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SELECTION AND PRIORITIZATION OF ORGANIC CONTAMINANTS FOR MONITORING IN THE DRINKING WATER VALUE CHAIN

By

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DECLARATION

"I declare that the thesis, "Selection and prioritization of organic contaminants for monitoring in the drinking water value chain" **Protocol no. 22/2007** that I hereby submit to the PhD in Public Health degree at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution. All the sources used or quoted in this research study have been indicated and reflected".

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Esper Jacobeth Ncube

Student no. 99130590

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Witness's signature

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Date signed

DEDICATION

I dedicate this Thesis work to those that have worked very hard to prove the causal link between the exposure to contaminated water and human health especially through the ingestion route and still fight to ensure successful Public Health Protection for the vulnerable and defenceless masses.

New diseases, including water-related diseases, periodically "emerge" either because they are newly recognized or because their importance increases.

http://www.who.int/water_sanitation_health/emerging/en/last visited 6 Sept 2007

ABSTRACT

The occurrence of organic contaminants in the drinking water value chain (from source to tap) is a growing concern for the Drinking Water industry and its consumers given the high risk these contaminants can cause to the general public. These adverse health effects include such as endocrine disruption, toxicity teratogenicity, mutagenicity and carcinogenicity. Some of these organic contaminants are included in national and international drinking water quality guidelines or standards. However, although there are similarities in the list of organic contaminants used by each organization or country, the organic contaminants are never the same given the local conditions. There are also noticeable differences in the concentration limits set as targets or criteria for organic contaminants for public health protection via the use of drinking water. A further question requiring the response from drinking water regulators was whether the standards listed in the international literature would be applicable in other countries like South Africa. Complicating this decision is the fact that the South African National Drinking Water Standard (SANS 241) does not adequately address this component of drinking water quality management. The current standard only provides for dissolved organic carbon (DOC), total trihalomethanes (TTHMs) and phenols. However, the standard contains a statement which specifies that if there is a known organic contaminant, that may pose a health threat, it should be included in the monitoring programme and evaluated against World Health Organization (WHO) guidelines. To safeguard Drinking Water industry customers, it was deemed necessary to investigate this matter and establish a tool to assist with the identification of a list of organic contaminants to be monitored in the drinking water value chain.

To achieve this a specific procedure/protocol needed to be developed, hence the aim of this study which was to develop a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain (from source to tap). To achieve this, a critical evaluation and synthesis of the available literature on the approaches for the selection and prioritization of organic variables of priority to the drinking water industry was undertaken as a first step. From the literature review it was evident that there are currently many selection and prioritization approaches which are characterized mainly by the purpose for which the exercise has been conducted for. Approaches that prioritize chemicals according to their importance as environmental contaminants have been developed by government agencies and private industries such as the Health Canada's Canadian Environmental Protection Agency (CEPA), the United Kingdom's Institute for Environmental Health (IEH), the European Community's Oslo and Paris (OSPAR) convention exercise for the protection of the Northeast Atlantic marine environment and the European Union (EU)'s combined monitoring based and modelling based priority setting scheme (EU-COMMPs). A few approaches such as ones published by the United States Environmental Protection Agency (USEPA), address the needs of the Drinking Water industry and there is no generic approach to the selection, prioritization and monitoring of organic contaminants in the drinking water value chain.

From the review of selection and prioritization approaches, a generic model was developed. The model consists of three main steps, the compilation of a "pool of organic contaminants, the selection of relevant parameters and criteria to screen organic contaminants and finally the application of criteria to select priority organic contaminants. It was however realized that these steps were not enough if the protocol to be develop will serve its purpose. Selection and prioritization approaches are typically intended to be fairly simple and quick methods for determining the health and environmental hazards posed by the use and release of chemical substances into different environmental systems. This was taken into account during the development of the current protocol. Understanding that a protocol is a predefined written procedural method in the design and implementation of tasks and that these protocols are

written whenever it is desirable to standardize a method or procedure to ensure successful reproducibility in a similar set up, a generic protocol was developed based on the model. The protocol developed in this study, operates as a multidisciplinary contaminants management and proactive protocol, thus exchanges toxicological, water quality, agricultural, chemical and public health information. The protocol uses previous or readily available information as a point of departure. It seeks to address the challenge facing the water industry in managing the current and emerging organic contaminants that are relevant to public health protection via the use of drinking water.

Once the protocol was developed, it was validated in a prototype drinking water value chain. The exercise comprised of testing each step of the protocol from the selection of the "pool of organic contaminants (Step I) to recommending the final priority list of organic contaminants (Step VII). The implementation was successfully conducted in the Rand Water drinking water value chain. Emphasis of expert judgment was made as each step was validated and the opinion of key stakeholders used to shape the process. During Step III of the protocol, an intensive literature review was conducted to determine organic contaminants that have been identified in ground and surface water systems across the world. As a result of this review, major groups of organic contaminants that have been found to occur in source water resources across the world were identified. The identified groups of organic contaminants include, pesticides, polynuclear aromatic hydrocarbons, per and polyfluoroorganic compounds, polycyclic aromatic hydrocarbons, alkanes and alkenes, C10-C13 Chloroalkanes, pharmaceuticals and personal care products [PPCPs], surfactants, benzotriazoles, cyanotoxins and Carbon-based engineered nanoparticles. The risk profile of the identified organic contaminants was established using the persistence, bio-accumulation and toxicity criteria and the development of water quality monographs as an information dissemination tool. A conceptual framework for the implementation of the protocol by water utilities and relevant institutions has been developed from the experiences learnt during the validation exercise and a priority list of organic contaminants for the monitoring in the drinking water value chain to be used by Rand Water and other water utilities was identified. Some of the organic contaminants on this are currently being analyzed for in The Rand Water's routine organic monitoring programme.

During the validation exercise, the following were noted,

- During the identification of the "pool of organic contaminants" from the consulted information sources such as the WHO guidelines for drinking water quality, Health Canada drinking water quality guidelines, the USEPA drinking water quality standards, the New Zealand drinking water quality standards, USEPA IRIS database, the PAN-UK list of registered pesticides for South Africa, the IARC list for recognized carcinogens and the Department of Agriculture pesticides manuals duplications were observed.

- The time allocated could not allow for the development of water quality monographs for all organic contaminants of concern but for a few selected contaminants whose information was inadequate to allow for decision-making.

- The determination of concentration levels of organic contaminants in fish, sediment and water samples could have been limited by the failure of current analytical instruments to go down to lower levels at which they occur in the drinking water value chain.

- Only two events could be planned, during the wet season (high flow) and dry season (low flow) based on time and budget constraints.

- Although various experts were consulted and invited to attend workshops in order to validate the process, the attendance could not be extended to all nine provinces given the time and budget constraints.

Based on the above, recommendations were made for the dissemination and use of the products emanating from this study. For example, it is recommended that the current protocol be made available to water utilities and the process of revising the current priority list be repeated every 5 years. Further research should be conducted to obtain full coverage of organic contaminants impacting on source water quality in all ground water and surface water systems used as sources for drinking water production. Another major recommendation is the investigation of potential analytical methods that current chromatographic methods with high resolution mass spectrometry to ensure that organic contaminants can be detected at the ng/l to ρg/l using a single enrichment method in order to make sure that those organic contaminants that occur at very low concentration in environmental samples can be detected. For example, the realisation that compounds such as synthetic organic polymer residues, emerging disinfectant by-products, detergent metabolites, chlorinated benzenes**,** alkyl phenol**,** polyethoxylates**,** their metabolites and cyanotoxins are continuously discharged into the environment via wastewater and industrial effluent discharges which increases their concentration in aquatic environment and concomitantly their potential to exert adverse health effects in water used as source for the production of drinking water necessitates that each of these groups be added to the current monitoring programme. The current water quality monographs can be used for the benefit of the Drinking Water industry. It is also recommended that a training manual on the production and use of water quality monographs is produced to facilitate their dissemination. CD-ROMs on the water quality monographs can be produced and distributed with the manual.

Key words
Organic contaminants, selection and prioritization, drinking water value chain, adverse human health effects, pool of contaminants, screening, protocol

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CONCEPTUAL DEFINITIONS

Water quality: the physical, chemical, biological and organoleptic properties of water that makes it fit for its intended use. Organoleptic properties are understood as those properties, which involve the use of senses, such as taste, smell, feel, sight in order to describe them. These are collectively, taste, odour, colour and turbidity.

The toxicity of a compound is its intrinsic capacity to cause injury, including the potential to induce carcinogenic, mutagenic and teratogenic effects.

The hazard presented by a compound is the capacity of that compound to cause injury under the circumstances of exposure. A toxic compound found in water does not necessarily present a hazard. It will present a risk only if exposure to the target organ(s) of an organism occurs.

Risk: The probability that in a certain time frame, an adverse outcome will occur in a person; group of people, plants, animals and/or the ecology of a specified area that is exposed to a particular dose or concentration of a hazardous agent, that is, it depends on both the level of toxicity of the agent and the level of exposure.

Validation: is an element of system assessment. It is undertaken to assess the feasibility of the protocol. It is also done to assess if the information supporting the protocol is correct and is mainly concerned with the assessment of the scientific and technical inputs into the protocol.

Prioritization: A prioritization exercise's function is to identify a short list of chemicals that rank highest when scored against a number of different screening criteria.[98] It gives an idea of magnitude of the problem associated with a potential contaminant and allows energy and resources to be directed to better understanding, regulating or engineering control measures for the most serious threats.[98] To produce an overall ranking of chemicals, scores resulting from application of individual screening criteria are weighted and the chemicals are ranked in order of increasing total score.

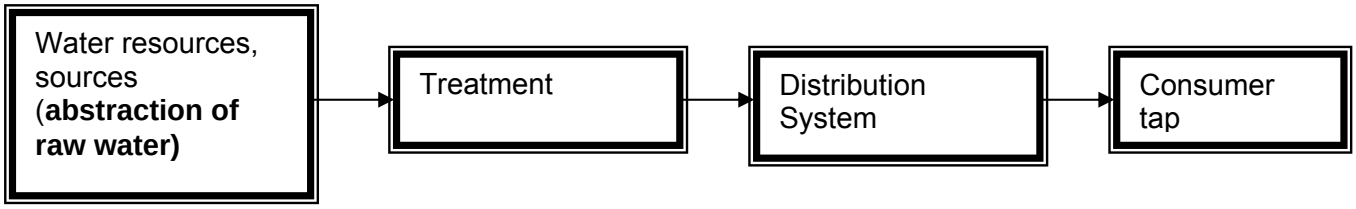
Critical control point: an activity, procedure at which control can be applied and which is essential to prevent a hazard or reduce it to an acceptable level. In the drinking water value chain, this will be the point at which the quality of water is expected to change. Hence, control at this point is crucial in terms of all system parameters.

Expert opinion

Expert opinion usually refers to the views of professionals who have expertise in a particular form of practice or field of inquiry, such as clinical practice or research methodology. Expert opinion may refer to one person's views or to the consensus view of a group of experts. When the concept of evidence based practice was first introduced, expert opinion was identified as the least reliable form of evidence on the effectiveness of interventions, and positioned at the lowest level in "levels of evidence" hierarchies. Other developments have determined that ranking expert opinion with levels of evidence is not useful or appropriate because expert opinion is qualitatively different to the forms of evidence that are derived from research.

Drinking water value chain (from source to tap)

This is traditionally known as the drinking water supply chain. The word "value" is added to emphasize the value add from one step to another from a process and water quality point of view. As the water progresses from the source, the water quality improves until it reaches the consumer at a quality that is acceptable and complies with the drinking water quality guidelines or standards. The figure below illustrates the chain.



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SYMBOLS AND ABBREVIATIONS

ADI	Acceptable daily intake
AhR	Aryl hydrogen receptor
AI	Adaptive implementation
$Al_2 (SO_4)_3$	Aluminium sulphate
$Al_2 (SO_4)_3.18H_2O$	Hydrated Aluminium sulphate
ANN	Artificial Neural Network
AOP	Advanced oxidation process
AOS	Alpha-olefin sulfonates
APs	Alkylphenols
APCI	Atmospheric chemical ionization
APE	Alkyl phenol ethoxylate
APPEOs	Alkyl phenol polyethoxylates
ARC	Agriculture Research Council
Arg	Arginine
As	Arsenic
AS	Alkyl sulfonates
ATSDR	Agency for Toxic Substances and Disease Registry
BBP	Butylbenzylpthalate
BPA	Bisphenol A
BTEX	Benzene, toluene, ethylbenzene and xylenes
BA	Bioassay
BaP	Benz[a]pyrene
BCF	Bioconcentration factor
BCF_{fish}	Bioconcentration factor in fish
BDEs	Brominated diphenyl ethers
BHC	Benzene hexachloride
BOC (M)	Biodegradable organic carbon (matter)
BP	Butyl phenol
BT	Benzotriazole
CAFOs	Confined animal feeding operations
CART	Classification and regression tree
CASRN	Chemical abstracts services registration number

CCL	Contaminants candidate list
CDBPs	Chlorinated disinfectant by-products
CEC	Commission for Environmental Cooperation
CEPA	Canadian Environmental Protection Agency
CH_3Sn^{3+}	Monomethyl tin
$(CH_3)_2Sn^{3+}$	Dimethyltin
ChV	Chronic values
Cl_2	Chlorine
ClO_2	Chlorine dioxide
COMMPS	Combined monitoring and modelling based priority setting
CPAM	Cationic polyacrylamide
CSIR	Council for Science and Industrial Research
CTP	Cyanotoxin poisoning
CYN	Cylindrospermopsin
C10-C13-	Ten carbon atoms to thirteen carbon atoms chained hydrocarbons
C_{60}	Fullerene
DADKM	Deaminodiketometribuzin
DADMAC	Diallyldimethylammonium chloride
DAM	Deamino metribuzin
DBCP	Dibromochloropropane
DBP	Di-n-Butylphthalate
DBPs	Disinfection by-products
DBP-CAN	Disinfection by-products with carcinogenicity estimates
DBT	Dibutyltin
DDA	Didealkyl atrazine
DDD	(1,1-dichloro-2,2-bis(p-chlorophenol) ethane
DDE	(1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene
DDHA	Didealkylhydroatrazine
DDT	Dichlorodiphenyltrichloroethane
DEA	Deethylatrazine
DEHA	Di-(2-ethylhexyl)adipate
DEHP	Di-(2-ethylhexyl) phthalate
DEP	Diethylphthalate
DES	Diethylstilbestrol
DIA	Deisopropylatrazine
DIHA	Deisopropylhydroatrazine

DKM	Diketo metribuzin
DMP	Dimethylphthalate
DMT	Dimethyltin
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DOH	Department of Health (RSA)
DOP	Di-n-octylphthalate
DWAF	Department of Water Affairs and Forestry
DWI	Drinking Water Inspectorate (UK)
DES	Diethylstilberol
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DsPH	Directors of Public Health
DSL	Domestic substances list
DYNAMEC	Dynamic Mechanism
E_1	Estrone
E_2	17-ß-Estradiol
EAWAG	Swiss Federal Institute for Environmental Science and Technology
EC	Effect concentration
ECB	European chemicals bureau
EDB	Ethyl dibromide
EDC	Endocrine disrupting compounds
EDCs	Endocrine disrupting chemicals
EDTA	Ethylene dinitrotetraacetic acid
EE_2	17α-ethynylestradiol
EEC	European Economic Community
EFS_d	Direct effect scores
EFS_i	Indirect effect scores
EFS_h	Effects on human
EHOs	Environmental health officers
EPA	Environmental Protection Agency
ESI	Electron spray ionization
EU	European Union
EURAM	European Academy of Management
FA	Fulvic acid
FAO	Food and Agriculture Organization

$FeCl_3$	Ferric chloride
GAC	Granular Activated Carbon
GC	Gas Chromatography
GC-MS	Gas Chromatography with Mass Spectrometric detection
GDWQ	Guidelines for Drinking Water Quality
GLI	Global leachability index
GUS	Groundwater ubiquity score
HA	Humic acid
HAA	Haloacetic acid
HAA5	The five regulated haloacetic acids
HABs	Harmful algal blooms
HANs	Haloacetonitrile
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HDPE	High density polyethylene pipes
Hg	Mercury
Hg^{2+}	Mercury ion
HKs	Haloketones
HMW	High molecular weight
H_2O	Water molecule –Chemical formula
HRA	Health Risk Assessment
Hu	Humin
HS^-	Hydrogen sulphide ion
Hy	Hydrophilic factor
IARC	International Agency for Research on Cancer
2-IBMP	2-Isobutylmethoxy-pyrazine
IEH	Institute of Environmental Health
IMAC	Interim maximum allowable concentration (Canada)
IPCS	International Programme on Chemical Safety
2-IPMP	2-Isopropymethoxy-pyrazine
IRIS	Integrated Risk Information System (USEPA)
IS	Internal standard
ISCW	Institute for Soil, Crops and Water
IUCLID	International Uniform Chemical Information Database
IUPAC	International Union of Pure and Applied Chemistry
JMPR	The Joint FAO/WHO meetings on Pesticide Residues
KCl	Potassium chloride

LASs	Liner alkyl sulfonates
LC	Liquid chromatography
L_c	Lethal concentration
LC-MS	Liquid chromatography, Mass spectrometry
LD_{50}	Lethal dose (death of 50% of a group of test animals)
LD_{Lo}	Lowest dose of a toxic material at which the death of the exposed test animal occurs
LIN	Leaching indices
LOEL	Low observed effect level
LOAEL	Low observed adverse effect level
LSE	Liquid solid extraction
MAC	Maximum Allowable Concentration (Canada)
MAV	Maximum Acceptable Value (New Zealand)
MBT	Methylbutyltin
MCL	Maximum Contaminant Limit (USEPA)
MCLG	Maximum Contaminant Limit goal (USEPA)
MC-LR	Microcystin-LR (L-Leucine, R-Arginine)
MCF-7 cells	A breast cancer cell line
MCPA	Monochlorophenoxy acetic acid
MCYST	Microcystins
MDL	Method detection limit
MDS	Multi-dimensional scaling
MDPE	Medium density polyethylene
MeHg	Methylmercury
2-MIB	2-Methylisoborneol
MRL	Minimum Reporting Limit
MTBE	Methyl tertbutyl ether
MX	Mutagen X
NDMA	Nitrosodimethylamine
NGOs	Non-governmental organizations
NHMRC	National Health Medical Research Council (Australia)
NOAEL	No observed adverse effect level
NOC	Natural Organic Carbon
NOEC	No-observed-effect concentration
NOM	Natural organic matter
NP	Nonylphenol
NPEOs	Nonylphenol ethoxylates

NSC	North Sea conference
NTA	Nitrilo acetic acid
NTP	National Toxicity Programme
O_2	Oxygen molecule, Chemical formula
O_3	Ozone molecule, Chemical formula
OC	Organic carbon
OECD	Organization for Economic Cooperation and Development
OECD-SIDs	Organization for Economic Cooperation and Development Screening Information Databases
OP	Octylphenol
OH	Hydroxyl group
OM	Organic matter
OPEOs	Octylphenol ethoxylates
OSPAR	OSLO PARIS
PAC	Powder activated carbon
PAHs	Polynuclear aromatic hydrocarbons
p-$AlCl_3$	Polyaluminium chloride
p-AlSiS	Polyaluminium silicate sulphate
PAM	Polyacrylamide
PBB	Polybrominated biphenyl
PBDEs	Polybrominated diphenylethers
PBT	Persistence, Bioaccumulation and Toxicity
PCB	Polychorinated biphenyl
PCBs	Polychlorinated biphenyls
PCBEs	Polychlorinated biphenyl ethers
PCCL	Preliminary Candidate Contaminant List
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzo-p-furans
PCE	Perchloroethylene
PCP	Pentachlorophenol
PDADMAC	Polydiallyldimethylammonium chloride
PEX	Cross-linked (X) Polyethylene pipe
PFAs	Polyfluorinated alkyl substances
PFACs	Perfluoroalkyl carboxylates
PFASs	Polyfluoroalkyl sulfonates
PFBES	Polyfluoro biphenyl ethers
PFOA	Perfluorooctanoic acid

PFOC	Polyfluorinated organic compounds
PFOS	Perfluoroorganic sulfonates
PFOSA	Perfluorooactane sulfoamide
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PNECs	Predicted no effect concentrations
POC	Particulate Organic Carbon
POPs	Persistent organic pollutants
PPCPs	Pharmaceuticals and personal care products
PPOPs	Priority persistent organic pollutants
PPU	Plant Protection Unit
PSL	Priority Substances List
PSPs	Paralytic shellfish poisons
PTB	Persistence, Toxic and Bioaccumulation
PVC	Polyvinyl chloride
PWSs	Public Water Systems
QSARs	Quantitative Structure Activity Relationships
QUEST	Quick, Unbiased and Efficient Statistical Tree
R_fD	Reference Dose
RDA	Regularized discriminant analysis
RQ	Risk quotients
RSA	Republic of South Africa
RW	Rand Water
SABS	South African Bureau of Standards
SANS	South African National Standard
SAR	Structure Activity Relationship
SCs	Sulfophenyl carboxylates
SCCPs	Short chain chlorinated paraffins
SDWA	Safe Drinking Water Act
Se	Selenium
Sn	Tin
sp	Species
SPE-GC-MS	Solid phase extraction Gas chromatography Mass spectrometry
SPM	Suspended particulate matter
STP	Sewage Treatment Plant
SWT	Sewage Water treatment

2,4,5-TP	2,4,5-Trichlorophenoxyacetic acid
TBA	Terbutylazine
TBP	Tri-n-butylphosphate
TBT	Tributyltin
TBTO	Tributyloxide
TCA	Trichloroacetic acid (1,1,1-Tricloroethane)
TCDD	Tetrachlorodibenzo-p-dioxin
TCE	Trichloroethylene
TD	Tumorigenicity dose
TDS	Total dissolved solids
TEFs	Toxic equivalent factors
THMs	Trihalomethanes
TOC	Total organic carbon
TOX	Total organic halide
TPP	Triphenyl phosphate
TT	Tolyltriazole
TTS	Total toxicity score
TTHMs	Total trihalomethanes
Ui	Unsaturation index
UK	United Kingdom
UN	United Nations
UNEP	United Nations Environment Programme
USEPA	United States Environment Protection Agency
VIN	Volatile indices
VMS	Volatile methylated siloxanes
VOCs	Volatile organic compounds
WHIM	Weighted holistic invariant molecular descriptors
WHO	World Health Organisation
WRC	Water Research Commission
WW	Water Works
WWTP	Waste Water Treatment Plant
XOCs	Xenobiotic organic compounds
=	Equal sign
≈	approximately
Atm.m^3/mol	Atmospheres. Cubic metres per mol
β	Beta
<	Less than

≤	Less or equal to
>	Greater than
%	Percentage
˚C	Degrees Celsius
g/mol	Gram per mole
H_c or K_h	Henry's law constant
K_d	Distribution coefficient
K_{oc}	Organic carbon-water partition coefficient
K_{ow}	Octanol/water partition coefficient
g/cm^3	Grams per cubic centimeter
lbs.yr	pounds/year
m	meter
mg/kg	Milligrams per kilogram
mg/kg/day	Milligrams per kilogram per day
mg/kg/day bw	Milligrams per kilogram per day body weight
mg/l	Milligrams per litre
MW	Molecular weight
ng/l	Nanograms per litre
ng/g	Nanograms per gram
Nm	Nanometre
ρ	Relative density
S_w	Water solubility
$T_{1/2}$	Half life
mg/l	Micrograms per litre
µg/kg	Micrograms per kilogram
µg/mol	Micrograms/mol
µm	Micrometer
V_p	Vapour pressure

CHAPTER 1 GENERAL INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Public health is a modern concept, although it has roots in antiquity. Early religions attempted to regulate behaviour that specifically related to health, from types of food eaten, to the extent to which certain behaviours could be indulged, such as drinking alcohol. [1] The establishment of government placed responsibility on leaders to develop public health policies and programs to gain some understanding of the causes of disease to ensure stability, prosperity and maintain order. [2] The aim of these policies and programs concerning drinking water is to minimize health risks for water users. The use of groundwater or spring water is subject to very few regulations given the perceived low risk to public health. The produced water must comply with the drinking water guidelines or standards which most countries have or benchmark against the World Health Organization drinking water quality guidelines.[3] Production of drinking water from surface water is covered by more complex regulations because of the perceived health risk. Apart from the application of the drinking water standards, regulations exist on source water and on the minimal treatment to be applied to the surface water. [3-8]

From the early beginnings of human civilization, it was recognised that polluted water and inadequate waste disposal may spread water-borne diseases. [1] Access to a safe drinking water is thus essential to human life and well being and today it is still a key public health issue. [3-4] However, many communities in various countries both rural and urban areas are still unable to access drinking water that meets national or international guidelines and standards. This undermines the protection of public health. Given that the provision of safe drinking water is a fundamental driver of public health, addressing water quality issues is increasing in importance on a global scale. [9]

The publication of Rachel Carson's "Silent Spring", [10] can be seen as a possible catalyst for an increase in global awareness concerning the pollution of surface and groundwater. This has lead to increased public concern for clean water, air and unpolluted soil [3] resulting in the growth of scientific investigations, public debate and media attention over the possible deleterious effects in humans and wildlife that may result from exposure to inorganic and organic contaminants. [11-23] As a consequence of these publications drinking water consumers worldwide are becoming more and more aware of the health effects of these organic contaminants.

1.2 HUMAN EXPOSURE TO ORGANIC CONTAMINANTS IN THE DRINKING WATER VALUE CHAIN

The significance of trace concentrations of organic contaminants in drinking water to public health has been largely inconclusive and controversial, since there is a general paucity of information concerning human health effects from which to draw via the drinking water ingestion route. Despite this observation, many initiatives have been undertaken to address the challenges. [24,25] Both direct and indirect assessments on human exposure to organic contaminants in water have been conducted [26-31] particularly in order to understand the relevance and public health significance of certain classes of organic contaminants'. [26-32] Figure 1.1 presents the environmental health paradigm and its relationship to the risk assessment framework as presented by Sexton et al. 1995 [33]

It is important to understand the public health significance of these contaminants in order to be able to manage and control them throughout the drinking water value chain. This understanding will contribute to the development of appropriate tools for adequate management of potential for hazards to exist. The exposure of humans to organic contaminants is complex and is in most cases through multiple ways.

It can be seen from Figure 1.1 that the effects of human exposure to any hazardous substance depend on the exposure dose, duration, personal traits, habits and interactions with other chemicals present. [33] The relative importance of these pathways has been considered as potentially important for volatile organic compounds.[27] Exposure to volatile chemicals from routes other than direct ingestion may be as large as or larger than exposure from ingestion alone. [27] This applies to compounds such as carbon tetrachloride, chloroform, ethylene dibromide (EDB), dibromochloropropane (DBCP), 1,1,1-trichloroethane (TCA) or methylchloroform, tetrachloroethylene (perchloroethylene or PCE) and trichloroethylene (TCE) collectively known as disinfection by-products. [27]

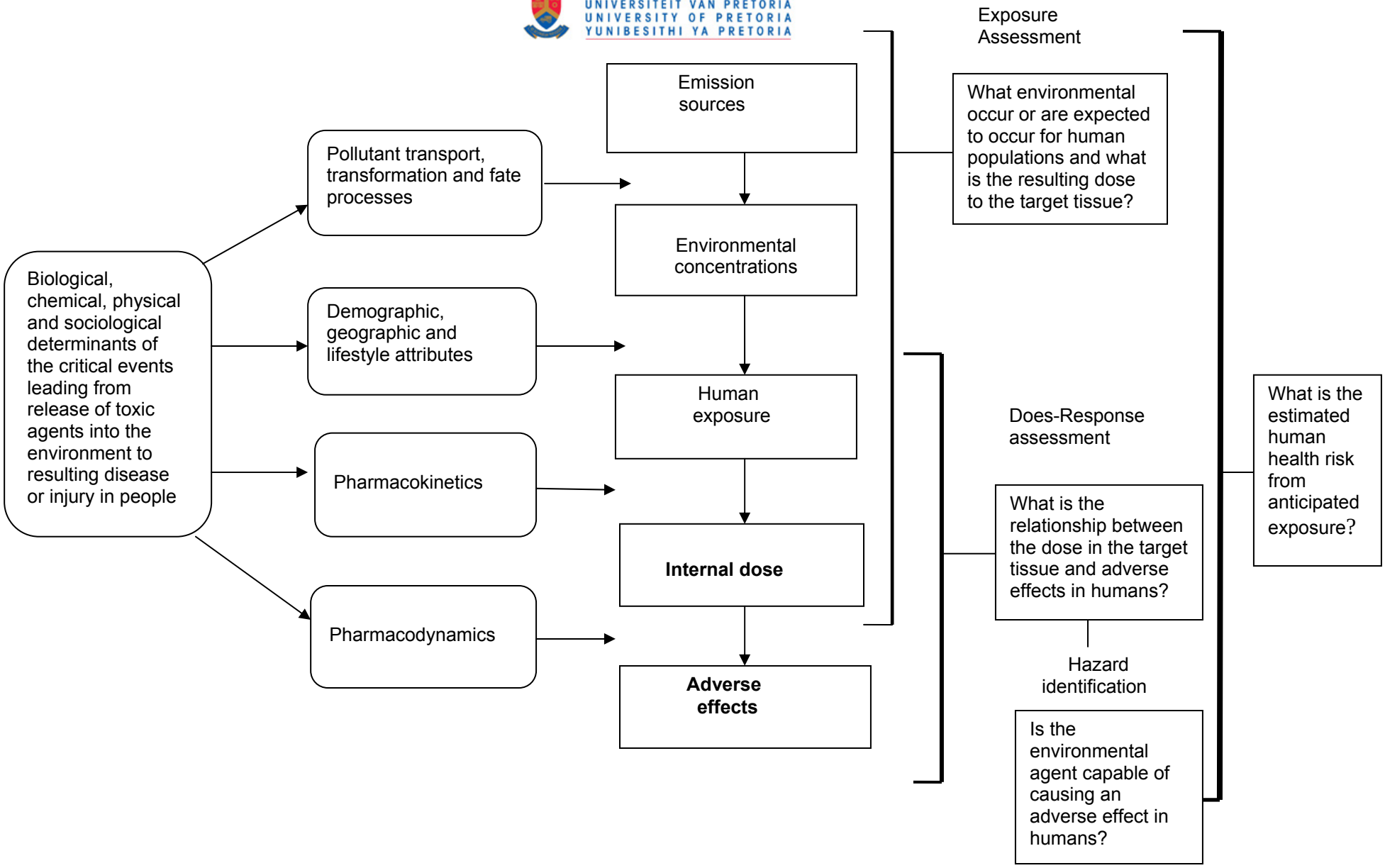


Figure 1.1**:** An environmental health paradigm and its relationship to the risk assessment framework adopted and modified from Sexton et al. 1995 [33]

1.2.1 The human risk

The human risk of long-term exposure to the low levels of most organic contaminants, especially emerging contaminants such as Pharmaceuticals and Personal Care Products (PPCPs), natural and synthetic hormones, Polyfluoro biphenyl ethers (PFBEs), Linear Alkyl Sulfonates (LASs) among others, through the drinking water ingestion route, inhalation or dermal contact from bathing or showering in the case of VOCs is essential unknown. [35-51] It is critical for the Drinking Water industry to understand the various sources, routes of entry, fate and behaviour, potential human health impacts, analytical and regulation requirements of organic contaminants that can enter freshwater water systems used for drinking water production. This will enable the various water services providers to select appropriate tools, methods and techniques for source water protection, treatment and removal of organic contaminants from source waters, monitoring of organic contaminants in the drinking water value chain and more importantly to select those that are relevant for the protection of public health through the drinking water value chain.

For a chemical agent or organic contaminant to reach target tissues in humans, there must be a source or sources producing it. The exposure of humans through drinking water is a direct result of the contamination of water systems that are used as source water for the production of drinking water, use of organic compounds such as synthetic organic polymers as coagulant aids, formation of organic contaminants during treatment and the ineffective removal of organic contaminants by conventional treatment plants.

1.3 SOURCES AND PATHWAYS OF ORGANIC CONTAMINANTS IN THE DRINKING WATER VALUE CHAIN

1.3.1 Sources of organic contaminants

The major sources from which organic contaminates can enter freshwater systems and thus enter the source water used for drinking water production are classified in two major groups namely; point sources and non-point sources. [Table 1.1 and Table 1.2]

Point Sources

Point source means any discernible, confined and discrete conveyance including but not limited to any pipe, ditch, channel, tunnel, conduit, well, container, rolling stock, discrete fissure, concentrated animal feeding operation or vessel or other locating craft from which pollutants are or may be discharged. The term does not include agricultural storm water discharges and return flows from agriculture. For these types of sources, contributions of contaminants originate from discrete sources whose inputs into aquatic systems and can

often be defined in a spatially explicit manner through measurement of chemical residues [Table 1.1] Point sources usually result in direct discharges to water courses, [Figure 1.1] whereas the route for non-point sources may involve partial deposition before reaching the water course. [52]

Non-point sources

These sources are diffuse in nature, occurring over broad geographical scales. Because of the diffuse nature, often cannot be readily delineated in a specially or temporally explicit manner. These include agricultural storm water discharges and return flows from agriculture. Non-point sources have the following characteristics;

- They respond to hydrological conditions
- Not easily measured or controlled directly, hence difficult to regulate
- Focus on land and related management practices
- Controlled by education, promotion of appropriate management. [52]

From Tables 1.1 and 1.2 below, it can be seen that sources and types of individual or group of organic compounds capable of contaminating source waters that could be used for drinking water production is diverse. It is therefore crucial that their routes and pathways into freshwater systems be understood.

Table 1.1: Major point sources of organic contaminants to surface waters, groundwater, treated waters and sediments

SOURCE	ACTIVITY	EXAMPLES OF CONTAMINANTS
Industrial (manufacturing and processing industries.)	Process effluents from pulp and paper, chemical manufacturers, food processing plants, petroleum industry	Organochlorine dyes, pharmaceuticals, Polychlorinated biphenyls (PCBs), Polycyclic aromatic hydrocarbons (PAHs), Polychlorodiphenyl furans (PCDFs) and Polychlorodipnenyl dioxins (PCDDs [3-8, 36-37,52]
Municipal Sewage treatment plants	Public sewage treatment plants that may receive indirect discharges from industrial facilities or businesses	Pharmaceuticals and personal care products, synthetic hormones, detergent degradates such as alkylphenols and their esters, pesticides, flame retardants and plasticizers such as tributylphosphate and bisphenol A [35-37]
Combined sewer overflows	Discharge of untreated water especially during floods into surface waters	Pesticides, pharmaceuticals, Polycyclic aromatic hydrocarbons (PAHs), greases and oils containing Polychlorinated biphenyls (PCBs) [35-37,40]
Resource extraction	Petroleum drilling	PAHs [3-8]
Natural occurring	Rocks, soils, decaying plant and vegetable material, effects of geological setting and climate, nutrient loading in catchments	Natural occurring organic matter (NOM), Humic and fulvic acids, algal toxins (saxitoxins, anatoxins, microcystins, cylindrospermopsins); geosmin, 2-methylisoborneol (2-MIB)[3-8,21,53,54,58]
Water treatment or material in contact with drinking water	Use of natural and synthetic organic coagulants, piping materials, disinfection of drinking water, distribution of potable water in PVC pipes	Diallyldimethylammonium chloride (DADMAC), dimethylamine, Allylchloride, diallylether, 5-hexanal, epichlorohydrin, glycidol, 1,3-dichloro-2-propanol, 2,3-dichloro-1-propanol, 3-chloro-1,2-propanediol, acrylamide, disinfection by-products, PAHs, organotins, volatile organic compounds (VOCs)[53-57]
Land disposal (landfills)	Leachate or discharge from septic tanks, landfills, industrial impoundments and hazardous waste sites	Pharmaceuticals, PAHs, tert butyl methyl ether (MTBE), organotins, mixture of hazardous chemicals[35-37,52,59]

Table 1.2: Examples of non-point source pollution

SOURCE	DESCRIPTION	CONTAMINANTS
Agricultural/ forestry	Run-off from all categories of agriculture: Crop production, pastures, confined animal feeding operations (CAFOs). Vegetable handling especially washing in polluted surface waters, irrigation return flows	Agrochemicals such as pesticides, pharmaceuticals such as steroids and growth promoters, sheep dip chemicals, antibiotics[36-38, 43-48, 52,60,61-69]
Storm sewers/urban run-off	Run off from impervious surfaces including streets, parking lots, buildings, roofs, cleaning for urbanization.	PAHs, pesticides, greases and oils, pharmaceuticals[39-41,49,61-64]
Transportation	Roads, railway lines, pipelines	Solvents, greases and oils, examples from PCBs and PAHs such as benzo [a] pyrene, fluoranthene [3-8,42]
Atmospheric deposition	Emissions from industrial stacks, municipal incinerators, pesticide applications, human activities such as combustion and pyrolysis	Priority Persistent Organic Pollutants (PPOPs) and Persistent Organic Pollutants (POPs), PCBs, Dioxins and furans, PAHs, persistent pesticides[27,29,50,52]

1.3.2 The major routes of entry and pathways into the drinking water value chain

The major routes by which organic contaminants enter the aquatic compartment from the sources mentioned above are too numerous to list. [52] Figure 1.2 summarizes the main generic pathways. It is evident from this figure that most organic contaminants enter watercourse ways from wastewater treatment plant (WWTP) effluents. [61] Hence, the WWTPs removal efficiency is crucial in making sure that organic contaminants levels in effluent waters are low to avoid contamination of receiving water bodies. Other categories of emerging contaminants such as veterinary pharmaceuticals can contaminate farmland when manure is used as fertilizer and are likely to enter the rivers as a result of run-off from the fields. [52, 61, 70] Another route of contamination is leakage into groundwater that may originate from disposal of household products such as domestic waste in landfills. [52]

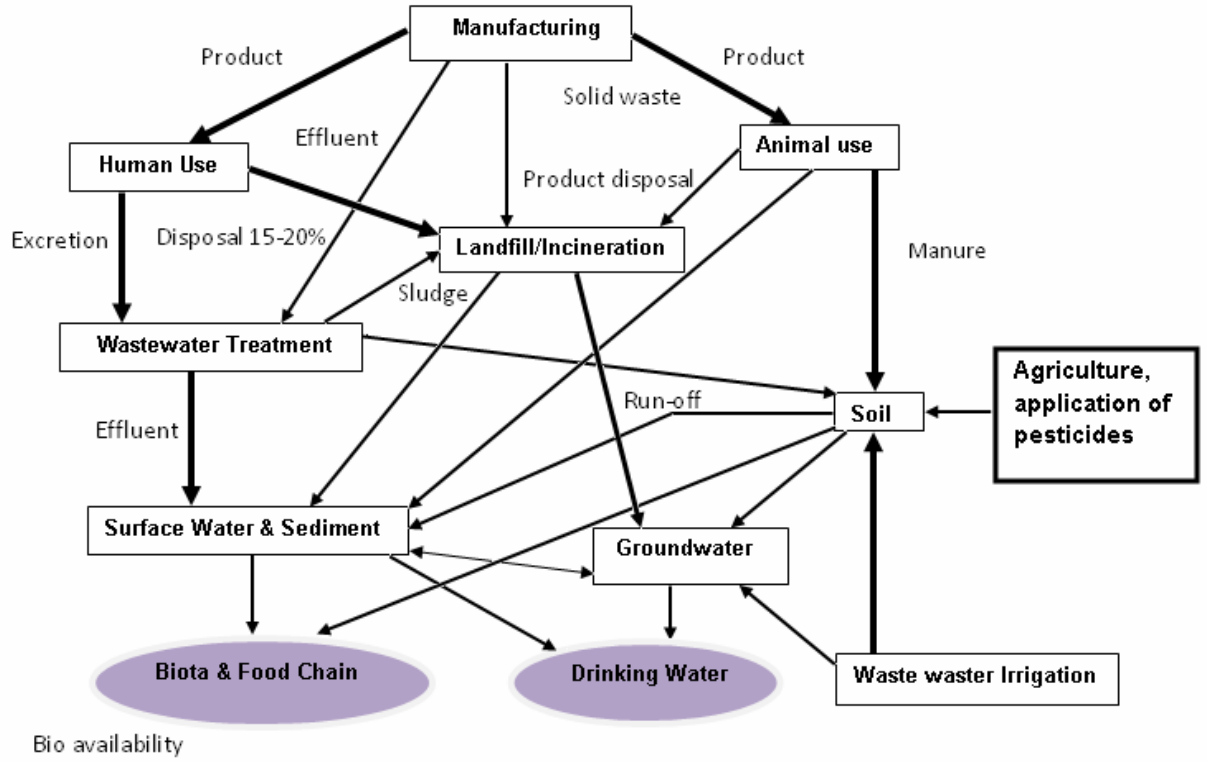


Figure 1.2: Potential sources, pathways and sinks of organic contaminants in the environment, adopted and modified from Schnoebelen et al. 2006 [70]

Organic contaminants occurring through atmospheric deposition

Atmospheric deposition is not just important as a direct pathway of contaminants from the atmosphere to the ocean but may also substantially contribute to the contaminant input via rivers, lakes, run-off from soil deposition such as spills. [2, 71] Much of what the rivers may import may be not derived from industrial and agricultural sources along rivers themselves. Organic contaminants occur in the environments in various forms for example, dissolved in the water and compartments (air, water, sediments). The contaminants do not necessarily remain in the same compartment during its transport from source of production to catchments from region to region or throughout the year. [52, 71] Contaminants interact with each other and may be transferred between the atmosphere and the water column, dissolved in water, sorbed to biota, organic or inorganic particles and sediments all according to variations in the physical and biological environment in space and time. [71] This is a major diffuse source of contaminants. Substances released to the atmosphere are present in gaseous and aerosol phases and are adsorbed to particles. [52, 71] One of the dominant deposition mechanisms to the ground is wet removal due to scavenging of particles and by partitioning of organic vapour into rain and snow. [52, 71] The extent of this process depends

on the distribution of the chemical between the gaseous and aerosol phases, particle size distribution and the Henry's Law constant. [52, 71]

Organic contaminants from surface run-off
Storm-water run-off can give rise to loading of organic contaminants not only to pollution incidents but also when collected in combined sewerage systems, [52, 61] and/or highway run-off (traffic, maintenance, accident and spills). [72] Factors such as population density, traffic density and farming intensity have an impact on the contaminant composition of run-off. Surface run-off and erosion due to natural or man-made drainage from agricultural land may end up in surface waters. [42-50, 52, 66, 67]

In addition to chemicals applied to crops, other agrochemicals used in animal husbandry such as cattle and sheep dip chemicals have been identified as major contaminants of surface water. [42-50] Run-off from surfaces treated with organic manure (a combination of dung and urine from household livestock and plant waste and municipal sewage treatment works sludge) usually applied to soils is regarded as an important route of entry of non-point source pollutants in surface waters in agricultural areas. [42-50, 66, 67] Pesticide quantities that enter farmland for replenishing nutrients and as soil conditioning can also be toxic organic contaminants. [52]

From this section it is evident that how and where a particular chemical is used determines the path by which it is introduced in the environment. It is evident from the above sections that different organic contaminants with varying characteristics and physico-chemical properties end up in freshwater systems. Depending on these properties and uses, organic contaminants follow different routes and pathways into source waters. The contaminants' chemical and physical properties are important determinants for their behaviour and fate in the environment.

1.4 FATE AND BEHAVIOUR OF ORGANIC CONTAMINANTS IN THE DRINKING WATER VALUE CHAIN

When released into the environment, substances are subjected to any one or a combination of a number of processes that may affect their fate and behavior. The effect of each of these processes on the concentration of a chemical in any given environmental compartment (such as water, air, soil, sediment, and biomass) depends on the chemical's physico-chemical properties, environmental conditions and the discharge pattern. [72] The major processes are:

- *Transport (that is volatilization, advection, dissolution, dispersion, adsorption, wet deposition, sedimentation, mixing and diffusion)*. [72]

Transport processes determine the variation in spatial and temporal distribution of a chemical in the environment. Rates of advection and dispersion are determined solely by environmental parameters such as current or wind speed. In air, rates are usually very fast while in water they may vary from very rapid in fast flowing rivers to very slow in stagnant lakes or ponds. In soil and sediment these rates may be insignificant.[72]

- *Transformation (biodegradation, hydrolysis, photolysis, speciation).*
  Transformation is of major importance in determining the persistence of a chemical. The mechanisms may vary depending on temperature, light intensity and numbers of competent bacteria. Dissolution is the route by which many other substances can enter a watercourse. For example the main source of organotins is from dissolution of tributyltin (TBT) and related compounds used as antifouling agents. [72]
- *Uptake (bioaccumulation, bioconcentration).*
  Two different modes of action of uptake can be distinguished, passive and active uptake. In fish, passive uptake occurs via the skin and or gills of the truly soluble fraction while active uptake occurs via the digestive tract. Uptake and subsequent concentrations in biomass depend on the bioavailability of the substance. [72] The measured total environmental concentration of a substance does not necessarily represent the actual concentration to which the individual species will be exposed. The most important physicochemical properties of a substance that impact on its fate and distribution in the environment are its molecular weight (MW), vapor pressure (V_p), water solubility (S), octanol/water partition coefficient (K_{ow}), organic carbon-water partition coefficient (K_{och}), Henry's Law Constant (H_c), bioconcentration factor in fish (BCF_{fish}) and half-life ($T_{1/2\ water,\ air,\ soil}$) in the compartment of interest. [52, 72] Based on these properties organic contaminants will fall into different categories or classes.

1.5 MAIN CATEGORIES OF ORGANIC CONTAMINANTS OF CONCERN

1.5.1 Classical organic contaminants

Until the beginning of the 1990s, non polar hazardous compounds such as persistent organic pollutants (POPs) and heavy metals were a focus of interest and awareness as priority pollutants, hence they were part of intensive monitoring programs. [73] Today, these compounds are as important as emerging contaminants for the industrialized countries since a dramatic reduction of emissions has been achieved through the adoption of appropriate measures and the elimination of the dominant sources of pollution. However, due to their persistence in the environment, ability to travel across the atmosphere and be deposited at distances far from their origin, bioaccumulation in fat tissues and toxicity to wildlife and human

beings this has led to their continuous regulation and monitoring in the environment which is evident in the contents of the Stockholm Convention of 2001 and other relevant conventions. [3-8] In this convention a group of organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins and furans are singled out as the "dirty dozen". These contaminants are listed in water quality standards and guidelines worldwide for safeguarding public health. [3-8]This group of compounds will be referred in this document as "classical organic contaminants". [Table 1.3]

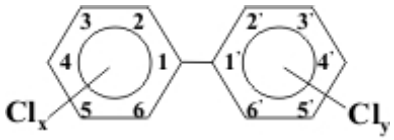
1.5.2 Emerging organic contaminants

While the number of known organic chemicals might seem large, the number of potential organic chemicals (those that could possibly be synthesized and those that already exists but which have not been identified) is unimaginably large. [73] The emission of so-called "emerging" or "new" unregulated contaminants [Table 1.4] has become an environmental problem, and there is widespread consensus that this kind of contamination may require legislative intervention. [49] Emerging contaminants are any synthetic or naturally occurring organic chemical(s) or microorganisms that are not commonly monitored but have the potential to enter the aquatic environment and impair the quality of raw water or cause known or suspected adverse human health or ecological effects.

This group mainly comprises products used in large quantities in everyday life, such as human and veterinary pharmaceuticals, personal care products, [78] surfactants and surfactant residues, plasticizers,[49] hormones, biocides, polyfluorinated compounds, polychlorinated biphenyl ethers (PCBEs), phosphoric esters and flame retardants and various industrial additives.[75] The characteristic of these contaminants is that they do not need to be persistent in the environment to cause negative effects, since their high transformation and removal rates can be offset by their continuous introduction into the environment. [49]

One of the main sources of emerging contaminants is untreated urban wastewaters and wastewater treatment plant [WWTP] effluents. [Figure 1.3] Current WWTPs are not designed to treat these types of substances and a high portion of emerging compounds and their metabolites. [49] These can escape elimination in WWTPs and enter the aquatic environment via the effluents, leach from WWTP sludge applied to land or solid waste disposal sites and finally find their way into the drinking water value chain. A detailed discussion of these groups will be given later this document.

Table 1.3: Examples of classical organic contaminants of concern

CLASS/TYPE OF ORGANIC CONTAMINANTS	DESCRIPTION/EXAMPLES
Natural occurring organic contaminants	Humic and fulvic acids, algal toxins, Dissolved organic carbon (DOC), particulate organic carbon (POC)
Agricultural chemicals	All organic chemicals used in animal and crop farming for example certain classes of pesticides and pharmaceuticals
Chlorophenols	Chlorophenols are synthetic organic compounds obtained from large industrial and commercial scales by chlorination of phenol or hydrolyzing chlorobenzenes. They consists of the benzene ring, the hydroxyl group (-OH) and atoms of chlorine.
Industrial chemicals	Compounds of industrial origin for example benzene and its substituents such as toluene, ethylbenzene and xylene isomers
Polychlorinated biphenyls(PCBs)	They are organochlorine compounds consisting of two benzene rings substituted by chlorine atoms. General structure :  Zhang et al. 2004 [95] Used in electrical transformers and large capacitors as hydraulic and heat exchange fluids and as additives to paints and lubricants. Also in carbonless copy paper and in plastics. Unintentionally produced during combustion.
Polychlorinated dibenzo-p-dioxins (dioxins)	This includes a group of over 75 different chlorinated dioxins Unintentionally produced during most forms of combustion, including burning of municipal and medical wastes and burning of backyard trash and industrial processes. Also can be found as trace contaminants in certain herbicides, wood preservatives and in PCB mixtures.
Polychlorinated dibenzo-p-furans (furans)	This includes over 135 chlorinated dibenzofurans. Unintentionally produced during most forms of combustion, including burning of municipal and medical wastes and burning of backyard trash and industrial processes. Also can be found as trace contaminants in certain herbicides, wood preservatives and in PCB mixtures.
Disinfection by-products	By-products of potable water disinfection using chlorine and other disinfectants, for example trihalomethanes (THMs), Haloacetic acids (HAAs), Haloketones (HKs), and Haloacetonitriles (HANs)

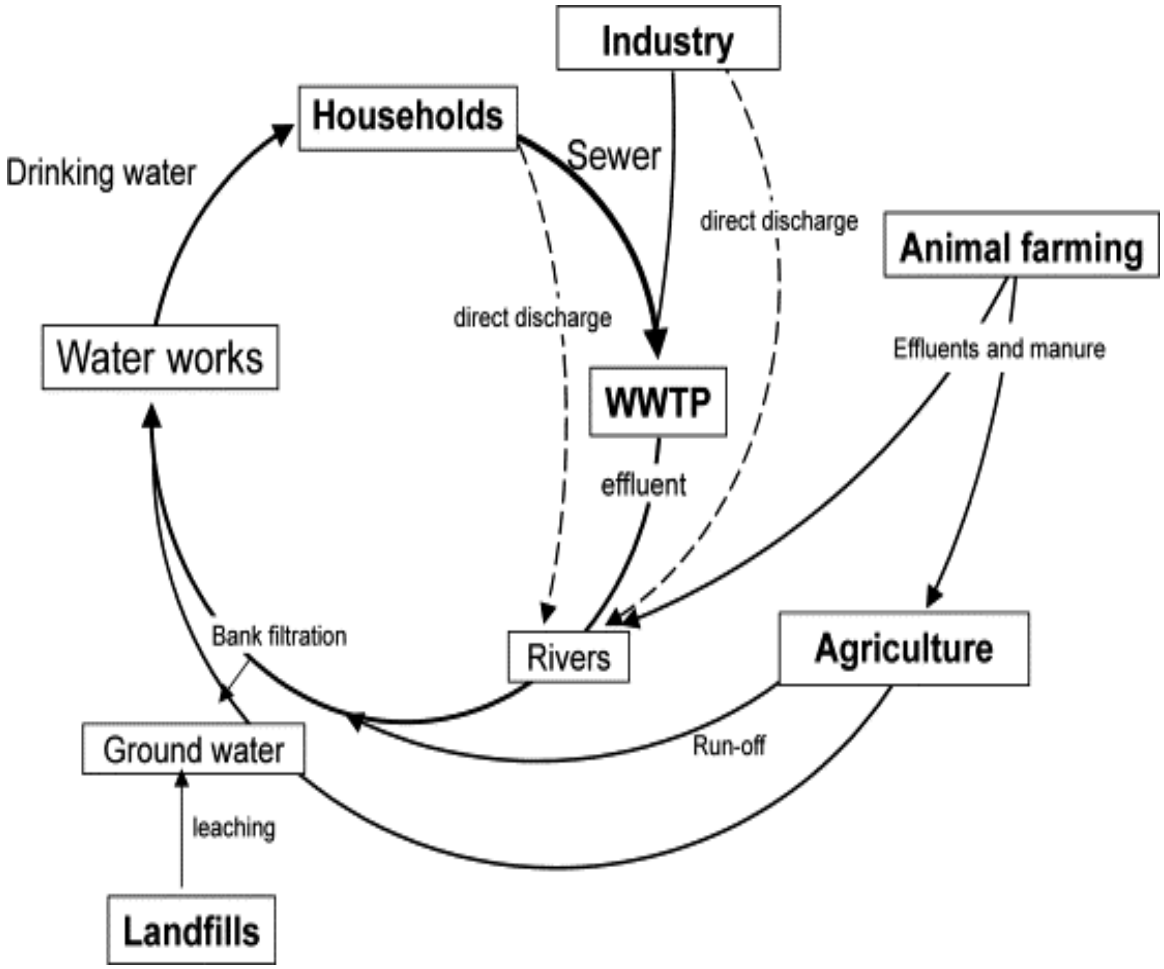


Figure 1.3 Routes of entry of emerging organic pollutants into the aquatic environment [49]

Table 1.4 : Examples of emerging contaminants, adopted and modified from Ellis, 2006 [61]

COMPOUND CLASS	EXAMPLES
Pharmaceuticals Veterinary and human antibiotics Analgesics and anti-inflammatory drugs **Psychiatric drugs** **Lipid regulators** **B-blockers** **X-Ray contrast media**	Trimethoprim, erythromycin, lincomycin, sulfamethoxazole Codeine, ibuprofen, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen Diazepam, Bezafibrate, Clofibric acid, Fenofibric acid Metoprolol, Propanolol, Timolol Iopromide, Iopamidol, Diatrizoate
Steroid and Hormones *(contraceptives)*	Estradiol, estrone, estriol, diethylstilbest**rol**
Personal care products Fragrances Sun screen agents Insect repellents	 Nitro, polycyclic and macrocyclic musks Benzophenone, methylbenzylidene camphor N,N-diethyltoluamide
Antiseptics	Triclosan, Chlorophene
Surfactants and surfactants metabolites	Alkylphenol ethoxylates, Alkylphenols (nonylphenol and octylphenol), Alkylphenol carboxylates
Flame retardants	Polybrominated diphenyl ethers (PBDEs), tetrabromo Bisphenol A, Tris (2-chloroethyl) phosphate
Industrial additives and agents	Chelating agents Edetic acid (EDTA), aromatic sulfonates
Gasoline additives	Dialkylethers, Methyl-t-butyl ether (MTBE)
Disinfection by-products	Iodo-THMs, bromoacids, bromoacetonitriles, bromoaldehydes, cyanoformaldehyde, bromate, NDMA

1.6 ASSESSMENT OF HUMAN HEALTH IMPACTS

In assessing the health impacts of organic contaminants, it is evident that various classes of organic contaminants cause an array of effects, contributing to the incidences of common diseases of multi-factorial etiology such as the different cancers, toxicity, neurobehavioral deficits, reproductive effects and endocrine disruption among others. [13,14,18,19,21-24,26,31] These include effects such as various cancers, allergies, damage to the central and peripheral nervous system, reproductive disorders, disruption to the immune systems or even death. [66, 68, 85-92]

Carcinogenic organic contaminants are those that cause or promote the growth of a malignant (cancerous tumor in which certain cells multiply uncontrollably). Examples include disinfection by-products (DBPs), PAHs, benzene and its analogs, 2, 4-D, some pesticides such as chlordane, simazine and 2, 3, 7, 8-tetrachloro dibenzo-p-dioxin (TCDD). [92] Recent studies have suggested that TCDD and dioxin like compounds may be important in the development of endometriosis. PAHs comprise the largest group of organic contaminants known to be cancer causing agents. Some PAHs have been demonstrated to be carcinogenic and mutagenic. [93] However, those PAHs that have not been found to be carcinogenic may act as synergists.[93] Exposure to PAHs is always due to a mixture making the assessment of exposure difficult hence the use of Benz[a]pyrene as a marker of exposure for the 16 priority unsubstituted PAHs which are considered to be possible or probable human carcinogens. [93] Another concern is the ability of PAHs to exert toxic effects through the aryl hydrogen receptor (AhR) mediated mechanism, similar to that of dioxins. [94]

Some organic contaminants act as **mutagens** that is, as agents that cause mutations. These are changes in the DNA molecules found in cells. Mutations in a germ cell (sperm or egg) can be inherited by offspring; those in other cells are not inherited but may cause harmful effects such as tumors. PAHs are a good example of such group of compounds. Others act as **teratogens,** that is**,** as agents that cause deformation in the fetus**.** [94] These organic contaminants are capable of causing birth defects while the human embryo is growing and developing during pregnancy especially during the first three months, Organic contaminants known to cause birth defects in laboratory animals, include PCBs and steroid hormones. Organochlorine pesticides and PCBs are a concern since they act as environmental hormones which disrupt reproductive cycles of humans and wildlife. [23,95] Some developing countries are still using these compounds because of their low cost and versatility in industry, agriculture and public health for example DDT for malaria control. [95]

A range of organic contaminants have the potential to cause toxic effects resulting in liver and kidney damage. These include chlorobenzenes, organochlorine pesticides such as Lindane, Hexachlorobenzene, Toxaphene, Heptachlor and its epoxide, Endrin. [92] Other individual compounds or groups include Dalapon, Diethylhexyladipate (DEHA), 2,4,5-TP (Silvex), ethylbenzene and 2,4-D are also capable of causing the same effects.[92] Others such as Carbofuran, THMs and toluene have the potential to affect the nervous system resulting in neurobehavioral effects. [92] The concerns about emerging DBPs include adverse reproductive and developmental effects recently observed in human populations. [21] The change of disinfectants from chlorine to ozone, chlorine dioxide and chloramines which is intended to reduce the levels of regulated DBPs such as trihalomethanes and haloacetic acids has been found to increase levels of other potentially toxicologically important DBPs. Examples include bromo trihalomethanes, iodotrihalomethanes, dihaloaldehydes. [21]

Of increasing concern are the emerging organic contaminants. [Table 1.4] Most of the emerging organic compounds have been found to have effects on the endocrine system. [85-92] Compounds that affect the endocrine system are called **endocrine disruptors**. The WHO defines an endocrine disrupting substance as “an exogenous substance that alters the function of the endocrine system and consequently causes adverse health effects in an organism or its progeny or subpopulations”. [3, 87] Disrupting the endocrine system can occur in various ways. Some organic contaminants can mimic natural hormones, [85-87] signaling the body into over-responding to the stimulus (e.g., a growth hormone that results in increased muscle mass) or responding at inappropriate times (e.g., producing insulin when it is not needed). Some endocrine disrupting chemicals can block the effects of a hormone from certain receptors, [85-92] while other organic contaminants can directly stimulate or inhibit the endocrine system, causing overproduction or underproduction of hormones. [85-92] Selected drugs are used to intentionally cause some of these effects, such as birth control pills. In many situations involving environmental chemicals, an endocrine effect may not be desirable. [85-92, 98-99]

Organic contaminants are capable of causing other problems other than adverse human health effects. These problems include impairing the organoleptic properties of drinking water such as taste, feel, physical appearance and occurrence of offensive odours. These properties constitute the aesthetic aspects of water which consumers are capable of identifying. Examples include, the visual nuisance causing discolouration, offensive taste and odours and high turbidity in water bodies. The presence of high organic content in water bodies can result in de-oxygenation, resulting in oxygen depletion and death of some organisms. Disturbance of temperature and pH regimes and promotion of eutrophication

could result in nutrient loading in water supplies resulting in the release of algal toxins into the water. This has resulted in a shift in environmental research to try and ameliorate these effects and protect not only source water resources but the entire drinking water value chain.

1.7 OVERALL ASSESSMENT

From the preceding discussions it is evident that organic contaminants in water bodies intended for use as sources of drinking water occur as a result of both natural and anthropogenic origins. These origins can be point or non-point sources of pollution. The organic contaminants find their way into sources by a variety of routes and pathways which include effluent discharge from manufacturing processes and households, wastewater treatment plants, run-off from agricultural fields, roadways, animal farming, leachates from solid waste disposal sites and atmospheric deposition.

The fate and distribution of all emissions depends on the hydrology, geochemistry and biological characteristics of the receiving environment. The occurrence of organic micro-contaminants in raw water and their removal in the course of drinking water production and possible formation of disinfection by-products are key issues in relation to the quality of drinking water and the impact thereof on human health. Although most organic contaminants discussed in this document are currently not regulated in drinking water directives, [3-8] precautionary principles should be employed and the removal of all organic micro-contaminants should be as high as possible. [21, 49]

However, several studies have shown that the removal of emerging polar contaminants such as those given in Table 1.4, during water treatment is incomplete. [21,96,97] The occurrence of some organic contaminants in finished water may indicate that drinking water is a source of exposure although some individual or classes of organic contaminants have been detected through biomonitoring indicating environmental exposure. This is however, an indication that organic contaminants of concern are found in the natural environment and in the drinking water value chain. Such are contaminants introduced by the use of synthetic organic polymers, use of alternative disinfection chemicals to chlorine such as ozone, chlorine dioxide and chloramines, the formation of organotins and VOCs in the distribution due to leaching from pipes used to deliver potable water.

The need for monitoring some important potentially hazardous organic contaminants in surface waters by state-of-the-art methods is now recognized as being essential for achieving good water quality objectives and protecting public health through the delivery of

chemical safe water. [74, 76, 77, 80, 81, 83, 84] The application of advanced LC-MS, GC-MS techniques, rapid assessment techniques [81, 80] and predictive models has allowed the determination of a broader range of organic contaminants and as a result revealed a comprehensive list of potential organic contaminants that can be found in the drinking water value chain. More than 1000 organic contaminants of concern to human health have been identified in source water resources some of which have the potential to persist in the drinking water value chain. Mass spectrometry is a highly sensitive and specific technique suitable for use in environmental organic analysis. GC-MS is widely used and a well known technique and allows identification and determination of for example pesticides in several matrices and is still the most popular technique for this purpose in most countries. However, owing to their thermal instability and polarity, many pesticides are not directly amenable to GC analysis. Liquid Chromatography [LC] coupled with Atmosphere Pressure Chemical Ionization [APCI] and Electron Spray Ionization [ESI] offers new opportunities for the determination of a wide range of organic contaminants. [75]

However, this achievement in Analytical Chemistry and in the field of organic analysis comes with a number of key analytical challenges. In practice, it is not feasible to monitor for hundreds of compounds due to the following;

- **Occurrence levels of organic contaminants in environmental samples especially in the water matrix;** Most organic contaminants occur at trace levels µg/l or ng/l. This makes it difficult for their successful detection and quantification. This holds true for hydrophobic pesticides, surfactants and plasticizers, natural and synthetic hormones, PPCPs, PAHs which are mainly lipophilic, hence found in trace amounts in water samples.
- **Different fate and behavior characteristics based on different physicochemical properties;** Some groups of organic contaminants will behave differently in the drinking water value chain depending on geographical conditions and their physicochemical properties. It is crucial to understand these properties in order to decide whether they are typical water contaminants or not.
- **Unavailability of reference materials and analytical standards for certain groups of concern;**

  There is lack of reference methods for certain groups of concern. For example, the European Union in its implication of the European Water Framework Directive [82] has been able to identify the need for the development of reference methods for four priority substances namely nonylphenol, octylphenol, polybrominated diphenyl esters (PBDEs) and C10-C13 chloroalkanes which consists of groups of chemicals

consisting of a large number of congeners and isomers. [82] Available monitoring data for these groups of chemicals often refer to different congeners so that it is difficult to compare data. [82] Enough effort should be made to identify indicator substances and reference materials whenever possible and secondly to define a consensus reference method for each of these priority substances. [82] Where there are available, the cost to purchase them has been high.

- **Unavailability of analytical or toxicity data** for certain classes of contaminants limiting decision making exercises. For example, monitoring for most organic contaminants in addition to pesticides, such as hormones, PPCPs are generally poor in much of the world and especially in developing countries. [98-101] Key pesticides are included in the monitoring schedule of most western countries. [3-8] However, the cost of analysis and the necessity to sample at critical times of the year (linked to periods of pesticide use) often preclude development of an exclusive data set. Many developing countries have difficulty carrying out organic chemical analysis due to a skills shortage, inadequate facilities, unavailability of certified reagents reference material and financial constraints. [42-46,75,101]
- **Unavailability of appropriate internationally accepted analytical methods for certain classes of concern;**

  There is currently no analytical method available for the C10-C13 chloroalkanes. [82] Reference methods for the determination of contaminants in complex matrices such as sediment, Suspended Particulate Matter (SPM) and biota need to be developed. Current standard methods for organic contaminants do not offer any clear advice for waters with elevated SPM levels. [82]
- **Unavailability of suitable indicator substances for certain classes of organic contaminants**

  The C10-C13 chloroalkanes (polychloro-n-alkanes), also known industrially as short-chain chlorinated paraffins (SCCPs) are the most challenging group of substances with respect to analysis and quantification[82]. This class of compounds has no well defined set of indicator substances. This is because, this family comprises complex technical mixtures containing a large number of isomers (C10, C11, C12, C13) with varying number of chlorine atoms and chlorine atom positions.[82]
- **Unavailability of drinking water guidelines or standards;** Most water quality regulation bodies such as the WHO, EU, USEPA and Health Canada, have developed water quality criteria for some organic contaminants.[82] However, most organic contaminants of concern especially those currently known, as emerging contaminants have no guidelines nor standards yet due to the paucity of toxicity data,

lack of potential threat given the quantities of a particular organic contaminant or group of organic contaminants produced on a local or national scale, the levels at which the contaminants occur in environmental samples for successful quantification using available analytical tools.[3-8]

1.7.1 Key challenges for the Drinking Water Industry

In order for water utilities to provide safe drinking water for human consumption and use, it is critical that organic contaminants which are potentially hazardous and can impact on the quality of drinking water and the health of consumers be identified. From the preceding discussions, it is evident that a number of analytical techniques that allow successful detection of these compounds have been developed although key analytical challenges still exist as explained in the above section. [75,79] In practice, it is impossible to monitor for hundreds of compounds and the concept of reducing the number of organic contaminants to analyze for in a particular class of organic compounds or mixture of compounds is included in each of the above approaches. This emphasizes the need for the selection and prioritization initiatives. Various selection and prioritization schemes have been developed by various governmental organizations and institutions. [102-105] these are discussed in detail in Chapter 2 of this document. In the absence of such schemes, the use of WHO guidelines for drinking water quality as a benchmark to determine parameters of concern to the drinking water industry including organic variables has been the norm. However, member states are still faced with the challenge of assessing local conditions and selecting those parameters that are relevant for the country or region.

As a result, there is a need for a generic protocol that will develop a criterion for all relevant classes of organic contaminants in the drinking water value chain. The protocol will describe a prototype procedure for the selection and prioritization of organic contaminants for use by the Drinking Water industry. It will emphasize the system assessment approach from catchment to tap in order to consider all organic contaminants of relevance to the drinking water value chain. Emphasis is made on assessing local conditions and determining the relevant potential environmental stressors and comparison with similar situations elsewhere in order to compile the “pool of organic contaminants” from which to select. The protocol will also contain summarized tailor made water quality monographs for immediate use by water utilities. This will be achieved through the following aims and objectives. However, it should be acknowledged that mixture effects which are usually accounted for using biomonitoring methods will not be accounted for in this study which will be based on chemical analysis and evidence from the literature. Such effects are not within the scope of the current study.

1.8 PROBLEM STATEMENT

In South Africa, drinking water utilities mainly monitor the water quality variables as stipulated in the South African National Standard. [106] However, organic variables are neglected since only a few variables are listed for compliance monitoring. Furthermore, worldwide, there are many approaches for the selection, prioritization and subsequent monitoring of organic variables. It is evident that there is no generic approach to the selection, prioritization and monitoring of organic variables by the Drinking Water industry. Of these approaches, none of them has considered the drinking water value chain with emphasis on the system assessment from catchment to tap.

1.9 AIMS AND OBJECTIVES

1.9.1 Aim

The aim of this study is to develop a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain (from source to tap). To achieve this, the following specific objectives need to be accomplished.

1.9.2 Objectives

- Critical evaluation and synthesis of the available literature on the approaches for the selection and prioritization of organic variables of priority to the drinking water industry
- Develop a generic protocol for the selection and prioritization of organic variables for monitoring in the drinking water value chain.
- Define the criteria for inclusion and exclusion of organic contaminants in the protocol.
- Validate the generic protocol in a selected drinking water value chain.
- Re-assessment of the developed generic protocol for the selection and prioritization of organic variables for monitoring in the drinking water value chain.
- Compile the final generic protocol for the selection and prioritization of organic variables for use by the drinking water industry

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CHAPTER 2 SELECTION AND PRIORITIZATION APPROACHES FOR ORGANIC CONTAMINANTS: A REVIEW

2.1 INTRODUCTION

Selection and prioritization approaches are typically intended to be fairly simple and quick methods for determining the health and environmental hazards posed by the use and release of chemical substances into different environmental systems. [1,2] Approaches that prioritize chemicals according to their importance as environmental contaminants have been developed by government agencies and private industries such as the Environment Canada's Canadian Environmental Protection Agency (CEPA), [3] the United Kingdom's Institute for Environmental Health (IEH),[4] the European Community's Oslo and Paris (OSPAR) [5] convention exercise for the protection of the Northeast Atlantic marine environment and the European Union (EU)'s combined monitoring based and modeling based priority setting scheme (EU-COMMPs). [6]

In drinking water quality monitoring programs, the focus is on the detection, prevention and management of all contaminants that pose a threat to human health. In order to protect the health of consumers and ensure that drinking water is clean, free from any substance that can be deleterious to health and has an acceptable appearance (in terms of taste, odour and colour), standards are set for the most common substances (parameters) that can be found in drinking water, and require regular monitoring and testing. Hence, the approach taken must be health risk assessment. From the above discussion, it is evident that using the occurrence, exposure or health effects criteria or a combination of either of the three one can successfully select and prioritize organic contaminants for a particular purpose. This purpose is usually a risk management action designed to protect public health. However, there is a need to use criteria that is reflective of the characteristics and needs of the Drinking Water industry.

In this chapter, these schemes and others specifically intended for drinking water contaminants are reviewed. The objective is to understand the extent to which existing selection and prioritization approaches provide relevant guidance for developing a generic protocol for the selection and prioritization of organic variables for monitoring in the drinking water value chain. The assumption is that current selection and prioritization methodologies are not suitable for addressing the present challenges faced by water services providers in managing organic contaminants that threaten drinking water supplies and pose health risks for consumers especially in developing countries.

Based on the various elements mentioned above, a criterion for reviewing the various selection and prioritization methodologies presented in the literature has been summarized. [Figure 2.1]

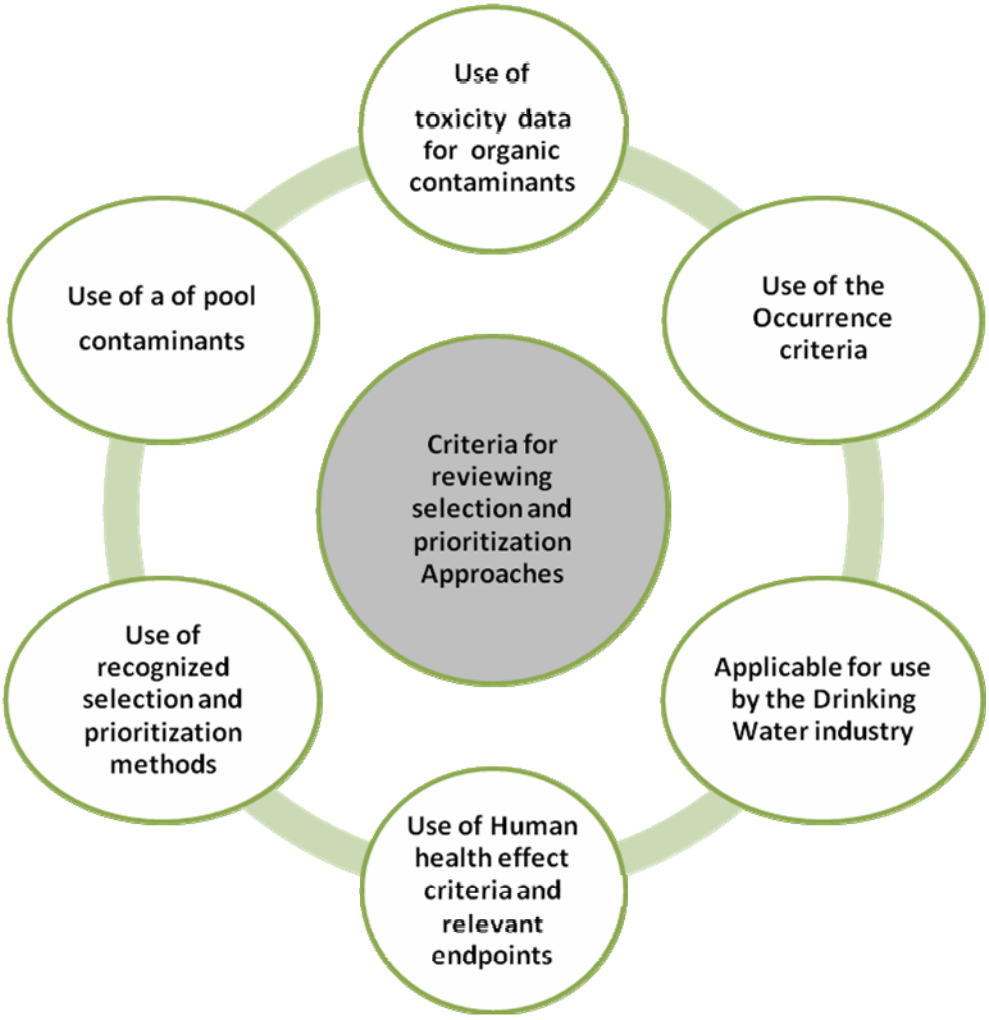

Figure 2.1: Review criteria for the selection and prioritization Approaches

2.2 SELECTION AND PRIORITIZATION APPROACHES BY GOVERNMENT AGENCIES AND PRIVATE INDUSTRIES

2.2.1 The United States Environmental Protection Agency (USEPA) approach

In the United States of America, the Environmental Protection Agency (EPA) is responsible for researching and setting national standards for a variety of environmental programs, and delegates to states and tribes the responsibility for issuing permits, monitoring and enforcing compliance. [7] Where national standards are not met, EPA can issue sanctions and take other steps to assist the states and tribes in reaching the desired levels of environmental quality. [7] The Safe Drinking Water Act (SDWA) directs the Agency to consider health effects and occurrence information for unregulated contaminants to identify those contaminants that present the greatest public health concern related to exposure from drinking water.[7-10] The USEPA uses a three step approach to the selection and prioritization of contaminants for analysis in drinking water. [Figure 2.2]

2.2.1.1 Step I: Compiling the universe "Pool of contaminants" to select from

The USEPA proposes that in order to identify the universe of potential contaminants there is a need to identify data sources, retrieve data elements, identify supplementary data sources, implement surveillance processes and evaluate nominations. Two hundred and eighty four (284) data sources were assessed for compiling the universe of potential drinking water contaminants. According to their procedure the pool of contaminants will include among others, naturally occurring substances, water-associated microbial agents, chemical agents, and products of environmental transformation of chemical agents, reaction by-products, and metabolites in the environment, radio nuclides, biological toxins and fibres.[10] The focus of the method is on the wider spectrum of all potential drinking water contaminants. [Figure 2.2]

The "universe" of potential contaminants is compiled based on two principles;

- The universe should include those contaminants that have demonstrated or have potential ***occurrence in drinking water***.
- The universe should include those contaminants that have demonstrated or have the potential ***to cause adverse health effects***.

Active surveillance and nomination/evaluation processes need to be conducted to ensure timely identification of information relevant to new and emerging agents. The contaminants not passing the screening criteria remain in the universe. [10]

2.2.1.2 Step II: From the "universe" of potential contaminants to Preliminary candidate contaminant list (PCCL)

The next step in the CCL selection approach involves narrowing the universe of chemicals compiled above to a PCCL (Figure 2.2). The USEPA maintains that the screening process be based on a contaminant's potential to occur in public water systems and the potential for public health concern. [10, 11]The screening approach identifies;

- Contaminants that are demonstrated to have relatively high toxicity with high potential to occur in Public Water Systems (PWSs) (I in Figure 2.3).
- Contaminants that are demonstrated to have relatively high toxicity with minimal actual or potential occurrence in drinking water (II in Figure 2.3).
- Contaminants that are demonstrated to have high potential to occur in PWSs with relatively moderate toxicity (III in Figure 2.3) and
- Contaminants that are demonstrated to have high potential to occur in PWSs with relatively moderate toxicity (IV in Figure 2.3)

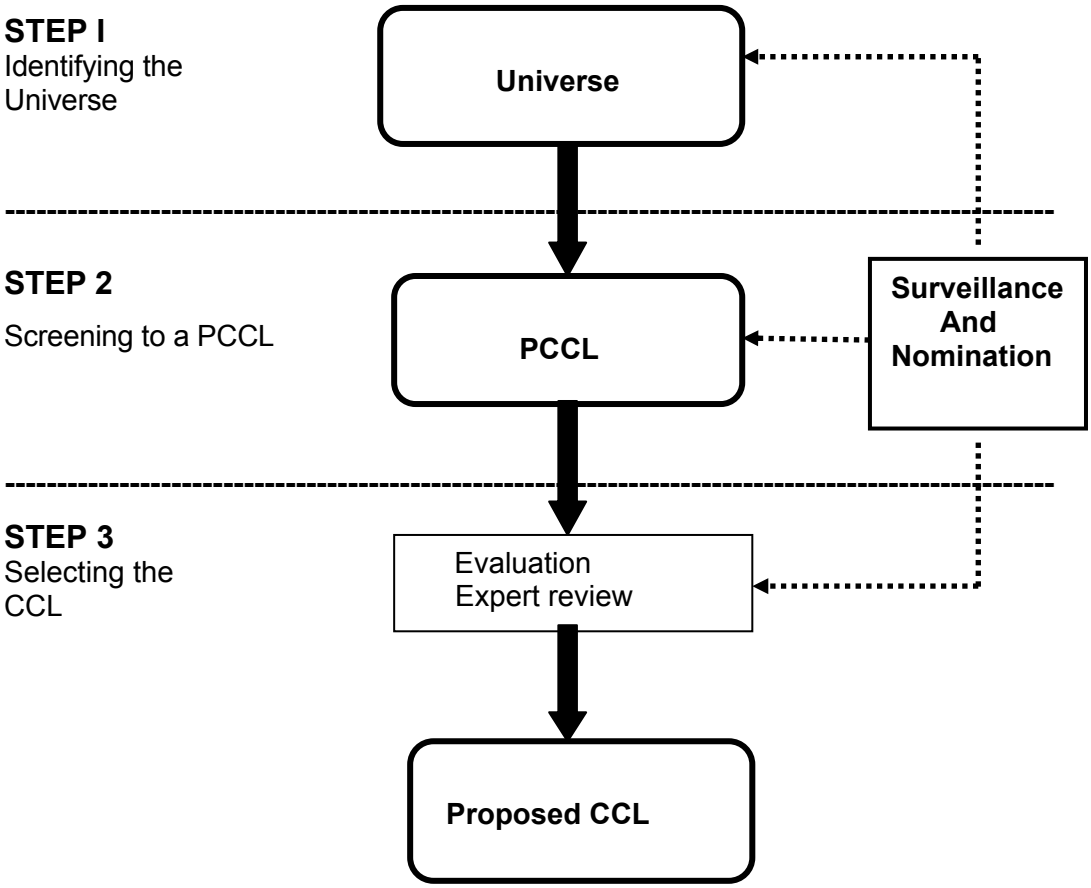

Figure 2.2: USEPA selection and prioritization approach for drinking water contaminants, schematic of CCL classification process. [10]

The basic framework used by the USEPA in screening the universe is shown in Table 2.1.

Occurrence data elements

The USEPA evaluated the occurrence data elements for each chemical and placed them on the horizontal axis of the screening table. [Table 2.1] In assessing the data, the USEPA found that the data elements that represent a chemical's potential to occur in drinking water vary greatly. However, the goal of the organization was to determine which data elements best represented the potential to occur in drinking water. [10]

The data evaluated included;

- Finished water-measures of concentration and frequency detections
- Total Releases into the environment-pounds per year and number of states releasing the chemical
- Pesticide application-pounds per year and number of states applying the pesticide
- Production volume-pounds per year
- Descriptive data-likelihood of occurring in drinking water, for example characterization as a disinfectant by-product or a drinking water treatment chemical.

Table 2.1: The basic framework used by the USEPA in screening the universe [Step I] [10]

	Occurrence
Health effects	Low to high occurrence →
Increasing Toxicity ↑	Pass to the PCCL Do not pass to PCCL

The approach considers and uses as many of the available types of health effects and occurrence data identified in the data source evaluation as practical. [Figure 2.3]

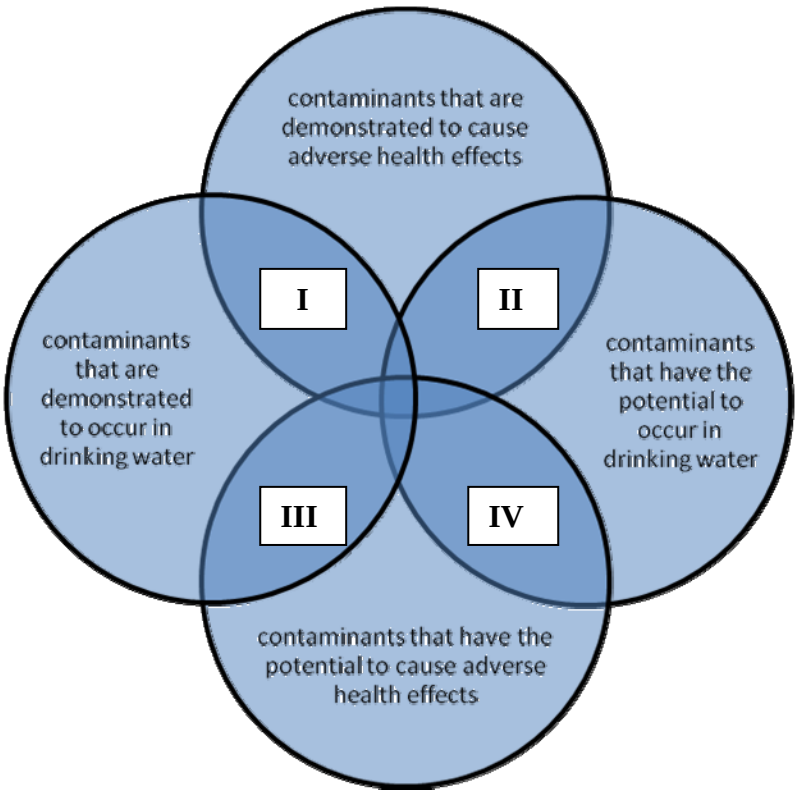

Figure 2.3-USEPA Screening criteria for drinking water contaminants-modified from EAWAG, 2002. [11]

In addition to the occurrence and health effect criteria, the USEPA uses the availability of treatment methods for the removal from drinking water and analytical methods for successful measurement of the contaminant in drinking water. The later are used as the screening criteria. The health effect information included quantitative, descriptive or categorical information. To obtain a final Preliminary Candidate Contaminant List (PCCL), consultation with experts in the various fields and the public is also done. [10]

The attributes used to score health effects and pass screening to the PCCL are given in Table 2.2. The table gives the health effects data elements that are potency measures for the universe data elements partitioning based on toxicity. To determine whether a contaminant will pass to the PCCL, environmental release and production volume were used. [10]

The hierarchy used in importance followed; finished water or ambient water > environmental release data > production data.

Table 2.2: Criteria for a chemical to pass screening to the PCCL [Step II] [10]

Health effects	Occurrence by data type		
	Finished ambient water concentrations	Release amount per year	Production volume per year
Toxicity Category 1	All concentrations	All amounts	All amounts
Toxicity Category 2	≥ 1 µg/l	≥ 10,000 lbs/yr	≥ 500,000 lbs/yr
Toxicity Category 3	≥ 10 µg/l	≥ 100,000 lbs/yr	≥ 10 M lbs/yr
Toxicity Category 4	≥ 100 µg/l	≥ 1M lbs/yr	≥ 50 M lbs/yr

The USEPA used descriptive cancer data to group data elements into toxicity categories [Table 2.3] that provide gradation based upon the strength of the data. [10] The health effect data such as the R_fD, NOAEL, LOAEL, MRDD and LD_{50} values were used. [Table 2.4]

Table 2.3: Partitioning of cancer data based on Tumorigenic dose [TD50]

	TD50	**EPA**	**IARC/HC**	**NTP**	**NCI**	**DSS-Tox**
Toxicity Category 1**	<0.1	Group A, human carcinogen	Group 1	CE 2 species/2 sexes or 2 species, or 2 sexes	P 2species/2 sexes or 2 species, or 2 sexes	H
Toxicity Category 2	0.1-100	Group B1 & B2 likely carcinogens	Group 2A	Combinations of CE, SE, EE and NE	Combinations of P, E, and N	HM
Toxicity Category 3	>100	Group C suggestive of carcinogenicity	Group 2B	Combinations of CE, SE, EE and NE	Combinations of E and N	M & LM

** cancer data placed data in only three highest toxicity categories CE-Clear evidence, SE-some evidence, EE-equivocal evidence, NE-no evidence, P-positive, N-negative, E-Equivocal, H-high probability, HM-high to medium probability, M-medium probability, LM-Medium to low probability.

Sources for the descriptive cancer data included, USEPA cancer groupings, IARC cancer groupings, the National Toxicity Programme (NTP) weight-of-evidence findings from cancer bioassays and the USEPA water disinfection by-products with carcinogenicity estimates (DBP-CAN) groupings based on carcinogenic potential derived from Quantitative Structure Activity Relationships (QSARs) projections. The cancer data is based on Tumorigenic dose (TD_{50}) .[Table 2.3] This is the dose-rate which if administered chronically for the standard life span of the species will have a 50% probability of causing tumours at some point during that period. [10]The USEPA chose a conservative approach in the screening process to categorize each

chemical's toxicity and evaluated all the available health effects dose-response and categorical data elements for a given chemical.

Table 2.4: Health effect data elements (potency measures for universe data elements partitioned based on toxicity, mg/kg/d or mg/kg) [10]

	RfD	NOAEL	LOAEL	MRDD	LD50
Toxicity Category 1	<0.0001	<0.01	<0.01	<0.01	<1
Toxicity Category 2	0.0001- < 0.001	0.01-<1	0.01-<1	0.01-<1	1-<50
Toxicity Category 3	0.001- < 0.05	1-<10	1-<10	1-<10	50-<500
Toxicity Category 4	0.05- <0.01	10-<1000	10-<1000	10-<1000	500-5000
Toxicity Category 5	> 0.1	>1000	>1000	>1000	>5000

Disinfection by-products (DBPs) and drinking water additives that lacked quantitative occurrence data but fell in the toxicity category 1 or 2 were added because of their high probability for being present in disinfected and treated drinking water. All toxicity category 1 chemicals (most toxic) were captured regardless of their occurrence category. **From a universe of 6000 the USEPA ended up with 532 chemical contaminants in the PCCL.**

2.2.1.3 Step III: PCCL to Candidate Contaminant List (CCL)

Once the PCCL has been identified and agreed upon by all stakeholders, the USEPA proposes the use of a prototype classification tool for the prioritization of contaminants on the PCCL to obtain priority contaminants that will be listed on the Candidate contaminant list (CCL). The following steps would be involved in the development of the classification process;

- Development of attribute scoring protocols
- Application of the classification models
- Evaluation of the classification model output and selection of the CCL
- Development of the training data set

At this stage, the expert judgment is important because occurrence and health effects data may not be known, even for some of the most harmful contaminants. These contaminants should not be overlooked due to a lack of information. According to the USEPA, the CCL selection process should be repeated for each list development cycle to consider any new information that may have become available since the last CCL was finalized. [10]

The five hundred and thirty two (532) chemical contaminants obtained from the universe were considered. The USEPA used structured classification model as tools to evaluate and identify drinking water priority contaminants. The model results were used to prioritize the chemicals and the best available data to identify contaminants that may occur in public water systems and

cause adverse health effects. The USEPA used the health effects and occurrence attributes to develop the scales and scoring protocols. [10]

Health effect attributes

Potency and severity are the attributes used to describe health effects. USEPA defines potency as the lowest dose of a chemical that causes an adverse health effect (LOEC) and severity is based on the adverse health effect associated with the dose used to define the measure of potency. [10] Potency was scored based on the dose that produced the adverse effect and severity was scored based on the health related significance of the adverse effect e.g. from dermatitis to organ effects to cancer. These two attributes are linked in that the severity is linked to the measure of potency. [10] The R_fD, cancer potency (concentration in water of 10^{-4} cancer risk), the NOAEL, LOAEL and LD_{50} were used to evaluate potency. The EPA selected 200 chemicals to calibrate the potency scoring protocols. [10] The organization used a log-based distribution to establish a potency scoring equation for each toxicity parameter. [10] This was accomplished by assigning the most frequent (modal) value in each distribution a score of 5 on a 10 point scale. [10] For example, when the toxicity parameter was one log more toxic than the modal value a score of 6 was assigned. Similarly, when the parameter was one log less toxic than the modal value the score of 4 was given and so on. A different equation was used for each measure of toxicity. [10] The scoring equations for potency are shown in Table 2.5

Table 2.5: Scoring equations for potency proposed by the USEPA

• R_fD score	=	10 - (log10 of R_fD + 7)	(2)
NOAEL score	=	10 - (log10 of NOAEL + 4)	(3)
• LOAEL score	=	10 - (log10 of LOAEL +4)	(4)
• $LogLD_{50}$ score	=	10 - (log10 of LD_{50} + 2)	(5)
• 10^{-4} cancer	=	10 - (log10 of the 10^{-4} cancer risk +6)	(6)

Scoring severity

Severity refers to the relative impact of an adverse health effect. Just as toxicity increases with dose, the severity of the observed effect also increases for example, a low dose effect could be a simple increase in liver weight while the same chemical could cause cirrhosis of the liver. LOAEL was used to score severity. [Table 2.5, 10]

Occurrence Attributes

Detections in drinking water or amount released into the environment were used to determine the prevalence which measures how widespread the occurrence of the contaminant is in the environment or how widely the contaminant may be distributed based on the spatial distribution

and magnitude based on the amounts. [10] However, where production data were used to determine prevalence there was no corresponding direct measure of magnitude, so persistence and mobility data were used as surrogate indicators of potential magnitude. Two hundred and seven (207) chemicals with available data were used. [10] The relationship between production or even environmental release data and actual occurrence in drinking water is complex. Where actual water measurements are available, they are the preferred data element to score prevalence because they are the most direct measure of occurrence in drinking water. The USEPA selected the following hierarchy for scoring;

- Percentage of Public Water Systems with detections (national scale data)
- Percentage of ambient water sites or samples with detections (national data scale)
- Number of states reporting application of the contaminants as a pesticide
- Number of states reporting releases (total) of the chemical
- Production volume in pounds/year.[10]

The USEPA used the persistence and mobility for chemicals with only production data as the basis of the magnitude attribute. The same scale was used for both organic and inorganic contaminants. The organization based the persistence and mobility scores on chemical and physical properties combined with environmental fate parameters. [10] Persistence and mobility act as measures of potential magnitude because both fate and transport or mobility affects the amount of a contaminant to be found in water. The length of time a chemical remains in the environment before it is degraded (persistence) affects its concentration in water. [10] The EPA used organic carbon partition coefficient (K_{och}), the octanol/water partition coefficient (K_{ow}), the soil/water distribution coefficient (K_d), Henry's law coefficient (K_h or H_c) and solubility to measure mobility of a chemical in the environment. [10] For persistence, half life ($T_{½}$), measured and modelled degradation rate were used. Classification models were then applied to training data sets (TDSs). [10] The classification models used statistical approaches for pattern recognition and derivation of mathematical relationships. Lists or not list (de L? or NL?) decisions were made. Using the parameters for mobility in the environment and persistence, five models were evaluated of which three models, Artificial Neural Network (ANN), Quick, Unbiased and Efficient Statistical Tree (QUEST) and Linear regression models demonstrated consistent performance when trained and evaluated with the training data set (TDS).[10]

Both a straightforward, additive approach and a collective rank-order approach were initialized to provide a prioritized listing of contaminants to be considered further and evaluated for possible inclusion on the draft CCL. **Out of the 532 chemicals on the PCCL, thirty two chemicals did not have data; hence 500 were considered [10].** The PCCL consisted of chemicals with variable health data, ranging from reference doses (R_fD) to lethal doses (LD_{50}) and occurrence

data ranging from measured water concentration data from public water systems to production volume data, the characterization tagged data elements with high certainty and low certainty. The combined certainty to measure for a single contaminant (i.e. health effects and occurrence tags) was used to place contaminants in bins of high, medium and low certainty. [10]

The high certainty bin consisted of chemicals with direct occurrence measured in water and well studied data for health effects. Four groups of chemicals were placed on the CCL based on their modelled scores, the potency-concentration ratios, where available and estimate of data certainty. 10] These included the chemicals in the high certainty bin with finished or ambient water data and potency/90th percentile concentration ratio of 10. [10] Pesticide chemicals in the medium certainty bin with modelled surface and/ or ground water data that yielded bin potency concentration ratios of 10 and chemicals in the medium certainty bin with release data that gave modelled L or L-L? Ranking and 27 chemicals in the low certainty bin that were added to the CCL as recommended by the public in response to EPA's Federal Register notice no. 71FR60704. [10] The potency and the concentration of the substance in water were used in the development of a ratio that was used to select contaminants for the draft CCL from the high certainty bin. Chemicals not selected from the draft CCL remained on the PCCL until additional occurrence or health effects data became available to support their re-evaluation. In selecting the CCL, adverse health effects that may pose greater risks to subgroups which represent a meaningful portion of the population were considered. Adverse health effects associated with infants, children, pregnant women, the elderly and individuals with a history of serious illness were evaluated. [10] The non-availability of toxicity data was a challenge. **Of the 500 chemicals on the PCCL, 44 were listed for the Contaminant Candidate List (CCL), 47 not listed and the rest were not well defined.** [10]

2.2.1.4 Assessment of the USEPA Approach [Figure 2.2]

The USEPA methodology uses a contaminant pool, the "universe" of potential contaminants for drinking water. [Step I, Figure 2.2] It is indicated in the approach that two hundred and eighty four (284) data sources were used and all chemical agents were targeted including biological, natural occurring and radiological parameters. The resultant "pool of contaminants" had 6000 entries. This data set is too big for this type of exercise especially considering the degree of heterogeneity. It would be difficult to manage given the diversity of physico-chemical properties and mechanism of action for toxicity or respective health effects on target organisms including human beings. It will therefore be difficult to apply common screening criteria to the whole set. This is seen in the way the group uses data sets for different criteria application. From these observations, the following disadvantages can be highlighted:

- There are biases since the screening criteria may not coincide with the user's goals.

- Subjective interpretations of data elements may skew results.
- Compounds with known issues/data more likely to be included than emerging contaminants.
- Certain databases are proprietary accessible only by subscription that could hinder transparency.
- Database incompatibilities. Nomenclature and search fields vary among databases
- Weak link issue-recombined databases are only as current and accurate as least robust sub-database.

The USEPA uses recognized selection and prioritization methods. This is reflected in the model used. [Figure 2.2] This is a positive aspect to note and it could be adopted in the current proposed protocol. Three steps, namely; "identifying the universe" which is synonymous to selecting the "pool of contaminants", screening to a preliminary contaminant candidate list (PCCL) and finally selecting the CCL which is the equivalent of the prioritization step.

The occurrence, toxicity and human health effects criteria and relevant end points are used to select, screen and prioritize chemicals. Hence, recognized selection and prioritization approaches are used. However, in step three of the method the use of many models is proposed which might hamper the objectivity and reliability of the method. This disadvantage emanates from the management issues mentioned in the preceding section. Many attributes used to select and prioritize contaminants leading to less objectivity of the approach. Use of training data sets for different criteria is proof that the occurrence and health effects attributes were not applied consistently across the same pool of contaminants. [10] This is also observed in the application of different attributes to different data sets. The distribution graphs used to estimate potency might give different potencies for different situations which constitutes a major disadvantage, for example, the distribution of the 10^{-4} values for cancer risk was skewed with values up to 5 orders of magnitude above the modal value (more potent carcinogens) but only 2 orders of magnitude below the mode (less potent carcinogens) . This particular criterion might be difficult to apply to non-carcinogens.

The following advantages are however, recognized in the USEPA programmes;

- Relevance-records are pre-screened for inclusion in discreet databases on the basis of key attributes.
- The use of stakeholder consultation and tacit knowledge within the Water industry to arrive to relevant conclusions on adoption of contaminants onto the PCCL or CCL, referred to as "expert judgement" in the methodology is an advantage as this allows all views to be taken into consideration and errors to be minimized.

- More robust search capabilities. Discrete databases are typically designed for special searches. [10]
- There is more data per record which is economical.
- Logistical benefits include potentially less cost per record, for publicly available databases.
- Modular approach possible can merge or recombine multiple databases if elements are consistent.

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However, the conceptual framework for the screening approach presented in Figure 2.2 is relevant and user friendly for use by water utilities. This should be followed by a careful selection of occurrence, health effect and/exposure attributes that will be used to prioritize the chemicals on the PCCL. These criteria must be applied to the whole set of chemicals and data set gaps attended to using appropriate procedures. The conceptual model and the approach used for the occurrence criterion [Figure 2.3] will be adopted for this study. Another positive aspect to adopt is the use of criteria reflective of the Drinking Water industry perspective such as the availability of methods for the removal of particular contaminants during drinking treatment and the availability of methods for measuring the contaminants in drinking water. Hence, the applicability of the approach for use by the Drinking Water industry is highly possible by adopting the positives that are highlighted in preceding sections.

2.2.2 THE UNITED KINGDOM, INSTITUTE FOR ENVIRONMENT AND HEALTH (UK, IEH) APPROACH

The IEH method for ranking chemicals by their fate in the environment and potential toxic effects in humans following non-occupational exposure was developed in 2004. [Figure 2.4] The IEH followed the steps shown in the model to select and prioritize the organic contaminants on the "existing chemicals list in the UK".

2.2.2.1 Selecting the "Pool of contaminants"

The IEH scheme during the first stage determines which of the many thousands of chemicals in the environment should be selected and incorporated into the screening process. As the scheme aimed to prioritise existing chemicals, substances that were subject to legislation, regulation or guidance or that had recently been reported as being of environmental concern were identified and incorporated into a spreadsheet. [4]

The different legislation, regulations or guidance documents from which the individual chemicals or groups of compounds were obtained were tabulated, indicating the country or organization of origin. [4] In total a pool of nearly 600 chemicals or group of chemicals were

added to the spreadsheet. In addition further information was obtained through a postal questionnaire survey of Environmental Health Officers (EHOs), Directors of Public Health (DsPH) in Great Britain and the general public on compounds that were perceived to be of greatest concern. [4] The objective of the survey was to identify specific compounds (and risk issues) that are the cause of concern to the general public as perceived by those who filled in questionnaires and those who are active in the field of environmental health during the course of their professional activities. [4]

2.2.2.2 Screening the "Pool of contaminants"

The IEH model uses physicochemical properties and toxicological data to assess the potential fate and transfer of chemicals between different environmental compartments and to predict the potential human exposure to toxic chemicals through the inhalation of contaminated air and the ingestion of water and food. [Figure 2.4] Physico-chemical properties were identified as in Tables 2.6 and 2.7. [4] Based on the values for each parameter, scores were assigned and chemicals ranked according to final scores. The preliminary list was prioritized according to their behaviour in the environment and mammalian toxicity to produce a short list. [4] The occurrence of chemicals in matrices of concern was considered as one of the major attributes. [4] The chemical's likelihood to partition between media [4] was considered. It was assumed that a compound once it gets to the environment, may behave in one or more of the following ways:

- Stay in the pure phase of the substance;
- Partition to the atmospheric environment;
- Partition to the water environment;
- Partition to the solid phase by sorption to a surface or formation of a solid in solution, solid organic matter phases. [Table 2.6]

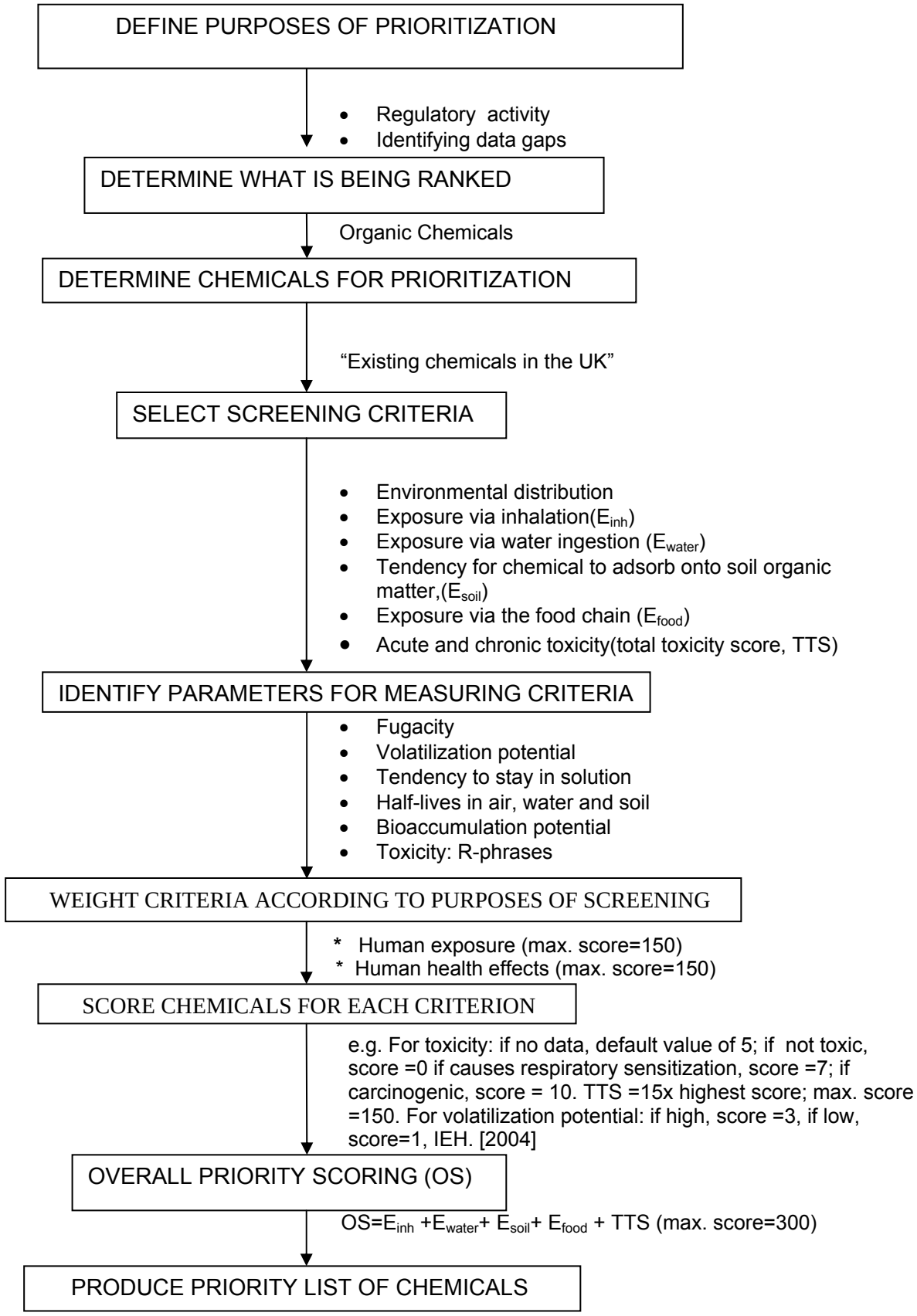

Figure 2.4: Model used in the prioritization scheme [4]

A new property, fugacity is introduced. [Figure 2.4] Fugacity is regarded as the escaping tendency of a chemical from a phase. [4] It is used to model the concentrations of a substance in different environmental compartments [water, air, soil, sediment, suspended solids and fish]. The model estimates the proportion of a compound likely to partition between these compartments based on a standard release of the chemical into the environment. [4]

A sequence of Level I, II and III calculations can be made, which have increasing data requirements that results in increasing information requirements about the chemical's partitioning, its susceptibility to transformation, transport and the environmental process and chemical characteristics that most significantly influence chemical fate. [Figure 2.4] Cut-off values used to determine the fate of the compounds are presented in Table 2.7. The scheme identified chemicals that are a potential risk to humans as a result of their presence in the environment by assessing their potential for human exposure using persistency in terms of half-lives in air, water and soil and their potential to cause human health effects as reflected in Figure 2.4.[4]

2.2.2.3 Prioritization of chemicals

Algorithms and scores were assigned to each of the above criteria in order to prioritize the chemicals [Figure 2.4], "score chemicals for each criterion". [4] An arbitrary score was assigned for a chemical for each criterion, for example bio-accumulative potential or carcinogenicity on the basis of its comparative importance or priority. [4] Scores for each of the criteria were then weighted according to the importance of each criterion and integrated using specially formulated mathematical model to produce a final overall priority score by which chemicals could be ranked in order of increasing importance. [Figure 2.4] The IEH performed at Level I and used "Risk" phrases (R-phrases) to rank environmental chemicals for human health effects. R-phrases are used to classify and label commercial substances according to the possible hazards to humans resulting from their general use. [Figure 2.4] The public and professional perceptions of chemical risks were taken into consideration when selecting the final list of compounds that required more detailed risk assessment. [4]

The main purpose of the exercise was to develop a dedicated priority setting method capable of identifying chemicals in air, water, soil and foodstuff that might pose a significant risk to human health following low level environmental exposure. It was also developed to identify compounds that required further assessment and those with data gaps. The approach proposes that more detailed risk assessments be conducted at a later stage on those compounds prioritized as being of high importance.

Table 2.6: Physico-chemical properties used in evaluating environmental fate and behaviour developed by the IEH [4]

Physico-chemical property	Description	Criteria
Water solubility, S_w, mg/l	Describes the amount of chemical that can dissolve freely in a known quantity of water.	Persistence
Vapour pressure, V_p, Pa (N/m2)	Saturation vapour pressure of compound at defined temperature, potential of chemical to evaporate, atmospheric transport	Persistence
Henry Law 's constant, H_c ($Pa.m^3$/mol or dimensionless)	Equilibrium partition between constant between air and water at a defined temperature. Indicates the tendency of a chemical to volatilise from soil, water and plant surfaces into the atmosphere.	Atmospheric transport
Half-life in soil,	Time for half of initial concentration to be lost due to aerobic or anaerobic biodegradation. The reaction is of first order kinetics	Persistence
Half-life in water	Time for half of initial concentration to be lost due to hydrolysis, aerobic or anaerobic biodegradation. The reaction is of first order kinetics	Persistence
Bioconcentration factor in fish (BCF_{fish}), kg wet weight fish/litre of water)	Indicates the tendency of a compound to partition between different environmental compartments and is defined as the ratio between the concentration of a chemical in biota and the concentration in water at equilibrium.	Bioaccumulation
Fugacity	It is regarded as the escaping tendency of a chemical from a phase. It has units of pressure and can be related to concentration.	Fate in the environment, partitioning, transformation, transport

Table 2.7: Cut-off values and chemical categories developed by the IEH. [4]

Chemical Category	Partition between phases	Partition data required	Example of organic contaminants
Type 1	Chemical partitions to all phases	Solubility (S) in water, fat or lipid, Vapour pressure (Vp), Henry's Law constant (Hc), Octanol-water partition coefficient (Kow)	Chlorobenzenes
Type 2	Chemical does not partition to air, i.e Vp $<10^{-7}$Pa	Partition coefficient to solid surfaces and to organic carbon, solubility in water and fat	Linear alkylbenzene sulfonates
Type 3	Chemical does not partition to water, i.e S$<10^{-6}$ g/m^3	Partition to solids from air or pure phase	Long chain hydrocarbons, silicones and polymers
Type 4	Chemical is not volatile and is insoluble Vp$< 10^{-7}$Pa and S$<10^{-6}$g/m^3	Sorption properties from a pure phase to various solids	Large molecular weight substances e.g polyethylene

2.2.2.4 Assessment of the IEH, 2004 Methodology [Figure 2.1]

The IEH methodology is primarily focused on the determination of human health exposure to organic contaminants released to the environment. The methodology achieves this by identifying a pool of contaminants and using the occurrence criteria and toxicity data to establish any exposure risks to human beings. Recognized selection and prioritization approaches such as screening, ranking and prioritization are used during the various processes commensurate with the criteria presented in Figure 2.1. The IEH approach has the advantage of combining the physicochemical properties for fate and distribution, toxicological data and algorithms to screen the chemicals. However, the approach has limitations.The method is a simple screening process. [4] A more detailed assessment is necessary to determine the potential transfer through the various environmental compartments and the full extent of any adverse health effects. Default values assigned for scoring chemicals for each criterion might reduce the objectivity of the method as these are arbitrarily assigned.

The other disadvantage is the use of R-phrases. Although they classify and label commercial substances according to the possible hazards to humans resulting from their general use, namely ingestion, skin contact and inhalation they have disadvantages. R-phrases are designed for the purposes of classifying and labelling commercial substances, to inform potential users of the substances about the possible adverse health effects that can be incurred. This implies that there are no R-phrases for chemicals that are not produced commercially, that are produced unintentionally or that have been banned. Most organic contaminants that are of concern to the Water Industry such as disinfection by-products, organochlorine pesticides and their metabolites such as DDT and its metabolites, toxins and products of combustion fall in this category. The other challenge is that of different values of the R-phrases for the same compounds. Hence the R-phrases are used by the IEH as a surrogate for the hazard potential of substances. The use of production volume, pattern of use or scores to assess potential human exposure is an oversimplified approach to exposure assessment, as the scores do not take into account the extent to which these chemicals may enter the environment and or the environmental matrix into which the chemicals are released (air, water, landfill site, fish consumption).

The IEH methodology ‘s applicability to the Drinking Water industry is the adoption of its clearly defined steps and the use of physico-chemical properties which are crucial for developing or choosing the appropriate screening criteria for a particular group of contaminants. The group chose organic chemicals for the exercise which is one of the areas the industry is receiving challenges from given the risks presented by emerging organic contaminants.

2.2.3 THE EUROPEAN COMMUNITY (EC), OSLO PARIS (OSPAR), DYNAMEC APPROACH

The OSPAR Commission was founded as a result of the 1992 Oslo and Paris (OSPAR) Convention for the protection of the Northeast Atlantic marine environment. It includes 16 Western European countries together with the European Community (represented by the European Commission). [12] In addition, more than a dozen non-governmental organizations representing various environmental groups and industry also contribute to OSPAR activities. [12] In brief, the purpose of Dynamic Mechanism (DYNAMEC) is to serve as a tool to enable the OSPAR Commission in a transparent manner and using sound information to identify and select those hazardous substances that have to be addressed by the commission as a whole. The tool is then used to determine those hazardous substances that should be given priority in OSPAR's activities. In broader terms, DYNAMEC should help the OSPAR Commission as a first step in the implementation of its long-term strategy on the elimination of anthropogenic inputs of hazardous and radioactive substances to the Northeast Atlantic Ocean "within one generation," that is, by 2020. [12]The DYNAMEC mechanism consists of several interrelated steps and procedures that are summarized below and illustrated in Figure 2.5.

The OSPAR selection and prioritization approach, DYNAMEC also comprises of basically three steps;

- Initial selection
- Establishment of a ranking list for potentially hazardous substances and
- Final selection of the chemicals for priority action. [12-14]

2.2.3.1 Initial Selection, Selection of a "pool of contaminants"

Available databases were consulted for the initial selection. These comprised of the Nordic Substance Database with 18,000 registered substances, the QSAR database of the Danish Environmental Agency with 16,000 entries and the Dutch BKH/Haskoning database with 180, 000 entries. Based on the PBT (Persistence, Bioaccumulation and Toxicity) selection criteria, a preliminary list of relevant substances was established. At the same time the "safety net procedure" was used to screen substances for hazardous properties not selected by the PBT criteria set. Substances thus determined to be similar were also added to this preliminary list. [DYNAMEC, 1999]. In a further evaluation step, experts scrutinized the individual entries on the list for the plausibility and concluded on the preliminary selection of a list of approximately 400 substances of possible concern. [Figure 2.5] To complete the subsequent prioritization, data profiles were established. [12-14]

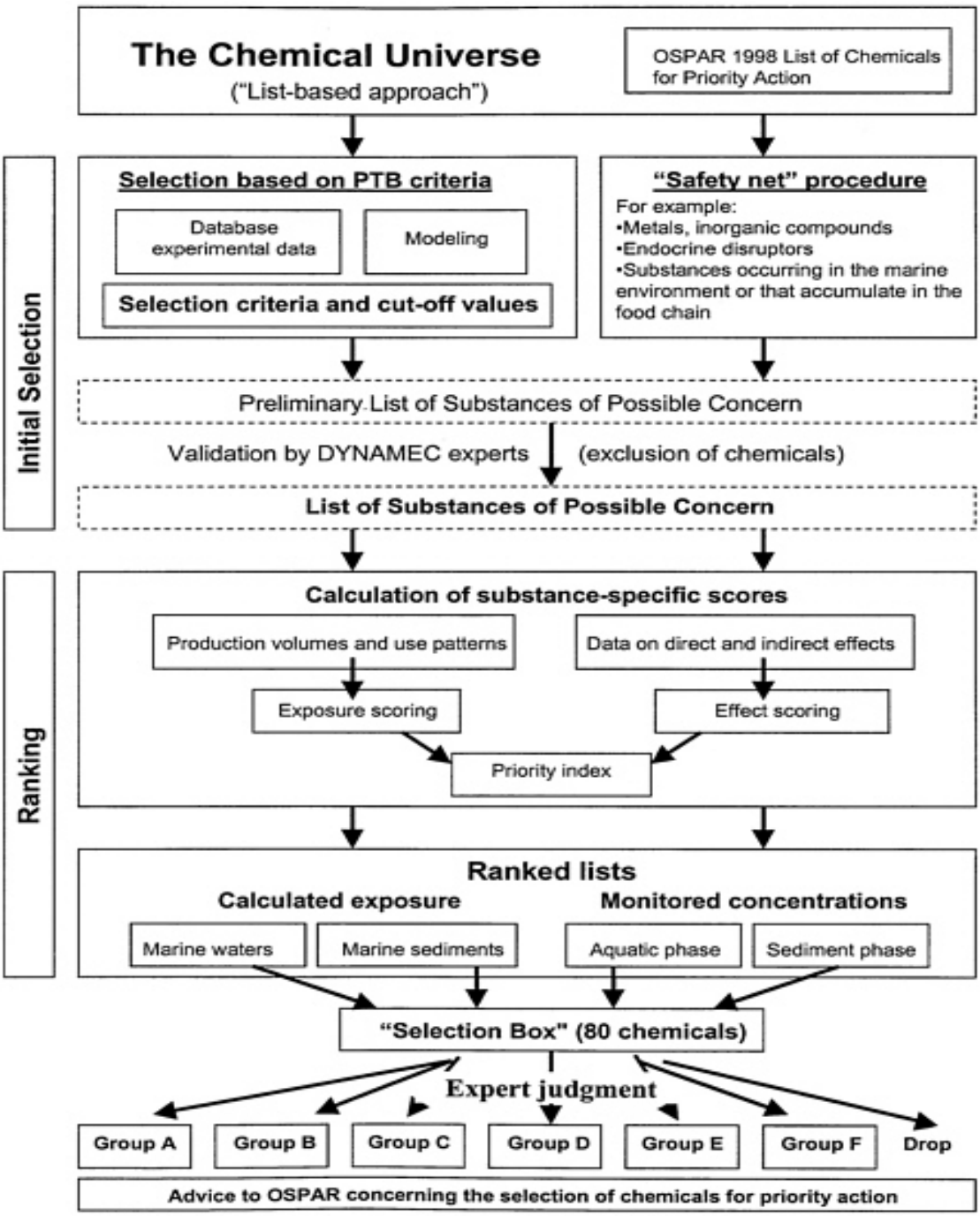

Figure 2.5: A dynamic Mechanism for the selection and prioritization of hazardous substances (DYNAMEC)-OSPAR COMMISSION [12]

2.2.3.2 Establishing a ranking list for substances of concern

After taking into account the overall structure and purpose of DYNAMEC, the least stringent selection criteria and corresponding cut-off values were ultimately applied to the hazardous substances under consideration. [Table 2.8]

Table 2.8: Categories of priority hazardous substances and cut-off values for PTB criteria according to the OSPAR-DYNAMEC procedure [12, 15]

Group	Description	Applied PTB cut-off values	Examples
I	Substances of very high concern(i.e ,POP-like substances or substances with severe PTB profile) and indication of production, use, or occurrence in the environment	P: not inherently biodegradable and B: log Kow ≥ 5 or BCF ≥ 5000 and Taq: acute L(E) C_{50} ≤ 0.1mg/l, long-term NOEC ≤ 0.01mg/l or Tmammalian: CMR or chronic toxicity	2,4,6-tris(1,1-dimethylethyl)-phemol,dicofol, endosulphan, methoxychlor, Octylphenol, EPN, Tetrasul, miconazole nitrate, Diosgenin, Trifluralin, Clotrimazole
II	Other initially selected substances with less severe PTB profile and indication of use or exposure	P: not inherently biodegradable and B: log Kow ≥ 5 or BCF ≥ 5000 and Taq: acute L(E) C_{50} ≤ 0.1mg/l, long-term NOEC ≤ 0.01mg/l or Tmammalian: CMR or chronic toxicity	Hexamethyldisiloxane, 1,2,3,4,5,5-hexachloro-1,3-cyclopentadiene, TBBA, 1,2,4-Trichlorobenzene, 1,2,3-Trichlorobenzene, 1,3,5-Trichlorobenzene 1-(1,1-Dimethylethyl)-4-methyl-benzene, Cyclododecane, Triphenylphosphine, Isododecane, Chlorpyrifos
III	Substances of very high concern (i.e ,POP-like substances or substances with severe PTB profile) but no indication of use or exposure	P: not inherently biodegradable and B: log Kow ≥ 5 or BCF ≥ 5000 and Taq: acute L(E) C_{50} ≤ 0.1mg/l, long-term NOEC ≤ 0.01mg/l or Tmammalian: CMR or chronic toxicity	Heptachloronorbornene, Flucythrinate, PCNs
IV	Other initially selected substances with no indication of use or exposure	-	Fenithrion, Isodrin, Pentachloroanisole, Fenpropimorph, Diazinon
V	Substances with PTB properties that are already heavily regulated or withdrawn from the market	P: not inherently biodegradable and B: log Kow ≥ 5 or BCF ≥ 5000 and Taq: acute L(E) C_{50} ≤ 0.1mg/l, long-term NOEC ≤ 0.01mg/l or Tmammalian: CMR or chronic toxicity	DDTs, Chlordane, PCTs,Aldrin, HCB,Toxaphene, Nitrofen, Heptachlor
VI	Endocrine disruptors that do not meet P or B criteria and are not natural hormones	-	Diethylstilbestrol, 17-ethynylestradiol, Butylphenol

P, Persistence, B, Bioaccumulation, Taq, Aquatic toxicity with L(E)C_{50} the lethal (L) or effect (E) concentration that affects 50% of the population;NOEC, No observed effect concentration; Tmammalian, Mammalian toxicity; BCF, Bioconcentration factor; CMR; Carcinogenicity, Mutagenicity and adverse effects on reproduction, Rose and Brinkman, 2005.

After establishing and applying the PTB criteria, the criterion for persistency was developed further to render it more specific to the marine environment. In a separate validation exercise, the cutoff criteria were also applied to the 246 substances (or groups of related substances) included on the OSPAR 1998 List of Candidate Substances. [12] The outcome of this exercise indicated that only 61 of the substances were identified as being of possible concern, while the remaining 185 were not due mainly to a lack of data and a very low potential for bioaccumulation. [12]

Under DYNAMEC, "hazardous substances" refers not only to substances or groups of related substances that are toxic, persistent, and liable to bio-accumulate, but also to those that are deemed by OSPAR to require a similar assessment approach, even if they do not meet the criteria for toxicity, persistence, and bioaccumulation. To select substances with an "equivalent level" of concern, DYNAMEC agreed to supplement the initial selections by a "safety net" procedure. [Table 2.9]

Table 2.9: Selection Box Groups. [12]

Group	Contents	Description
A	5(13)[a]	Substances of very high concern(i.e ,POP-like substances or substances with severe PTB profile) and indication of production, use, or occurrence in the environment
B	7(7)[a]	Other initially selected substances with less severe PTB profile and indication of use or exposure
C	8	Substances of very high concern (i.e ,POP-like substances or substances with severe PTB profile) but no indication of use or exposure
D	7	Other initially selected substances with no indication of use or exposure
E	20	Substances with PTB properties that are already heavily regulated or withdrawn from the market
F	6	Endocrine disruptors that do not meet P or B criteria and are not natural hormones
Drop	7	Substances that do not meet the initial selection criteria and should be deleted from the Draft Preliminary list of Substances of Possible Concern

[a]-These substances were initially selected as a result of reliance on QSAR data or experimental data, thus, the confidence in the assessment might be in doubt.

Specifically, DYNAMEC experts reviewed proposals from interested parties to include substances on the preliminary List of Substances of Possible Concern that they felt achieved such an equivalent level of concern. Thus, several substances were ultimately included on the

preliminary list using this mechanism. [12] The safety net procedure was also intended to address those substances such as metals, inorganic compounds and endocrine disruptors for which the criteria of persistency and bioaccumulation are generally not applicable. [12] The results of the initial selection of substances were examined by a group of experts established by DYNAMEC in order to check the plausibility and consistency of the substance-specific data and exclude those substances that had been incorrectly selected. [12] The ultimate outcome of the initial selection procedure was a List of Substances of Possible Concern for the marine environment. [Figure 2.5]

Use of Fact Sheets

DYNAMEC noted that the status of this list is not definite and could change as further information becomes available and in light of improved knowledge. The group decided that fact sheets should be prepared to aid further assessment of all listed substances of possible concern. [12] These fact sheets would provide comprehensive but concise background information, such as physical-chemical properties and production/use volume information where available. After producing and distributing the first set of fact sheets, subsequent work focused on expanding the fact sheets for 80 chemicals and groups of related chemicals that were later determined to require priority action [so-called “selection box” substances, Table 2.9]. DYNAMEC noted that additional related work would be necessary to complete fact sheets for all remaining substances of possible concern and to help locate and ascertain relevant data to fill gaps on the existing fact sheets. [12]

Flagging Substances

For a variety of reasons, the substances and groups of related substances identified by the initial selection, process will give rise to differing levels of concern. [12] In particular, a given substance may (1) have intrinsic properties similar to persistent organic pollutants (POPs) and fulfill the most restrictive set of cutoff points for PTB criteria; (2) have suspected endocrine disrupting properties; and (3) already be adequately addressed in other forums. Regarding the later, OSPAR could then evaluate whether to await the outcome of any relevant action or to initiate specific OSPAR action. [12] Since DYNAMEC sought to produce a comprehensive and feasible list of substances that are a threat to the marine environment, OSPAR agreed that any substances falling into one or more of these three categories should be “flagged” to ensure consideration in the revision of the existing List of Chemicals for Priority Action. [12]

2.2.3.3 Ranking of Substances on the list of substances of concern

In order to rank all substances or groups of related substances on the Preliminary List of Substances of Possible Concern, each was characterized with respect to its production

volumes, patterns of use, and/or measured occurrence in the environment. [12] The level of potential concern for each substance was assessed through use of an effect score (relative toxicity and liability to bio-accumulate) and an exposure score (relative level of predicted or measured occurrence in the environment). [12] The mathematical product of these two scores was used to help determine the relative risk for each listed substance. This process included automated data processing and was followed by expert judgment (that is on the basis of chemical fact sheets). In addition, DYNAMEC decided that calculated exposure estimations and monitored freshwater concentrations, both for the aquatic phase and in sediment, should be accounted for in the ranking process. [12-14] .

It is important to note that these ranking algorithms were based on those that had already been established for use in the previously reviewed COMMPS procedure. However, some algorithms or weighting factors were modified to render them more suitable for the marine environment. [12] In some cases, conservative default values were used when certain substance-specific data were not known or available. In addition, a significant obstacle that DYNAMEC had to overcome concerned restricted access to some data on production/use volumes for certain substances for reasons of confidentiality. [12] This meant that the application of the ranking algorithms, assessment of the outcome of the ranking, and the data used could be undertaken and validated only by a limited number of experts with unrestricted access to the data. [12-14]

For substances without sufficient information available to carry out the ranking, further action could not be undertaken until either adequate information became available or some other approach for determining the status of such substances was developed. [12] The ranking of the List of Substances of Possible Concern resulted in four lists:

- Substances associated with marine waters based on measured environmental concentration and the properties of the substances;
- Substances associated with marine waters based on modeled exposure scores (in turn based on calculation from production volume and use patterns);
- Substances associated with marine sediments based on measured environmental concentration and the properties of the substances; and
- Substances associated with marine sediments based on modeled exposure scores (in turn based on calculation from production volume and use pattern).[12-14]

The ranking however, also took into account effects of the so called CMR (carcinogenic, mutagenic, toxic to the reproductive system) substances that may enter the human body through the ingestion of contaminated sea food. Consideration was also given to persistence

in the calculation of the overall ranking score and differentiation of biodegradation was spread in the scaling. **Of the 400 substances in the preliminary selection list, only about 200 could be placed on the four ranking lists. [Figure 2.5, 12]**

To facilitate these discussions, a selection box of 80 substances (all chemicals) was extracted by combining the 48 top-ranked substances from the four ranked lists (excluding certain substances already included on the 1998 OSPAR List of Chemicals for Priority Action) with all initially selected substances that could fulfil the most stringent cut-offs for the PTB criteria or those that were previously flagged as endocrine disruptors.[12] DYNAMEC experts examined the 80 selection box substances on the basis of their expanded chemical fact sheets and established a basis for grouping these substances that is described in Table 2.9 above. Based on these groupings, DYNAMEC recommended that the OSPAR Commission consider adding the 12 substances included in Groups A and B when it revises the OSPAR List of Chemicals for Priority Action. Regarding the 20 total Group A and B substances that might be in doubt, DYNAMEC recommended that they should not presently be considered priority substances. However, interested parties were invited to provide more reliable data for these substances in 2000–2001 so that they might be considered with the rest of the Group A and B substances. DYNAMEC further recommended that the 15 substances in Groups C and D should not be considered as priority substances unless new data could be provided expeditiously to support their consideration. [12-14]

2.2.3.4 Assessment of the OSPAR COMMISSION METHODOLOGY [Figure 2.1]

The approach satisfies all elements prescribed in Figure 2.1 in that it proposes a pool of contaminants to be screened for the protection of the marine environment. A PTB screening criteria including cut-off values is proposed for persistence, bioaccumulation and toxicity as presented in Table 2.8. It is the only procedure which recognizes the fact that certain criteria can leave out contaminants of concern, hence the use of the “safety net” procedure which is used simultaneously with the PTB criteria to obtain the preliminary list of substances of possible concern. The approach also like the USEPA approach introduces validation of the lists by relevant stakeholders before confirming the list of substances of possible concern. Like the IEH methodology, the OSPAR DYNAMEC includes the scoring of exposure and human health effect for the substances. The product of the effect and exposure score gives priority index that will be used to rank the chemicals.

One unique feature of the DYNAMEC although similar to the IEH methodology is the fact that all matrices of concern are accounted for. The occurrence criterion is used both in a qualitative and quantitative manner through monitoring concentration levels in respective matrices of

interest. The lists ranked for each compartment is again verified by stakeholders before it passes on to the phase for priority action. Based on Figure 2.5, it is evident that the DYNAMEC procedure can be modified to suit the drinking water environment, where one will assess contaminants in the biota, sediment phase and aquatic phase. Also some of the steps in conceptual model can be adopted especially Step I of the model.

2.2.4 A USEPA approach using Quantitative Structure Activity Relationships (QSARs)

The U.S. EPA designed a simple prioritization scheme for determining which disinfection by-products (DBPs) may require additional research. [Figure 2.6] Quantitative Structure Activity Relationships (QSARs) were used. These are processes by which chemical structures are quantitatively correlated with a well defined process such as chemical reactivity or biological activity. A strong correlation may exist between structure and observed property, for example that of the number of carbon atoms in alkanes and their boiling points. There is a clear trend in the increase of boiling point with an increase in the number of carbon atoms and this can serve as a means to predict boiling points in higher alkanes. For example, a biological activity can be expressed quantitatively as in the concentration of a substance required to give a certain biological response. Additionally, when physicochemical properties or structures are expressed by numbers, one can form a mathematical relationship or quantitative structure activity relationship between the two. The mathematical expression can then be used to predict the biological response of other chemical structures. QSAR models usually work according to the following equation;

P = f (Dstructural, Delectronic, Dhydrophobic, Dx) + e
Where P is the properties (endpoint)
Ds,e,h,x are the descriptors of the molecule. [16]

Based on the preceding section, it is evident that QSARs represent predictive models derived from application of statistical tools correlating biological activity (including desired therapeutic effect and undesirable side effects) of chemicals such as drugs, environmental pollutants, toxicants with descriptors representative of molecular structure and/or properties. It is for this reason that QSARs/Quantitative Structure Property Relationships [QSPRs] are being applied in many disciplines such as risk assessment, toxicity prediction and regulatory decision in selection and prioritization exercises. [16]

2.2.4.1 Mechanism-Based Structure-Activity Analysis

Essentially, mechanism-based Structure Activity Relationship [SAR] analysis involves comparison of an untested chemical with structurally related compounds for which

carcinogenic activity is known. Considering the most probable mechanism(s) of action, the structural features and functional properties of the untested compound are evaluated and compared with reference compounds.[16] All available knowledge and data relevant to evaluation of carcinogenic potential of the untested chemical are considered. These include *a*) SAR knowledge base of the related chemicals; *b*) toxicokinetics and toxicodynamics parameters (including physicochemical properties, route of potential exposure, and mode of activation or detoxification) that affect the delivery of biologically active intermediates to target tissue(s) for interaction with cellular macromolecules or receptors; and *c*) supportive non-cancer screening or predictive data known to correlate to carcinogenic activity. A prediction of carcinogenic potential involves integration of all this available information with human expert intuition and judgment. [16]

In evaluating the DBPs both structural and functional criteria are applied. Basically, the structural moieties or fragments that may contribute to carcinogenic activity through a perceived or postulated mechanism are identified, and the modifying role of the rest of the molecule to which the structural moiety/fragment is attached is evaluated. [17] Whenever possible, comparison is made to a structurally related reference compound with known carcinogenic activity (tested preferably by the same route of administration as the chemical in question) to evaluate whether the difference in chemical structures may lead to an increase or decrease in carcinogenic activity. [17]

Functional criteria involve consideration of all the available short-term non-cancer predictive data and pharmacologic and toxicological capabilities correlated or associated with carcinogenic activity. Functional criteria complement structural criteria because structural considerations alone cannot forecast entirely new types of carcinogens. [17] Furthermore, functional criteria may serve as a means to confirm or cast doubt on the mechanistic assumptions made in applying structural criteria. Information that is highly useful for predicting carcinogenic potential includes data on oncogenes, tumour suppressor genes, genotoxicity and/or ability to bind covalently to DNA, apoptosis, cellular proliferation, immunosuppressant, and sub-chronic toxicity end points that are indicative or suggestive of carcinogenic potential. [17]Ideally, all of the available data should be evaluated with respect to predictive capability, strength of evidence, and relevance to the carcinogenic process and then integrated. Positive predictive tests and data covering all aspects of the carcinogenic process (initiation, promotion, and progression) should be given more weight than multiple tests detecting the same mechanistic end point. It is based on these principles that the USEPA developed the method for prioritizing DBPs. [12,18]

2.2.4.2 Selection of a "Pool of contaminants"

First, the U.S. EPA compiled a list of more than 600 DBPs from various disinfectant combinations that have been identified and cataloged by the U.S. EPA to serve as an important reference. [17] Additional DBPs were subsequently added as new information became available. Of these DBPs, the U.S. EPA considered only those DBPs found or detected in actual drinking water samples. DBPs found only through laboratory experiments were excluded because these experiments are often performed under conditions that are not representative of actual water treatment practices.[17] Thus, there is uncertainty as to whether DBPs identified in laboratory experiments can actually be found in drinking water samples.

2.2.4.3 Screening the "Pool of contaminants"

Several additional criteria included eliminating DBPs with incomplete chemical structure characterizations. [17] In addition, chemicals believed to be impurities from processes other than disinfection, such as leachates from treatment plant materials and laboratory equipment (e.g., naphthalene, 3-ethyl styrene), were eliminated. The list of 252 remaining DBPs was peer reviewed by chemists with expertise in DBP formation and identification to ensure, to the extent possible, that the chemicals in the list were all actual or probable DBPs. After these criteria were applied, 239 DBPs remained for research prioritization (Figure VIII).

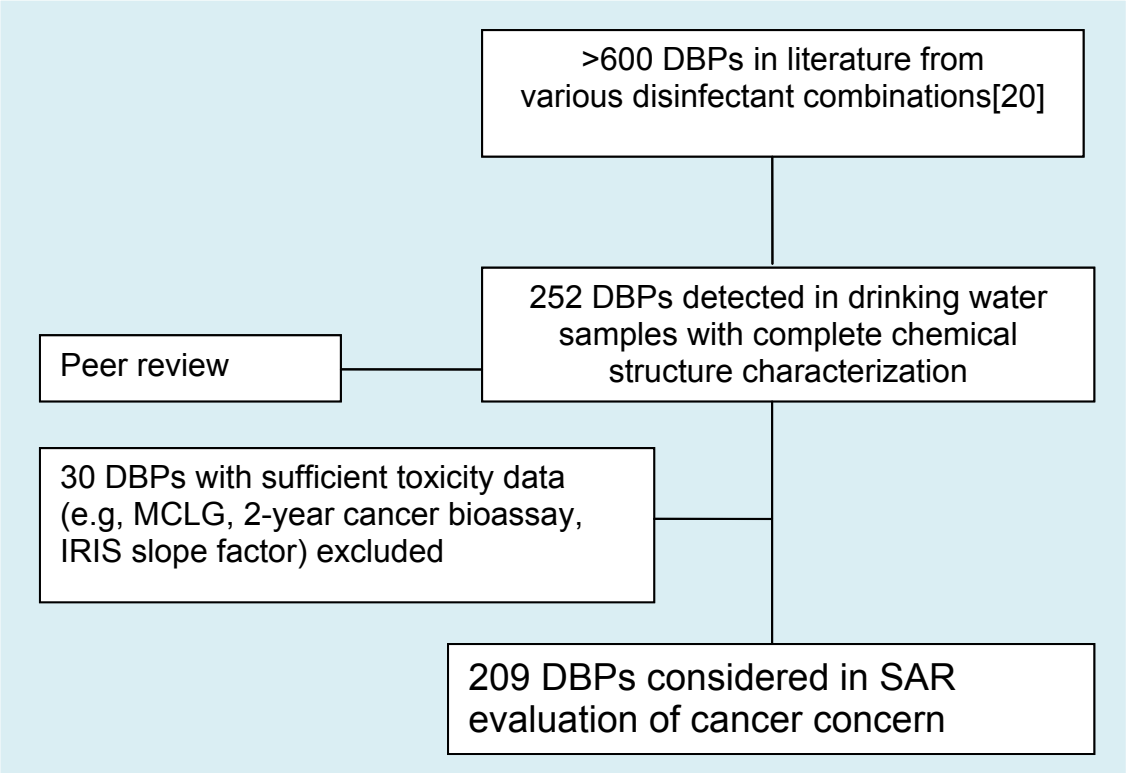

Figure 2.6: Selection of DBPs for SAR analysis, Woo et al. 2002 [17]

2.2.4.4 Prioritization, identification of those DBPs that have or will have a 2-year cancer bioassay data and occurrence data sufficient for making a Hazard assessment

The U.S. EPA identified those DBPs that have or will have 2-year cancer bioassay data and occurrence data sufficient for making a hazard assessment, and those DBPs for which sufficient bioassay data are/will be available but insufficient occurrence data currently exist. [17] The criteria for judging if sufficient toxicity data exist to conduct a cancer assessment were as follows:

- There is an MCLG from the Stage 1 DBP rule or past drinking water rules;
- The National Toxicity Programme (NTP), the U.S. EPA, or others have conducted or will conduct a 2-year cancer bioassay or
- There is an oral slope factor on the agency's Integrated Risk Information System (IRIS). [19]

The criteria for judging if sufficient occurrence data exist to derive a national estimate of exposure were as follows:

- There is an MCLG from the Stage 1 DBP rule or past drinking water rules, or
- The DBP is included in the information collection rule for DBPs that is collecting national occurrence data. Thirty DBPs were identified in this step and eliminated from SAR consideration.[Figure 2.6]

Two hundred and nine [209] DBPs were considered in the Structure Activity Relationship (SAR) evaluation. This involved comparison of an untested chemical with structurally related compounds for which carcinogenic activity is known. Considering the most probable mechanism(s) of action, the structural features and functional properties of the untested compound were evaluated and compared with reference compounds. [17] The functions involved ranking the carcinogenic potential of DBPs that met the following criteria:

- Detected in actual drinking water samples
- Have sufficient cancer bioassay data for risk assessment and
- Have structural features/alerts or short-term predictive assays indicative of carcinogenic potential. [17]

A semi quantitative concern rating scale of low marginal (M), Low-moderate (L-M), moderate (M), High-moderate (H-M) and high (H) was used along with delineation of scientific rationale. Of the 209 DBPs analysed, 20 were of priority concern with a moderate or high moderate rating. Of these, four were structural analogues of MX and five were haloalkanes that presumably will be controlled by existing and future THM regulation.[17] The other 11 DBPs, which included halonitriles (6), haloketones (2), haloaldehyde (1), halonitroalkane (1) and

dialdehyde (1) are suitable priority candidates for future carcinogenicity testing and/or mechanistic studies. [17]

2.2.4.5 Assessment of the USEPA QSAR Approach [Figure 2.1]

The USEPA method for the selection and prioritization of DBPs using QSARs starts with the compilation of a pool of contaminants for the exercise using sources relevant to the drinking water concerns. For example, the USEPA considered only those DBPs found in actual drinking water samples. [17] In this case the occurrence criterion, human health effects and applicability criteria are also satisfied. The USEPA considered the conditions for hazard expression by taking into consideration the appropriate routes of exposure for DBPs. An individual may be exposed to DBPs by different routes of exposure such as inhalation from showering, dermal from bathing or oral from tap water consumption. It is evident in the methodology that in evaluating the carcinogenic potential of each compound, the main routes of exposure were evaluated.[17] The SAR predictions presented focused mainly on the hazard potential via ingestion of drinking water, a major route of exposure to DBPs. A semi quantitative concern rating scale is used of low marginal (M), low-moderate (L-M), moderate (M), high–moderate (H-M) and high (H) has been used to prioritize the selected disinfection by-products. [17]

The USEPA approach has the advantage of readily available national data on the National toxicity programme (NTP) and the US IRIS database. [17] The group can be praised for attempting to find a solution to a problem on deciding on which DBPs are priority for analysis in the drinking water value chain. This is a cost-benefit analysis which will face the Drinking Water industry for centuries to come. That is the formation of DBPs known to have detrimental human health effects which is chronic in nature and can affect a small portion of the population than the control of water borne diseases through the use of disinfectants such as Chlorine.

However, like any other QSAR approach it is challenged by a number of factors. [17] Assumptions are made during the calculations since models are used. There is therefore unavoidable and variable margin of error associated with toxicity predicted using SARs since there are generally no real data from an *in vivo/in vitro* toxicity data or bioassay of the chemical in question. [17] Although SARs are calculated from chemicals with highly similar structures, small differences between chemicals in chemical-receptor molecular interactions may cause significant differences in the resultant toxicity response at a higher level. [17] There is also a problem of extrapolating from high concentrations that cause mortality in animals to low-level environmental exposure and hence concentrations to which human beings are exposed especially through drinking water. The approach does not allow for natural defence

mechanisms to be accounted for. Therefore one cannot contract the various predictions in terms of potency with respect to either cancer or developmental toxicity. [17]

The approach uses appropriate selection and prioritization methods in that the "pool of contaminants" which is the selected 600 DBPs is used. This is screened using available cancer data and the resulting 209 DBPs of concern prioritized further using the Structure Activity Relationship attributes. The occurrence and other criteria as envisaged in Figure 2.1 are not apparent in the method.

2.2.5 A QSAR/QSPR APPROACH FOR RANKING AND CLASSIFYING NON-IONIC ORGANIC PESTICIDES BASED ON ENVIRONMENTAL DISTRIBUTION, GRAMATICA, et al. 2004

QSAR/QSPR approaches have been used to prioritise organic pollutants according to their environmental distribution tendency.[16] Gramatica, et al. 2004 screened 54 non-ionic organic compounds which constituted of organic pesticides of different classes, namely, acetanilides, carbamates, dinitroanilines, organochlorines, organophosphates, phenylureas and triazines. [16] Like in the method by Gramatica et al. 2001, this approach was based on the fact that the behaviour of most organic pesticides is controlled by a variety of physical and chemical properties of the compounds. It is based on the distribution, fate and behaviour of compounds in the environment. [16] Using multivariate statistical approaches applied to the physicochemical properties of the pesticides and QSARs the compounds were ranked into four a priori classes. [16] The basis on which this is based on is the fact that the molecular structure of a chemical influences its physico-chemical properties and biological activity and structurally similar compounds behave similarly. [18] Considering the relationship between one or more independent variables (the theoretical structure descriptors) and a categorical response variable of integer numerical values (the a priori classes), the QSAR approach was applied to prioritise the compounds according to their partitioning tendency in the environment. This shows the broad application scope for the QSARs methods. The partitioning of pesticides into different environmental compartments depends, mainly on the physico-chemical properties of the studied chemicals. [16, 1 8, 20] The QSAR approach allows a rapid indication of environmental distribution of pesticides starting only from their molecular structure. [16]

2.2.5.1 Selection of a "Pool of contaminants"

The data set of 54 non-ionic organic pesticides comprising of acetanilides, carbamates, dinitroanilines, organochlorines, organophosphates, phenylureas and triazines was selected from a bigger data set studied in previous years. [16]These pesticides have already been the subject of QSPR studies using theoretical molecular descriptors in modelling the Koc, the

leaching and volatility indices (LIN and VIN).[16] The main goal of the authors was to develop a simple procedure based on a QSAR/QSPR (Quantitative Structure Activity or Property relationships) approach for a preliminary screening, ranking and classification of organic pesticides (including those not yet synthesized) according to their environmental partitioning using only the knowledge of their chemical structure.[16]

2.2.5.2 Ranking of pesticides

To rank pesticides according to their distribution tendency in various media a combination of two multivariate approaches: Principal Component Analysis and Hierarchical Cluster Analysis were used. In such methods physico-chemical properties are taken into consideration. [16] These include:

- The organic carbon partition coefficient, Koc
- The n-octanol/water partition coefficient, Kow
- Water solubility (Sw), mg/ℓ, data obtained from Water and solubility data from the pesticides manual molecular descriptors [computed using DRAGON package of Todeschini and Consonni, downloadable from the Web].
- Vapour pressure, Vp (Pa of mmHg) [16]

The partitioning of pesticides into different environmental compartments depends mainly on the physico-chemical properties of the studied chemical. Henry's law constant, K_H which are the more relevant in the determination of the environmental partitioning. [16] Based on this, the 54 studied pesticides of various chemical categories were thus ranked in 4 a priori classes according to their environmental behaviour (sorbed, soluble, volatile and non-volatile/medium class) and finally assigned to the defined four classes by different classification methods such as Classification and Regression Tree (CART), K-Nearest Neighbour (KNN) and Regularized Discriminant Analysis (RDA) using theoretical molecular descriptors. [16]

Use of molecular descriptors

Two hundred and thirty six (236) descriptors were used to describe compounds structural diversity and to elect those useful for the studied classification. The following were calculated using the HYPERCHEM package. [16]

- Constitutional descriptors (OD and ID-descriptors) i.e. counting of atoms, bonds and fragments, MW and sum of atomic properties
- Topological descriptors (2D-descriptors from molecular graphs)

- WHIM (Weighted Holistic Invariant Molecular Descriptors) that contain information on the whole 3D-molecular structure in terms of size, symmetry and atom distribution.

- Empirical descriptors: unsaturation index (Ui) and hydrophilic factor (Hy).[16]

They also added the number of hydrogen bonds (nHDon) and the number of atom acceptors of hydrogen in the same type of bonds (n HAcc).

Use of Chemo metric methods

Data exploration and multi active analysis of physico-chemical properties by Principal Component Analysis and Hierarchical Cluster Analysis was performed on auto scaled data by SCAN program for the definition of a priori classed. In the Cluster Analysis the complete linkage and the Euclidean distance among the chemicals on the auto scaled variables (the five studied physic-chemical properties) were applied. [16]

- The classification strategy, CART was also used. This is a non parametric classification strategy that makes an automatic, stepwise variable selection (among the 236 molecular descriptors used as input) and displays, as the final result, a binary classification tree that is applicable immediately. The proportional class prior and the splitting criterion of Gini were applied to auto scaled variable.[16]

- The second classification method used on the descriptors selected by CART was the KNN a classification method that searches for the K-the nearest neighbour of each object in the data set, performing the classification of the considered object by considering the majority of the classes to which the K-the nearest objects belong. The predictive power of the method was checked for K values between 1 and 10.[16]

- The third classification method applied was Regularized Discriminant Analysis (RDA) , Optimal λ = 0.25 and γ =0.00 all the objects are considered as belonging to the most numerous class and the misclassification risk is calculated as the ration between the number of these objects and the total number of objects. [16]

2.2.5.3 Assessment of the Gramatica et al 2004 QSAR Approach [Figure 2.1]

The Approach by Gramatica et al. 2004 uses recognized and appropriate selection and prioritization methods. The approach is a simple procedure based on a QSAR/QSPR approach for a preliminary screening, ranking and classification of organic pesticides. [16] The chemicals were ranked in 4 a priori classes according to their environmental behaviour (sorbed/soluble, volatile/non-volatile/ medium class and finally assigned to the defined four classes by different classification methods (Classification And Regression Tree (CART), K-Nearest Neighbours (K-NN), Regularized Discriminant Analysis (RDA) using molecular

descriptors such as molecular weight and hydrogen bonding with water.[16] The approach uses the screening, ranking and classification procedures for selecting and prioritizing compounds.

Since leaching in water is much more evident for chemicals that have simultaneously high solubility and low sorption capacity, the authors realized the need for a multivariate approach such as PCA analysis. The use of PCA ranks the 54 pesticides into four *a priori* classes, namely, most soluble/least sorbed (Class 1), most sorbed/least soluble (Class 2), most volatile (Class 3) and non-volatile/medium (Class 4). Some compounds were not well separated from each other using this approach, which called for a refining step like the HCA analysis. [16]

The indication of occurrence in water does not inform about the hazard or potential harm to human beings via the ingestion of water. Once the chemical has been identified as having potential to be taken up by humans, (first step) the question then asked is whether the chemical is toxic to man at a specified environmental level and duration of exposure or not. The approach under discussion is successful as far as determining the persistency and bioaccumulation potential of the organic pesticides but not estimating their toxicity to human beings via the consumption of drinking water. Hence, the human health effect criterion is not satisfied in this approach although it is true that contaminants with high leaching tendency will have high potential for recharge and hence the perceived health risk the contaminant can exert once it reaches the water body.

The toxicity criterion as implicated by Figure 2.1 was also not satisfied as the approach purely screens and ranks the pesticides for the potential to leach into source water systems once released into the environment using a set of physico-chemical properties. Hence, the applicability of the approach for use by the industry will be only by adopting the physico-chemical properties, the types of organic contaminants and their importance as drinking water quality contaminants needing adequate management for the protection of public health.

2.2.6 IDENTIFICATION AND RANKING OF ORGANIC PESTICIDES IN RETURN WATERS TO THE RIVER FROM IRRIGATED LAND, PAPA et al. 2004 [21]

The Amu Darya River, one of the most important water resources for Uzbekistan and Turkmenistan was declared a world disaster zone in 1991. [21] The great increase in irrigation and the use of pesticides had led to both a lack of water and drinking water contamination. The aim of the study by Papa et al. 2004, part of an EU project on water management guidelines, was to evaluate the Leachability of 71 organic pesticides commonly employed in the area and to assess the compounds that could potentially contaminate the river and impair

drinking water [21]. The most important problem was the drying up of the Aral Sea and "returning water". This is water withdrawn from the river for irrigation purposes that returns to the river from irrigated land, in lower volumes but enriched with a large content of salts and other pollutants, especially pesticides. [21] Pesticide pollution and salination had led to lack of groundwater resources for drinking water purposes, cancer was reported to be under spread and the areas had the highest level of child mortality in Central Asia. [21] A multi active approach is proposed for pesticide screening, condensing information from different environmental partition indexes (groundwater ubiquity score (GUS), modified LEACH (modified leaching index and leach ability index (LIN) into a single ranking, the Global Leachability Index (GLI). [21]

2.2.6.1 Selection of a "Pool of contaminants"

Seventy one compounds, organic pesticides commonly used in the area were selected. [21] Because of the lack of analytical facilities and the high cost of performing analyses, the project adopted the strategy to identify from among the list of chemicals applied in the area, those pesticides with the highest probability of being present in the river water, such probability was assessed according to physico-chemical properties and environmental persistency. [21] The data was built up by identifying, from trade formulation names, the active ingredient of the parent molecule in the pesticides molecules. [21] The 71 compounds of the selected data set were characterized by the Chemical Abstract Services registry number (CASRN), the organic structure and the principal physico-chemical properties and literature search was done to collect data on water solubility, vapour pressure n-octanol/water partition coefficient, organic carbon partition coefficient, Henry's law constant and half-life in soil. [21] A range of minimum and maximum half-life values(mainly field data) was collected, the maximum being used to calculate indexes considered for 'a worst case' scenario, when there are no available half-life experimental data (12 compounds) the analysis considered PBT profiler predicted data (medium value in soil). [21]

2.2.6.2 Screening of pesticides

Three indexes were used to calculate leachability. Two traditional, the Groundwater Ubiquity Score (GUS) and the Leaching Index (LEACH) and a third, recently introduced by Gramatica and Di Guardo (LIN-Leachability Index), based on principal component analysis (PCA) of pesticides physico-chemical properties. [21] The basis of this method is the fact that environmental behaviour is strongly influenced by properties inherent in the compounds themselves, particularly physico-chemical properties [Table 2.10] such as solubility in water, vapour pressure and partitioning coefficients between organic matter in soil or biota and water. [4,16, 20] All the indexes were calculated using models and trigger values used to classifying pesticides. [Table 2.10] The GUS index was used to assess the leachability of molecules and

the possibility finding these compounds in groundwater. This index is based on two parameters: mobility in soil, given by the organic carbon partition coefficient (Koc, adimensional) and soil persistence, quantified by the disappearance half-life in the soil, defined in field conditions and expressed in days ($t_{1/2}$). [21]

The LEACH index, leaching index was used to assess the potential degree of groundwater and river water contamination. [21] The LEACH index has no trigger value and the lower the LEACH value the lower the risk of contamination. The values are expressed on a logarithmic scale to allow comparison with other indexes. [21] Since the literature lacked experimental data for degradation half-life in soil for the compounds, disappearance half-life in soil, in field conditions, was considered for "a modified LEACH" calculation. [21] The original equation was then modified without taking vapour pressure into account, in order to avoid a double counting of volatilization which is already considered in disappearance half-life in the field. [Table 2.10]

Leaching index [LIN] is an environmental partition index derived from a linear combination by PCA of those physico-chemical properties more relevant to the determination of environmental partitioning (solubility in water (Sw, mg/l), organic carbon partition coefficient (Kow), vapour pressure (Vp, mmHg) and Henry's law constant (H, atm m^3/mol). [21] The data measured at 25˚C was transformed into logarithmic units. [21] The multivariate technique of PCA was performed for all indexes according to models and trigger values presented in Table 2.10. The PCA condensed the information from different environmental partition indexes (GUS, modified LEACH, LIN) into a single ranking, the Global Leachability Index (GLI) whose values were used to screen the pesticides according to their distribution tendency in the different media and rank them into the classes according to their water partitioning tendency obtained by different approaches with a risk potential for contamination as shown in Table 2.11. These classes are "leachers" with a high risk for contamination, borderline compounds and non-leachers. These classes will be used to generate a prioritized list of pesticides for further analysis in water. [21]

Table 2.10: Physico-chemical properties and models for calculating cross-compartmental transfer [21]

Physico-chemical property	**Model**	**Range**	**Function**
Henry Law 's constant, H_c ($Pa.m^3/mol$ or dimensionless)	$Hc = C_{air}/C_{water}$ Estimated Hc = Vp/Sw	High Hc, chemical is likely to volatilise, Low Hc chemical is likely to remain in solution	Assesses the tendency of a chemical to escape from the aquatic phase[14-15]
n-octanol-water partition coefficient K_{ow} or log K_{ow}	Kow = Coct/Cwater Log Kow = log (Coct/Cwater)	High Kow, lipophilic Low Kow, hydrophilic	Assesses the potential for the chemical to remain in the organic or aquatic phase [14-15]
Organic carbon-water partition coefficient, Koc (cm^3/g)	Koc = Coc/Cwater	High Koc, adsorbs onto organic carbon from solution Low Koc, leaches from organic carbon into solution	Assesses the potential of a chemical to adsorb onto the organic carbon[14-15]
Leaching Index (LEACH)	LEACH = $(Swx_{1/2})/(Vp \times Koc)$	Low LEACH, low risk of contamination and vice versa.	Assesses the potential degree of groundwater and surface water contamination [14]
Modified Leach Index	"Modified LEACH" = $(Swxt_{1/2field})/(K_{oc})$	Disappearance $T_{1/2}$ used due to lack of experimental data	Assesses the degree of volatilization[14]
Leachability Index (LIN)	Calculated by PCA on the physico-chemical properties selected.	Based on Sw, Hc, Vp, Koc, Kow	Assesses the leaching ability of chemicals from the soil into the aquatic phase[14]
Groundwater Ubiquity Score	GUS = $\log_{10}(t_{1/2}) \times (4-\log_{10}(K_{oc}))$	GUS>2.8 leacher, high risk for contamination 1.8<GUS>2.8, borderline cases GUS<1.8 non-leacher	Assesses the magnitude of groundwater contamination risk[14]

Table 2.11: Summary of leachability indexes calculated for 71 pesticides and risk classes [21]

ID	CASRN	Pesticides	LIN	GUS	Modified LEACH	GLI	Leaching risk	Class
1	030560-19-1	Acephate	4.02	3.70	6.61	3.50	High	1
2	135410-20-7	Acetamiprid	1.09	0.20	0.60	0.42	Medium	2
3	082657-04-3	Bifenthrin	-2.50	-2.89	-4.28	-2.56	Low	3
4	034681-10-2	Butocarboxim	2.15	2.20	3.88	1.94	High	1
5	000063-25-2	Carabaryl	0.76	2.32	1.13	0.98	Medium	2
6	002921-88-2	Chlorpyrifos	-1.39	0.62	-1.47	-0.70	Low	3
7	068359-37-5	Cyfluthrin-Beta	-2.13	-1.48	-6.22	-2.44	Low	3
8	091465-08-6	Cyhalothrin-Lambda	-3.20	-3.23	-6.05	-3.23	Low	3
9	052315-07-8	Cypermethrin	-2.78	-2.05	-5.35	-2.64	Low	3
10	052315-07-8	Cypermethrin-Zeta	-2.32	-0.75	-4.42	-1.96	Low	3
11	000050-29-3	p.p'-DDT	-3.22	-4.34	-4.56	-3.25	Low	3
12	052918-63-5	Delatamethrin	-2.96	-1.41	-7.37	-2.92	Low	3
13	000115-32-2	Dicofol	-0.56	4.25	0.03	0.84	Medium	2
14	000060-51-5	Dimethoate	2.44	3.25	4.30	2.40	High	1
15	000115-29-7	Endosulfan	-1.56	-0.17	-2.74	-1.22	Low	3
16	066230-04-4	Esfenvalerate	-2.23	0.68	-3.97	-1.45	Low	3
17	153233-91-1	Etoxazole	-2.20	-1.61	-5.10	-2.28	Low	3
18	064257-84-7	Fenpropathrin	-2.66	-0.33	-5.62	-2.19	Low	3
19	111812-58-9	Fenpyroximate	-2.55	-2.61	-5.68	-2.78	Low	3
20	051630-58-1	Fenvalerate	-2.18	0.00	-4.80	-1.78	Low	3
21	120068-37-3	Fipronil	-0.17	2.76	-0.08	0.55	Medium	2
22	002540-82-1	Formothion	2.13	0.00	2.41	1.06	High	1
23	078587-05-0	Hexythiazox	-1.32	0.19	-3.19	-1.13	Low	3
24	138261-41-3	Imidacloprid	2.03	-0.24	-1.71	0.16	Medium	2
25	144171-61-9	Indoxacarb DPX-JW062	-0.26	0.29	-3.19	-0.75	Low	3
26	173584-44-6	Indoxacarb DPX-KN128	-0.26	0.29	-3.19	-0.75	Low	3
27	000121-75-5	Malathion	0.43	0.77	-0.06	0.22	Medium	2
28	000298-00-0	Parathion-Methyl	-0.22	0.49	-0.48	-0.15	Medium	2
29	002310-17-0	Phosalone	-0.79	0.45	-2.17	-0.69	Low	3
30	002312-35-8	Propargite	-1.14	0.79	-1.91	-0.66	Low	3
31	024017-47-8	Triazophos	-0.61	-0.54	-1.83	-0.82	Low	3
32	000052-68-6	Trichlorfon	2.93	4.96	5.73	3.30	High	1
33	034256-82-1	Acetochlor	0.21	0.81	0.25	0.22	Medium	2
34	120162-55-2	Azimsulfuron	2.90	3.93	2.99	2.48	High	1
35	083055-99-6	Bensulfuron-methyl	1.94	3.07	1.66	1.67	High	1
36	025057-89-0	Bentazone	1.29	2.62	2.20	1.44	High	1
37	001689-84-5	Bromoxynil	0.82	1.36	0.48	0.61	Medium	2
38	099129-21-2	Clethodim	-0.33	0.13	-3.11	-0.80	Low	3
39	000094-75-7	Desormone (2,4 D)	0.90	1.88	1.90	1.05	High	1
40	079241-46-6	Fluazifop-p-butyl	-1.18	0.35	-2.31	-0.87	Low	3
41	098967-40-9	Flumetsulam	2.18	3.61	1.50	1.87	High	1
42	002164-17-2	Fluometuron	0.95	4.00	2.04	1.67	High	1
43	077501-90-7	Fluoroglycofen-ethyl	-0.84	0.06	-4.76	-1.31	Low	3
44	069377-81-7	Fluroxpyr	2.75	2.73	0.78	1.68	High	1
45	069806-34-4	Haloxyfop	1.46	4.10	1.69	1.80	High	1
46	002212-67-1	Molinate	0.42	2.91	2.46	1.28	High	1
47	001836-75-5	Nitrophene	-1.21	0.21	-1.82	-0.82	Low	3
48	040487-42-1	Pendimethalin	-1.54	0.63	-2.14	-0.88	Low	3
49	000709-98-8	Propanil	0.58	2.15	1.19	0.88	Medium	2
50	094051-08-8	Quizalofop-p	0.39	2.36	-1.39	0.37	Medium	2
51	100646-51-3	Quizalofop-p-ethyl	-0.91	0.00	-4.13	-1.23	Low	3
52	101200-48-0	Tribenuron-methyl	2.69	1.98	1.63	1.63	High	1
53	017804-35-2	Benomyl	0.61	-0.07	-2.80	-0.48	Medium	2
54	116255-48-2	Bromocunazole	-0.16	-0.95	-0.68	-0.56	Low	3
55	010605-21-7	Carbendazim	1.14	4.22	1.11	1.61	High	1
56	005234-68-4	Carboxim	1.08	0.00	-0.11	0.22	Medium	2
57	083657-24-3	Diniconazole	-1.21	-0.64	-1.63	-1.01	Low	3
58	106325-08-0	Epoxiconazole BAS 480F	0.01	1.47	-0.47	0.18	Medium	2
59	136426-54-5	Fluquinconazole	0.27	2.80	-0.39	0.64	Medium	2
60	076674-21-0	Flutriafol	0.65	-1.88	-0.07	-0.42	Medium	2
61	066246-88-6	Penconazole	0.17	3.50	1.78	1.22	High	1
62	060207-90-1	Propiconazole	0.24	2.18	1.07	0.75	Medium	2
63	107534-96-3	Tebuconazole	-0.18	-0.66	-0.68	-0.49	Medium	2
64	023564-05-8	Thiophamate-methyl	0.58	1.07	-1.27	0.11	Medium	2
65	000137-26-8	Thiram	0.84	-0.35	-1.65	-0.26	Medium	2
66	043121-43-3	Triadimemefon	0.87	1.91	0.63	0.81	Medium	2
67	026644-46-2	Triforine	0.72	2.25	0.50	0.82	Medium	2
68	000052-51-7	Bronopol	3.72	5.91	6.88	4.05	High	1
69	051707-55-2	Thidiazuron	1.72	4.61	1.79	2.04	High	1
70	004602-84-0	Farnesol	-1.70	1.30	-1.54	-0.64	Low	3
71	007212-44-4	Nerolidol	-1.62	1.83	-0.96	-0.36	Medium	2

2.2.6.3 Assessment of the Papa *et al* 2004 Approach [Figure 2.1]

The method has successfully screened and ranked the 71 pesticides by using their leaching tendency and other physico-chemical properties. The philosophy is similar to the preceding methodology discussed in **section 2.2.5**. Papa et al. [2004] found Bronopol, Acephate, Trichlorfon, Azimsulfuron, Dimethoate as the most leachable chemicals with the highest GUS, LIN and "modified LEACH" and GLI derived scores. [21] Some structural features account for this. They have structures characterized by electronegative atoms (O or N) relevant to hydrogen bonding with water and therefore give rise to an increase in solubility. Persistency of chemicals to remain in soils and thus be available for transfer to other environmental compartments like surface and groundwater manifested strongly as a criteria for screening pesticides. [21] Persistence of a chemical is therefore an important factor for estimating human exposure. [21] Half-life data are typically used to predict chemical persistence. Short half-lives ($T_{1/2}$) are indicative of extremely volatile, water-soluble and/or easily degraded chemicals.[21] Long half-lives ($T_{1/2}$) are indicative of non-volatile, relatively water insoluble, chemicals with high affinity for the solid phase.[21] This justifies the incorporation of half-life in models for calculating the various leachability indices. [Table 2.10]

In the method, clinical records were used to assess evidence of exposure to the toxic chemicals and the resultant adverse health effects. [21] Hence, the application of the toxicity and human health effects criteria has been satisfied. It was identified that cancer was widespread in the area and there was the highest level of child mortality in the Amu Darya Basin where pesticides and other organic compounds were highly used. [8] When there were no available half-life experimental data, the analysis considered the PBT profile predicted data medium value in soil. [21] A PCA multivariate approach allows the screening and ranking of pesticides by condensing information from different environmental partition indexes (GUS, "modified LEACH" and LIN) into a single ranking tool, the global leachability index (GLI). [21]

However, the comparison of these leachability indices values shows some discrepancies due to the mathematical algorithms and/or various properties included in their calculation giving rise to different ranking for the studied pesticides.

3 OVERALL ASSESSMENT OF REVIEWED APPROACHES

The approaches reviewed above satisfied most of the elements presented for review (Figure 2.1). Six methods were reviewed of which four were by governmental bodies and two from research groups. [Table 2.12] Although some of the approaches did not exclusively address drinking water contaminants, they were reviewed in order to obtain the generic conceptual framework within which chemical substances are selected and prioritized for various purposes.

Table 2.12: Prioritization schemes reviewed in this study

Prioritization scheme reviewed	Activity	Scope	Approach	Outcome
Gramatica et al. [2004]	Prioritization of compounds based on their environmental fate and behaviour.	Organic non-ionic pesticides of different classes, acetanilides, carbamates, dinitroanilines, organochlorines, organophosphates, phenylureas and triazines	Spreadsheet of physicochemical properties governing environmental fate and behaviour, followed by a multivariate approach (PCA).	The 54 pesticides ranked into four a priori classes.[9]
Papa et al. [2004]	Diffuse pollution resulting from agricultural activities impairing the river water quality	71 organic pesticides commonly employed on irrigated land next to a river used as raw water source for drinking water production.	Use of various Leachability models (Table III) followed by the application of multivariate approaches, such as PCA to the various indices of pesticide leachability.	A list of 19 priority organic pesticides [8]
OSPAR COMMISION-DYNAMEC	Nomination and selection to the Domestic Substance List, followed by a risk-based assessment	Nordic database comprising of 18000 registered substances, the Quantitative Structure Activity Relationships (QSAR) database of the Danish Environmental Agency with 166000 entries and the Dutch BKH/Haskoning database with 180000 entries.	PBT criteria, Exposure	List of toxic substance [1,2, 22, 24,25]
IEH-UK ranking method	Ranking Chemicals by their fate in the environment and potential toxic effects in humans following non-occupational exposure.	600 chemicals or group of chemicals, available on request from the MRC, Institute for Environmental Health, UK	Scoring each criterion to assess potential fate and transfer of chemicals between environmental compartments and using R-phrases to score toxicity.	A list of 100 priority organic chemicals produced.[4]
USEPA Prioritization approach for drinking water contaminants	A"universe" of potential contaminants	Drinking water contaminants to be monitored	Workshop, inputs from experts and public (water utilities, trade associations, environmental groups. Demonstrate occurrence in drinking water, potential to occur in drinking water, to cause adverse health effects and have potential to cause adverse health effects.	Preliminary candidate contaminant list [7]
USEPA QSAR approach for disinfection by-products	Use of Mechanism based QSARs to rank DBPs for carcinogenic potential	600 DBPs from various disinfectant combinations	Judgement if sufficient data existed for cancer assessment and occurrence data for exposure assessment followed by a semi-quantitative concern rating.	20 DBPs rated high for cancer causing potential [17]

All the methods attempted to produce a short list from their original lists used in the study although the focus was on individual chemicals other than group of compounds which is a reality in environmental samples. It was noted that there is no perfect, common scientific approach to weighting different selection criteria in prioritization processes due to the number of assumptions and diversity of confounding factors that are incorporated into such approaches. However, it is evident from the reviewed methodologies that selection and prioritization exercises are governed by a number of generic principles;

- A selection and prioritization approach is identified by its purpose. The purpose will inform the criteria that will be used for the selection of parameters to be used for the screening and prioritization exercise.
- Physico-chemical properties are most commonly used to predict environmental fate, behaviour of chemicals and toxicity data (e.g lethal concentration/dose causing 50% mortality; LC_{50}/ LD_{50} to protect human health effects). [Table 2.13] It could well be argued, however, that the results of acute lethality tests such as LC_{50}/ LD_{50} are not particularly relevant to the effects of low-level environmental exposure.
- To produce an overall ranking of chemicals, scores resulting from the application of individual screening criteria are weighted and chemicals are ranked in order of increasing total score. The criteria used should always be dependent on the purpose of the prioritization. For example, the environmental protection or monitoring of impairments for aquatic life requires the consideration of other organic contaminants other than those used for drinking water analysis which is assessed according to human health criteria.

Most of the approaches have been successful in selecting and prioritizing organic contaminants of concern based on the occurrence, persistence, bioaccumulation and toxicity and other human health effects criteria. However, challenges facing these approaches are;

- The lack of occurrence and toxicity data for some contaminants of health concern
- The time frame and resources needed for a full risk assessment and production of a "priority list"
- The fact that assessment of the toxicity of substances for example, organic contaminants will call for the analysis of exposure parameters which is often complicated by the generally low concentrations of chemicals in the environment especially in drinking water where some have been removed by treatment processes.
- Assessment of exposure to human beings is also complicated by the large size of human populations which Water utilities deal with. Each individual is subjected to multiple routes of exposure per contaminant or group of contaminants other than the drinking water ingestion or bathing. This warrants a full toxicity study or a risk assessment which all of the above methodologies did not handle.

Table 2.13: Physico-chemical properties used in evaluating environmental fate and behaviour

Physico-chemical property	Description	Criteria
Water solubility, S_w, mg/l	Describes the amount of chemical that can dissolve freely in a known quantity of water.	Persistence [1-4,22-25]
Vapour pressure, V_p, Pa (N/m2)	Saturation vapour pressure of compound at defined temperature, potential of chemical to evaporate, atmospheric transport	Persistence [1-4,22-25]
Henry Law 's constant, H_c ($Pa.m^3/mol$ or dimensionless)	Equilibrium partition between constant between air and water at a defined temperature. Indicates the tendency of a chemical to volatilise from soil, water and plant surfaces into the atmosphere.	Atmospheric transport[8,9]
n-octanol-water partition coefficient K_{ow} or log K_{ow}	Indicates the tendency of a chemical to partition between water and lipid/organic matter (lipophilicity), Alternate to BCF	Bioaccumulation [1,2,11,15,22-25]
Organic carbon-water partition coefficient, Koc (cm^3/g)	It is the ratio between the concentration of a compound on organic carbon and the concentration in water. It indicates the chemical's tendency to adsorb onto organic carbon from solution, tendency to become tightly bound on humic material of the soil or leach through it.	Bioaccumulation [1,2,11,15,22-25]
Hal-life in soil,	Time for half of initial concentration to be lost due to aerobic or anaerobic biodegradation. The reaction is of first order kinetics	Persistence [1,2,11,15,22-25]
Half-life in water	Time for half of initial concentration to be lost due to hydrolysis, aerobic or anaerobic biodegradation. The reaction is of first order kinetics	Persistence [1,2,11,15,22-25]
Bioconcentration factor in fish (BCF_{fish}), kg wet fish/litre of water)	Indicates the tendency of a compound to partition between different environmental compartments and is defined as the ratio between the concentration of a chemical in biota and the concentration in water at equilibrium.	Bioaccumulation [1,2,11,23,25]
Fugacity	It is regarded as the escaping tendency of a chemical from a phase. It has units of pressure and can be related to concentration.	Fate in the environment, partitioning, transformation, transport [1,2,11,23,25]
LD_{50}	Indicator of mammalian toxicity of substances, expressed in mg/kg	Toxicity [22]
LOAEL	Lowest Observed Adverse Effect level	Toxicity [22]
LC_{50}	Acute toxicity of substance resulting in mortality of 50% of test aquatic organisms	Toxicity [22]

Some of the reviewed approaches were based on molecular structure and properties of compounds, QSARs and/or QSPRs approaches for prioritization. It is evident from the review that these are models that enable prediction of physical, chemical and biological properties of non-assessed compounds by comparing structurally and or qualitatively similar accessed compounds based on the structure and composition of the molecules. QSAR modeling may a priori be applied in all cases where reliable experimental data is not available or in cases where decisions have to be made within a short time frame. The idea of using this approach is to reduce cost by reducing the number of chemicals that warrant full toxicity testing. This will then be done to a short-list of chemicals that will be obtained after applying a QSAR. For example carcinogenicity rating is assigned to a chemical, if it contains one or more molecular substructures that have been related to carcinogenicity, for example disinfection by-products or pesticides. [7, 9]

However, the models are faced with challenges. For example, because different parameters are needed, a single statistical model is seldom robust. They are also developed on assumptions, for example “structurally similar compounds behave similarly” implying that similar chemicals by definition invoke the same toxicity pathway (within a specified biological model) which might not be applicable to certain functional groups. It must also be remembered that a QSAR/QSPR is a model, thus it is an idealized representation of reality based on a set of criteria. Through careful selection of descriptors and model development, the resulting QSARs may lead to predictions that are more or less accurate.

4 CONCLUSIONS

Although, a few of the approaches reviewed address drinking water contaminants, they have illustrated how the complex and often contentious task of identifying, ranking and culling multitudes of substances to much smaller numbers that will receive regulatory and research consideration has been approached in various countries. They also served to illustrate how stakeholder consultation and expert judgement is vital and integral to the design, implementation and validation of these types of prioritization schemes. This is vital for the development of future priority lists of contaminants for monitoring in drinking water.

Environmental behaviour is strongly influenced by properties inherent in the compounds themselves particularly physicochemical properties. These properties play an important role in defining the environmental fate and distribution of organic contaminants. They include properties such as solubility in water, vapour pressure, partitioning coefficients between organic matter in the soil or biota and water. These properties are mainly used during the initial selection stages of the prioritization schemes. QSARs/QSPRs play a crucial role in

addressing of data gaps during selection and prioritization exercises. This includes toxicity data, emission data, environmental concentrations and structural similarities.

Three major generic steps could be identified in each selection and prioritization approach that was reviewed. These are summarised in Figure 2.7. This conceptual framework will serve as a model for the development of a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking value chain which is presented in Chapter 3 of this document.

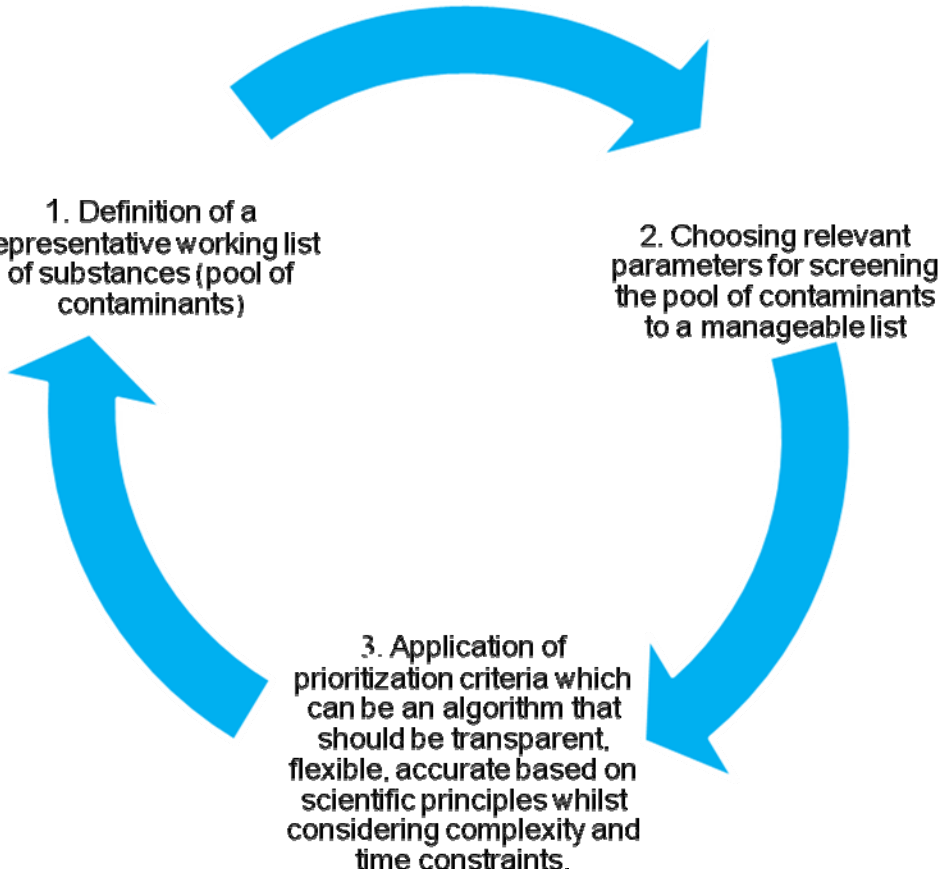

Figure 2.7: A generic conceptual framework for the selection and prioritization of contaminants as illustrated by reviewed methodologies.

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CHAPTER 3 A GENERIC PROTOCOL FOR THE SELECTION AND PRIORITIZATION OF ORGANIC CONTAMINANTS FOR MONITORING IN THE DRINKING WATER VALUE CHAIN

3.1 GENERAL INTRODUCTION

The contamination of drinking water supplies by trace organic contaminants from various manufacturing and processing industries, effluents discharged from wastewater treatment plants and anthropogenic activities remains a significant concern to public health throughout the world. Organic contaminants are released into the environment through a variety of human activities.[1,2] These activities include pesticide use in agricultural and public health programmes such as control of vector borne diseases.[1,3] Unfortunately, some of them have found their way into environmental and biological systems.[3] More vulnerable to pesticide contamination have been the surface water systems and the populations that depend on the water from these systems for domestic purposes.[3-6] This is mainly due to the fact that drinking water is generally considered as the highest and most direct source of human exposure to waterborne contaminants and accordingly it usually receives the most attention in water-related health risk assessment.[7]

Once discharged from the various sources organic contaminants find their way into source water resources.[3] The other complicating factor is their continuous addition into the environment given the fact that men in the 21st century have become reliant on a vast number of manufactured chemicals and substances to enhance the quality of life with little thought given to what happens to these chemical substances once they have been used and discarded.[8,9] The information contained in Table 3.1 illustrates the magnitude of this problem which now resides with Water Services Authorities that are charged with the responsibility of ensuring that the water that consumers receive on tap is safe and wholesome for lifelong consumption. The preventive management of these chemicals in drinking water requires practical and easily applicable tools for distinguishing the few chemicals of potential local or national concern from the unmanageably long list of chemicals of possible significance. [9-11]

It is evident from Table 3.1, that the number of organic contaminants of environmental concern is high. Emerging organic contaminants also receive more attention as they are often used in domestic, agricultural and general business.[8,9,12] They include household cleaning products, fragrances, over-the-counter medicines, disinfectants, pesticides, pathogens and organic nano- particles.[13,14]

Table 3.1: Industrially produced Chemicals

- 18 million substances are listed and described in the “Chemical Abstracts”
- 400 million tons of chemicals were produced worldwide in 2000. (Compared to 1 million ton manufactured in 1930)
- 100 000 chemicals were listed with the European Community in 1981 (old chemicals)
- 720 chemicals were listed under the Swiss Ordinance on Environmental Pollutants between 1988 and 2000
- 8 700 different food additives are known
- 3 300 substances are being used as drugs in human medicine
- 30000 organic chemical substances in wide commercial use (>1 ton/annum) not measured in environmental media and fate in the environment is not known
- 2004, The Stockholm Convention comes into force to regulate the “dirty dozen”
- 11,317 substances on its Domestic existing Substances List as meeting the Persistent (P) and bioaccumulation (B) criteria
- 8,4million substances are commercially available and 240,000 are reported to be inventoried/regulated chemicals according to Chemical Abstract Services website
- 82,000 industrial chemicals are in the US TSCA inventory. [13-16]

Although most emerging organic compounds have been identified in the drinking water supply chain, mainly in source waters they are currently not included in routine drinking water monitoring programs. Currently, there are over 100 health-related chemicals or group of chemicals for which guideline values have been set by the World Health Organization.[7] This list does not include emerging organic contaminants. Furthermore, there is a lack of accurate information about their fate in different aquatic environments and their effects on aquatic ecosystems or human health although some of the adverse health effects have been successfully identified.

The effects caused by organic contaminants have been and are still considered as a major risk to wildlife and human beings. The detection of pesticide residues in the drinking water supply chain due to use of pesticides in catchments from which source water is abstracted for drinking water production is of high importance. [17,18] Although not well studied possible health effects associated with long term exposure to drinking water containing low concentrations of pesticides include reproductive damage, birth defects, neurologic and endocrine abnormalities, effects on growth and development, cancer and other adverse effects.[17,18] Most of the adverse health effects associated with these compounds have been mentioned earlier in this document (**section 1.6 of Chapter 1**). These effects and the characteristics of organic

contaminants have compelled the authorities in various industries of the world to view the occurrence of organic contaminants in the environment as a global issue especially the risks these compounds are capable of causing. [1,2] It was not until the second half of the 20th century that various organizations acknowledged fact that many of these compounds cause severe environmental and health problems. [17,18] Any early response was to assess the environmental risk associated with selected chemicals. Depending on the results, various countries subsequently introduced regulations governing their use. For example, the Organization for Economic and Cooperative Development (OECD) has been engaged with risk assessment and risk management of chemicals for more than 40 years. [15] Today, there is a consensus that, at least in principle, all chemicals that are in use must be evaluated.

Various regulating bodies such as the World Health Organization (WHO),[7] the United States Environmental Protection Agency (USEPA) [19], the United Nations Environmental Programme (UNEP) [5,6] and the European Union (EU) [20,21] have also taken major actions. This has resulted in the development of guidelines and standards for organic chemicals in drinking water (see attached CD). Unfortunately, the number of chemicals to be tested is enormous (Table 3.1). From the preceding sections, it is apparent that characterizing all possible organic contaminants or organic chemical mixtures in drinking water is an overwhelming task. The exercise of assessing each chemical or mixture of chemicals' resultant toxicity on the other hand is more daunting. Therefore, appropriate prioritization procedures need to be employed that identify particularly dangerous substances, which may then be subjected to more extensive risk assessment.

Chapter 2 of this document presents a review of selected methodologies for the selection and prioritization of organic contaminants. This review showed that approaches used by different organizations vary widely, depending on the purpose for which the schemes were developed. Because of the high number of both classical and emerging organic contaminants that are a potential health risk through drinking water, it is necessary to develop a protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain. The basic information presented in the review has been used to develop a readily applicable model on which the current selection and prioritization protocol is developed taking into account the concerns and needs of the drinking water industry (Figure 3.1).

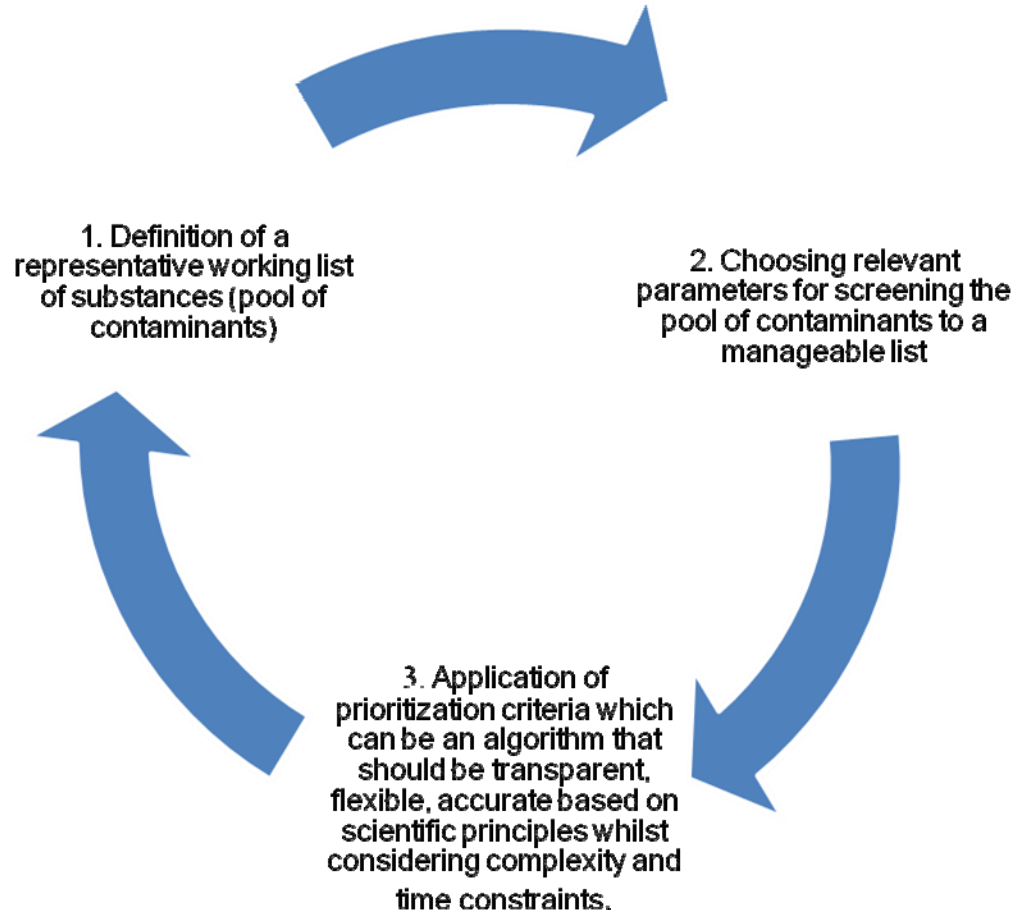

Figure 3.1: A generic conceptual framework for the selection and prioritization of contaminants as illustrated by reviewed methodologies.

3.1.1 Purpose of the protocol

The purpose of this protocol is to define a process for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain (from source to tap). The protocol is developed for the Drinking Water industry and other relevant industries such as agriculture and health. It operates as a multidisciplinary contaminants management and proactive protocol, thus exchanges toxicological, water quality, agricultural, chemical and public health information. The protocol uses previous or readily available information as a point of departure. It seeks to address the challenge facing the water industry in managing the current and emerging organic contaminants that are relevant to public health protection via the use of drinking water.

The protocol employs a multiple step (selection and prioritization process in which evaluation of each list by the Drinking Water industry experts and related stakeholders is emphasized. Validation of the protocol in a prototype drinking water value chain is viewed as one of the most important part in order to obtain a priority list relevant to local conditions. It is intended to provide guidance to Water Services Providers (WSPs), practitioners and their consultants on the selection and prioritization of organic contaminants for monitoring in the drinking water value chain.

3.2 Specific components of the protocol

3.2.1 General principles on which the protocol was developed

This protocol is based on the following principle assumptions;

- The two main criteria for identifying specific chemicals of concern to public health by the Water industry are; the probability of consumer exposure from drinking water and the occurrence of significant hazard to health. As a result, the chemicals identified as definitely occurring or more likely to occur and cause adverse health effects to human health will be given greater priority for monitoring than those less likely to occur in the drinking-water and to cause adverse health effects.
- Aesthetic qualities of water are very important to Water Services Providers from a business sustainability sense since some organic contaminants may significantly degrade aesthetic quality or cause significant problems for the operations and maintenance of water supply systems. While aesthetic considerations may not have a direct impact on public health, changes in taste, odour or appearance of drinking-water may prompt some consumers to turn to other sources of drinking-water that may be microbiologically unsafe [7,12] or cancellation of bulk water services contracts and migration to other WSPs resulting in loss of competitive advantage and business sustainability.
- Chemicals that cause operational problems, such as corrosion or encrustation of distribution systems, may have an indirect impact on public health by compromising the ability to maintain the water supply. [7,12]
- Drinking water is not the only route of exposure to organic contaminants. However, for the purpose of this protocol, only exposure via the drinking water ingestion route, dermal contact and inhalation during water use are going to be considered as exposure routes to contaminants in drinking water. Many different individual or group of contaminants may occur in the drinking water value chain (from source water to the tap), however, only a few may be important to the drinking water industry under different circumstances.

- What is relevant in one environment, may not be relevant in others, hence, it is important that water utilities in different countries identify those organic contaminants of concern according to their local conditions. The process outlined in this protocol provides guidance to assist water utilities in collaboration with relevant sectors such as public health authorities, national and provincial health, agriculture and environmental governmental departments, non-governmental organizations (NGOs) with interest in water, health and environmental issues, research groups, industries and relevant stakeholders in identifying those organic compounds that are likely to be present in an individual water supply and may present a potential health risk through the drinking water value chain.
- In identifying the "pool of contaminants", it is necessary to understand both local and international trends. It is necessary to develop an understanding of the characteristics of the catchment from which the source water is abstracted. This includes making an inventory of natural influences to ground and surface water, the types and size of industrial and agricultural activities, human settlements within a catchment.
- Treatment of source water in order to produce potable water also influences the final quality of water delivered to the consumer. Chemicals used for treatment such as disinfectants, coagulants, flocculants and coagulant aids can introduce impurities into the system or react with organic contaminants in the water to form undesirable disinfection by-products.
- The distribution of potable water also influences the final quality of drinking water delivered to the consumer. Chemicals in potable water continue to interact with pipe materials which might leach into the water and introduce organic contaminants of concern to human health.
- Extensive research should be conducted on organic contaminants of concern. Some international organizations have developed databases for exposure and toxicity data, priority lists of substances and their guidelines or criteria for drinking water. [7, 12,22,25] These information sources can be used for benchmarking and compiling the "pool of contaminants" from which selection and prioritization can be performed. There is no need to reinvent the wheel.

The criteria for the selection and prioritization of organic contaminants presented in this protocol were influenced by these generic principles and the needs of the Water Industry. It should be stressed that the protocol presents a tailor made screening process for the Water Industry, taking into consideration, the time constraints and limited resources and that a detailed assessment is necessary to conduct a full risk assessment for the prioritized organic contaminants. The model used in this selection and prioritization protocol is outlined in Figure 3.2.

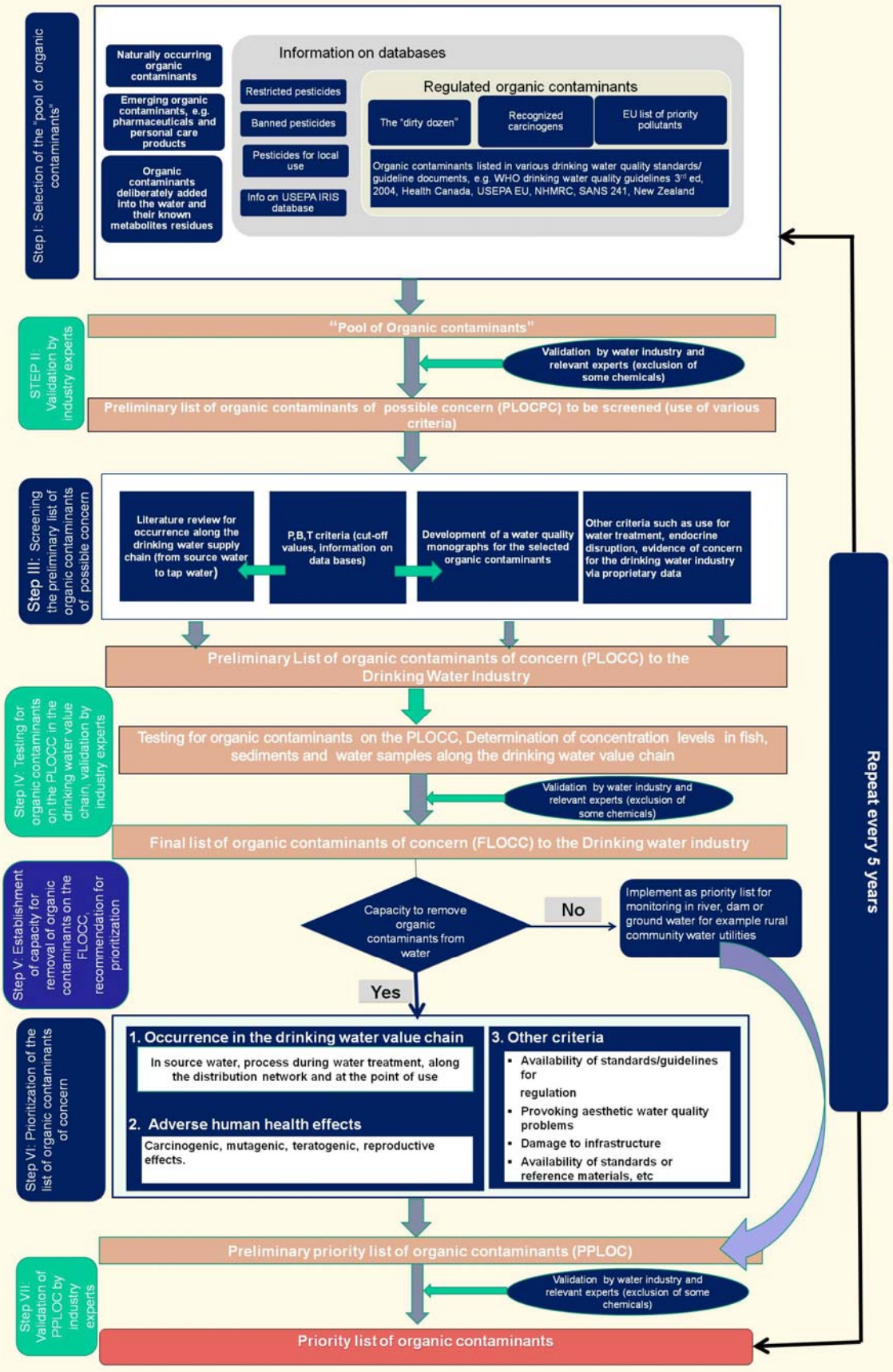

Figure 3.2 A generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain.

3.3 The selection and prioritization approach

3.3.1 Step I: Selecting the "Pool of organic contaminants"

The first step in a selection and prioritization exercise is to determine which of the many thousands of organic chemicals in the environment should be selected and incorporated into the prioritization process. Such information can be obtained from:

- Naturally occurring organic contaminants
- A group of organic contaminants known as the "emerging organic contaminants" such as the pharmaceuticals and personal care products (PPCPs) (section 1.5.2 of Chapter 1).
- Organic contaminants deliberately added during drinking water production to improve the efficiency of some unit processes such as coagulation and flocculation. This includes their metabolites or residues.
- List of pesticides registered for use, banned or restricted, for example the Pesticide Action Network administered by the United Kingdom (PAN-UK) database exists for most countries including South Africa. Confirmation with the national and provincial as well as local governments is necessary in order to obtain the current situation from the various agricultural departments (catalogues from the national Department of Agriculture in the case of South Africa).
- Organic contaminants of concern listed on databases such as the integrated risk information system (IRIS) of the USEPA (see Table 3.2)
- Substances that are subject to legislation, regulation or guidance or those that have been reported in the literature as of being of environmental concern, for example the "dirty dozen" from the Stockholm Convention signed in 2001 and recognized carcinogens as presented by the International Agency on Cancer Research (IARC), [2] substances that are listed in drinking water guideline documents as of health concern via the drinking water route such as those in the WHO guidelines for drinking quality 3rd edition,[7,12] EU list of priority substances as per the Water Framework Directive, [23] the United States Environment Protection Agency (USEPA),[19] the UK Drinking Water Inspectorate (DWI),[26] Australian drinking water quality guidelines,[22] and the New Zealand drinking water standards. [24]
- Interviews of environmental health officers, other water utilities, independent research groups, universities may also contribute positively to the compilation of a "pool of contaminants" or candidate list

It should be noted that local information should not be undermined during this step as it plays a crucial role in planning, especially the need to comply with national standards. WHO Guidelines for drinking water quality (current edition) is a very resourceful document for

global use by the Water Industry. However, member states should take into consideration the advisory nature and select organic contaminants that are relevant to their local conditions. Although the documents have adequate information on epidemiology and toxicology of contaminants, there is a lack of other aspects needed to establish guidelines. This information can only be available at local or national level.

Table 3.2 gives examples of possible information sources. It should be noted, however, that the compiled list must be reasonable given the main disadvantage of time constraint and lack of manageability. Applying a screening procedure to such large lists may involve serious practical difficulties to get data for all the substances. **The outcome of this step is a "pool of organic contaminants" arranged in an excel spreadsheet.**

3.3.2 Step II: The validation of the "Pool of organic contaminants" by Drinking Water industry experts and relevant stakeholders

The step is the validation of the "pool of organic contaminants by a group of experts from the Water Industry and relevant stakeholders. This can be in form of a workshop, meeting or use of questionnaires or a combination of these methods. The guiding principle is the relevance of the organic contaminants and their public health significance to the drinking water. During this step, some organic contaminants will be eliminated from the list based on the non-relevance to drinking water and the diversity of views and experience of the various experts. It is advisable that the group of participants cover all subject areas relevant to public health protection such as process engineers, toxicologists, medical experts, hydrologists, environmental health officers, water quality specialists, water treatment plant managers, operators, agricultural scientists and analytical chemists just to mention a few. During these interactions some organic contaminants are adopted as of concern while others are excluded resulting in a "**Preliminary list of organic contaminants of possible concern (PLOCPC)" (Figure 3.2)** to be screened in Step III of the Protocol using various criteria.

Table 3.2: Examples of possible sources of information for reference in selecting the "Pool of contaminants"

Content	Source	Country of Origin	Organization	Reference
Organic contaminants for monitoring in drinking water, fact sheets	Australian drinking water quality guidelines	Australia	National Health Medical Research Council (NHMRC)	http://www.nhmrc.gov.au/publications/synopses/eh19syn.htm confirmed on 01 September 2009
Organic contaminants for monitoring in drinking water	Canadian drinking water quality guidelines	Canada	Health Canada	http://www.hc-sc.gc.ca/ewh-semt/pubs/water_eau/development-elaboration/intro-eng.phpconfirmed on 01 September 2009
Drinking water quality guidelines/factsheets	WHO drinking water quality guidelines, 3rd edition	Geneva	World Health Organization (WHO)	http://www.who.int/water_sanitation_health/dwq/GDWQ2004web.pdf confirmed on 01 September 2009
Candidate contaminant lists	USEPA Website	United States of America	United States Environmental Protection Agency(USEPA)	http://www.epa.gov/safewater/contaminants/index.html confirmed on 01 September 2009
List of pesticide residues	PAN-UK website	United Kingdom (UK)	Pesticide action Network (PAN-UK)	http://www.pan_uk.org/reviews last visited on 12 August 2007
A-Z list of substances found in the environment, human health effects	Integrated Risk Information database	United States of America	USEPA	http://www.epa.gov/ncea/iris last confirmed on 01 September 2009
List of pesticides of concern	USEPA website	United States of America	USEPA	http://www.epa.gov/pesticides/a-z/index.htm last confirmed on 01 September 2009
List of potential hazards and types of exposure	Monographs	International	(International Agency on Research on Cancer (IARC)	http://www.monographs.iarc.fr/ENG/classification/crthallist.php last confirmed on 01 September 2009
Endocrine disruptors	Scientific facts	International	International Programme on Chemical Substances (IPCS)	http://www.greenfacts.org/en/endocrine-disruptors/endocrine-disruptors.htm last confirmed 02 September 2009
List of priority Substances	EU Website	Europe	European Commission (EC)	http://www.ec.europa.eu/index_en.htm last confirmed on 04 September 2009

3.3.3 Step III: Screening the Preliminary List of Organic Contaminants of Possible Concern (PLOCPC)

The list obtained in Step II is a list of organic contaminants that are perceived as of concern to drinking water and public health protection via potable water use. In this step, this list is checked and verified against the occurrence criteria and the potential to cause adverse health effects. In order to accomplish this, a literature review must be conducted. The focus of the review is on the occurrence of the organic contaminants in the drinking water value chain and their potential to cause adverse health effects. In order to accomplish this, the following need to be determined;

- The occurrence of organic contaminants in the drinking water value chain (from source to tap) (literature review) (Figure 3.2 Step III);
- The use of the persistence, bioaccumulation and toxicity (P,B,T) criteria (use of cut-off values) for screening the organic contaminants (Figure 3.2 Step III);
- The development of water quality monographs for selected organic contaminants in order to solicit more information on the occurrence, fate and behaviour of the organic contaminant in the drinking water value chain and confirm its relevance for adoption by the Drinking water industry(Figure 3.2 Step III) and
- The use of “other criteria”, such as endocrine disruption, relevance and concern to the Drinking water industry as evidenced by proprietary data, previous legislation and use during water treatment (Figure 3.2, Step III, Figure 3.3).

3.3.3.1 Step III: Potential organic contaminants in the drinking water value chain: a literature review

Occurrence in the drinking water value chain is important as it provides evidence for potential human exposure to organic contaminants. Since surface waters may be used for the abstraction of water intended for human consumption, it is important to identify those contaminants that may endanger human health through the drinking water ingestion route, dermal contact during the various domestic uses of water, recreational use or via the inhalation route. During this step, a literature review should be conducted with the aim of identifying individual or group of organic contaminants that have been found to occur in the aquatic environment throughout the drinking water value chain. At the end of this review, a list of organic contaminants that has been found to occur in the drinking water value chain should be compiled. The review should also cover the potential health effects that can occur as a result of exposure to these organic contaminants. It should be taken into account that

the occurrence of a chemical in the drinking water value chain will be largely influenced by its physico-chemical properties such as its solubility in water, vapour pressure, soil/sediment sorption/desorption. [28] Hence, these properties can be noted and used to predict the fate and behaviour of the contaminant in the drinking water value chain (Table 3.3). [28] The scope of the review should therefore cover the following organic contaminants;

- Naturally occurring organic contaminants or group of organic contaminants;
- Organic contaminants or group of organic contaminants that occur in groundwater and surface water resources that can be used as sources for drinking water production as a result of anthropogenic activities;
- Organic chemicals that are deliberately added to water during water treatment and have a potential to act as precursors for the formation of organic contaminants for example the use of synthetic organic polymers (both anionic and cationic);
- Organic contaminants that are produced as a result of reaction among chemicals such as disinfection by products, synthetic organic polymer residues of concern to human health;
- Organic contaminants that occur in the drinking water as a result of interaction between the chemicals in the water and internal contact material in distribution systems and
- Organic contaminants that can be produced at the point of use based on their physico-chemical properties, such as volatile organic chemicals (VOCs) or semi-volatile organic chemicals (SVOCs).

The list produced from the literature review is compared with the “Preliminary list of organic contaminants of possible concern (PLOCPC)” (Figure 3.2). Some organic contaminants can be eliminated at this stage based on the weight of evidence from the literature review. The compounds are arranged into a table according to their functional groups. It should be indicated at this stage if the organic contaminants are of health concern via the drinking water ingestion route. The fact that exposure to these contaminants can occur through other routes other than drinking water ingestion should be recognized. If there is any evidence from the literature review, it should be noted accordingly as this will assist in decision-making in future steps**.** The list obtained from this review will form part of the preliminary list of organic contaminants of concern (PLOCC) to the Drinking water industry after applying the P, B, T and other relevant criteria.

3.3.3.2 Step III: Application of the persistence, bioaccumulation and toxicity (P, B, T) criteria (use of cut-off values) to the list of organic contaminants obtained from the literature review

These parameters include: Persistence (P), which is the propensity for a substance to withstand degradation and therefore remain in the environment in an unchanged state for a prolonged period of time; bioaccumulation (B), the ability to build up in biota (through for example, accumulation in fatty tissues) resulting in higher tissue concentrations of which in turn can impact on top predators such as the consumption of contaminated fish by human beings and toxicity (T), resulting in measurable harm to organisms in the environment. The physico-chemical properties that characterize these parameters are described in Table 3.3. Cut-off values are used to decide whether a compound is persistent, bioaccumulative or toxic and the response is added to the table. Such cut-off values are presented in Table 3.4. Based on the cut-off values, it should be decided whether to keep the contaminant on the preliminary list of organic contaminants of possible concern (PLOCPC) or add it onto the preliminary list of organic contaminants of concern (PLOCC). Values for each of the contaminants obtained from the above step are obtained from the literature and using a "Yes" or "No" decision making process a contaminant is characterized as "persistent" or "not persistent". The same is done for other parameters. This information is added to the table of organic contaminants of concern.

Since not all the organic contaminants will have readily available data on the fate and behaviour in the aquatic environment, human exposure effects, fate and behaviour in the human body, interactions with other chemicals in nature, measurement in environmental samples, removal methods from source water, drinking water quality guidelines or standards to enable regulation, it was necessary to consult more information sources and proprietary data in order to collate relevant information. It was decided that water quality monographs be developed as a way of summarizing the findings in a format that could be user friendly for the Drinking Water Industry and relevant stakeholders. [Step III, Figure 3.2]

Table 3.3: Physico-chemical properties used to confirm the occurrence and P,B,T criteria [28]

Physico-chemical property	Description	Criteria
Water solubility, S_w, mg/l	Describes the amount of chemical that can dissolve freely in a known quantity of water.	Persistence
Vapour pressure, V_p, Pa (N/m2)	Saturation vapour pressure of compound at defined temperature, potential of chemical to evaporate, atmospheric transport	Persistence
Henry Law 's constant, H_c ($Pa.m^3/mol$ or dimensionless)	Equilibrium partition between constant between air and water at a defined temperature. Indicates the tendency of a chemical to volatilise from soil, water and plant surfaces into the atmosphere.	Atmospheric transport
n-octanol-water partition coefficient K_{ow} or log K_{ow}	Indicates the tendency of a chemical to partition between water and lipid/organic matter (lipophilicity), Alternate to BCF	Bioaccumulation
Organic carbon-water partition coefficient, Koch (cm^3/g)	It is the ratio between the concentration of a compound on organic carbon and the concentration in water. It indicates the chemical's tendency to adsorb onto organic carbon from solution, tendency to become tightly bound on humic material of the soil or leach through it.	Bioaccumulation
Half-life in soil,	Time for half of initial concentration to be lost due to aerobic or anaerobic biodegradation. The reaction is of first order kinetics	Persistence
Half-life in water	Time for half of initial concentration to be lost due to hydrolysis, aerobic or anaerobic biodegradation. The reaction is of first order kinetics	Persistence
Bioconcentration factor in fish (BCF_{fish}), kg wet fish/litre of water)	Indicates the tendency of a compound to partition between different environmental compartments and is defined as the ratio between the concentration of a chemical in biota and the concentration in water at equilibrium.	Bioaccumulation
Fugacity	It is regarded as the escaping tendency of a chemical from a phase. It has units of pressure and can be related to concentration.	Fate in the environment, partitioning, transformation, transport
LD_{50}	Indicator of mammalian toxicity of substances, expressed in mg/kg	Toxicity
LOAEL	Lowest Observed Adverse Effect level	Toxicity
LC_{50}	Acute toxicity of substance resulting in mortality of 50% of test aquatic organisms	Toxicity

Table 3.4: Cut-off values for selected parameters

Physico-chemical property	Cut-off values
Henry Law 's constant, H_c ($Pa.m^3/mol$ or dimensionless), volatilization potential	$H_c > 1 \times 10^{-4}$ High $H_c = 1 \times 10^{-4}$ Medium $H_c < 1 \times 10^{-4}$ Low [28]
n-octanol-water partition coefficient K_{ow} or log K_{ow}	$K_{ow} > 4$ low tendency to stay in solution $2.5 < K_{ow} < 4$ Medium tendency or possible $K_{ow} < 2.5$ High [28]
Mean Half-life in soil (persistence measure)	<0.042 days (1 hour) Very short-lived- Low 0.042-0.42 days Short-lived Low 0.42-4 days Moderately short-lived Medium 4-40 days Moderately persistent High >40 days Highly persistent High [28]
Mean Half-life in water (persistence measure)	<0.042 days (1 hour) Very short-lived- Low 0.042-0.42 days Short-lived Low 0.42-4 days Moderately short-lived Medium 4-40 days Moderately persistent High >40 days Highly persistent High [28]
Bio-concentration factor in fish (BCF_{fish}), kg wet fish/litre of water)	$BCF_{fish} < 10$ Bioaccumulation unlikely BCF_{fish} 10-100 Low bioaccumulation BCF_{fish} 100-1000 Bioaccumulation Moderately low BCF_{fish} 1000-10,000 Bioaccumulation Moderately High $BCF_{fish} > 10,000$ Bioaccumulation High [28]
log K_{ow} as an estimate of bioaccumulation potential	Log $K_{ow} < 2$ Bioaccumulation unlikely Log K_{ow} 2-3 Bioaccumulation low Log K_{ow} 3-4 Bioaccumulation Moderately low Log K_{ow} 4-5 Bioaccumulation Moderately high Log $K_{ow} > 5$ Bioaccumulation High [28]
LD_{50}	Acute LD_{50} < 0.1mg/l, Chronic or long term or Chronic toxicity NOEC ≤ 0.01mg/l [15]
LC_{50}	Acute LC_{50} ≤ 0.1mg/l, Long term or Chronic toxicity NOEC ≤ 0.01mg/l [15]

3.3.3.3 Step III: The development of Water quality monographs

The aim of this step is to gather additional information on each contaminant to further assist with the screening of organic contaminants. Hence, the development of water quality monographs is used as a screening and information elucidation tool. [Figure 3.2, Step III] The following outline is adopted to ensure maximum benefit.

Table 3.5: Water Quality Monograph template

A. GENERAL INFORMATION

Water quality variable	
CASRN	
Toxic	
Mutagenic	
Carcinogen	
Endocrine disruptor	
Teratogenic	
Priority pollutant	
Accumulative	
Persistent	
Essential element	
Aesthetic	
A.D.I	
L.O.A.E.L	
N.O.A.E.L	
LD_{50} mg/kg (oral)	
LD_{L0} mg/kg (oral)	
Trade names	

B. OCCURENCE

C. PROPERTIES/STRUCTURE

D. FATE AND BEHAVIOUR

E. MEASUREMENT

F. HUMAN EXPOSURE

G. TOXICOLOGY

REMOVAL DURING WATER TREATMENT

I. NATIONAL AND INTERNATIONAL DRINKING WATER CRITERIA

COUNTRY/ORGANISATION	CRITERIA	
WHO		
USEPA		
AUSTRALIA		
EEC		
SOUTH AFRICA, etc		

J. GENERAL DISCUSSIONS

K. REFERENCES

The following sections describe the content of each component used in the water quality monograph template (Table 3.5).

A. General information

The general information concerning the organic contaminant including its common name which should be stated under "water quality variable", and the chemical abstract services register number (CASRN) which is a unique number that identifies the chemical should be given. These name and number will serve to correctly identify the organic substance being represented and not confuse it with other similar compounds. Of particular value under this heading is the toxicological data. This should be summarized in form of "Yes or No" responses to each aspect such as whether it is toxic, mutagenic, carcinogenic, endocrine disruptor, teratogenic, of aesthetic concern, priority pollutant, accumulative, or essential element. The health effect indicators should be located numerical values. The test organisms on which the study was based on should also be indicated. The units of measurement are also crucial. These includes Reference dose (R_fD), Acceptable Daily intake (ADI), Low Observed Adverse Effect Level (LOAEL), No observed Adverse Effect Level (NOAEL), and toxicity parameters such as LD_{50} and LC_{50}. The persistence (P), bioaccumulation (B) and toxicity (T) attributes of specific organic substances as presented in the Stockholm Convention on priority organic pollutants (POPs) [7,12, 29] may be used. The description of each parameter is presented under the "Conceptual definitions" in Chapter I of this Thesis. Other names such as trade names and the international union of pure and applied chemistry (IUPAC) name are also included to help in soliciting more information as the chemical can be represented using these different names in the various sources of information.

B - Occurrence

This section should give a summary on the sources of the organic contaminant, its routes and pathways into freshwater systems or any part of the drinking water supply chain. In certain instances specific levels at which this contaminant has been found in water or other environmental matrices of relevancy should be given. This part of the document is very important as it defines the contaminant as a drinking water contaminant of concern.

C - Properties/structure

An organic contaminant can be classified as water based or atmospheric contaminant of concern based on its physical and/or chemical properties. In this section of the water quality monograph, the physical and chemical properties of the organic contaminant including its structure should be given depending on the availability of the information.

D – Fate and Behaviour

An organic contaminant may be known to be toxic or cause adverse human health effects in other forms such as particulate nature while in the atmosphere or as part of a food product and not in other forms. In the environment the parent compound can be broken down under both anaerobic and aerobic conditions or not at all. It is therefore crucial under this section to identify the degradation pathways, chemical reactions and products that can be formed as part of these interactions. The fate of the organic contaminant in the aquatic environment as well as along the drinking water supply chain should be summarized. This depends heavily on the type of information and availability of information. More attention should be given to the fate of the contaminant once it is in water under both aerobic and anaerobic conditions.

E - Measurement

The best analytical technique or screening method for the organic contaminant or group of organic contaminants should be given under this section. Such aspects as sensitivity accuracy, limit of quantification, recovery and method detection limit are taken into consideration. This will serve as evidence that the contaminant is already considered a concern for analysis in the drinking water value chain and the matrix should be indicated.

F - Human exposure

The various human exposure routes to organic contaminants including their effects should be discussed. The major route by which humans can be exposed should be stated.

G –Toxicology

The information summarized in Section A should be described in detail here giving examples.

H - Removal during water treatment

This section presents the techniques that can be used to remove the contaminant or group of contaminants during drinking water treatment as presented in the literature and to the specialist's best knowledge.

I - National and international drinking water quality criteria

Drinking water quality standards and guidelines values are very important in public health protection. These values themselves provide a basic risk assessment, since these are substances deemed likely to be present in drinking water and a health evaluation has been carried out. This includes an allowance for exposure from other sources, but still provides a basic health risk assessment and a first screen for prioritization. [30] Hence, the available national and international drinking water quality criteria should be presented. The WHO guidelines can be used as a benchmark. [7] This is because this document is produced after

consultation with specialist of different backgrounds relevant to public health protection. It undergoes continuous revision based on current challenges in the drinking water and public health protection areas. Standards/guidelines listed by other countries/organizations, [22, 25] should be consulted during the compilation of this part of the monograph. For example for South Africa, the South African drinking water quality guidelines from the Department of Water Affairs, regulations on industrial chemicals and pesticides residues allowed in water used for human consumption from the Department of Health and the South African National Standard, the national drinking water standard [106] should be consulted.

J - General discussion

This section represents the decision-making part on whether to include the organic contaminant or group of contaminants on the List of organic contaminants of concern. [Figure 3.2, Step III] The decision is based on the analysis of all information available from sections A to I of the water quality monograph. Special attention is given to the occurrence [Section B, Table 3.5], adverse health effects and exposure information as presented in sections A, F and G in Table 3.5. The availability of drinking water criteria in order to be able to regulate the contaminant is regarded in highest priority.

K-References

References are important for information retrival. The reader must be able to identify the origin of the summarized information should they want to read the full article or assess the authenticity of the source.

3.3.3.4 Step III Use of other criteria

Other than the use of water quality monographs, some organic contaminants might not have sufficient data to support the decision making process. “Other criteria” can therefore be used as presented in Figure 3.3. For example, questions as presented in Figure 3.3 can be asked and the answers could assist in deciding whether to list the organic contaminant as that of concern. The other criteria includes potential water quality problems which might occur as a result of the use of a chemical, its metabolites or residues during drinking water production, for example damage to infrastructure and evidence from other organizations such as the Departments of Agriculture and Health which are kept as proprietary data indicating organic compounds that have been used for human or animal poisoning as a result of contamination of drinking water. More of the evidence emanating from these criteria will be obtained during the validation of the preliminary list of organic contaminants of concern to the Drinking Water industry. The elements mentioned in Figure 3.3 should come from the local screening experts, hence the nature of being tailor made. The outcome of these four steps is a preliminary list of organic contaminants of concern (PLOCC) to the to the Drinking Water

industry. The organic contaminants on this list are going to be screened for occurrence in the drinking water value chain and validated by the Drinking Water industry experts and relevant stakeholders before being accepted as the final list of concern to drinking water safety. (Step IV)

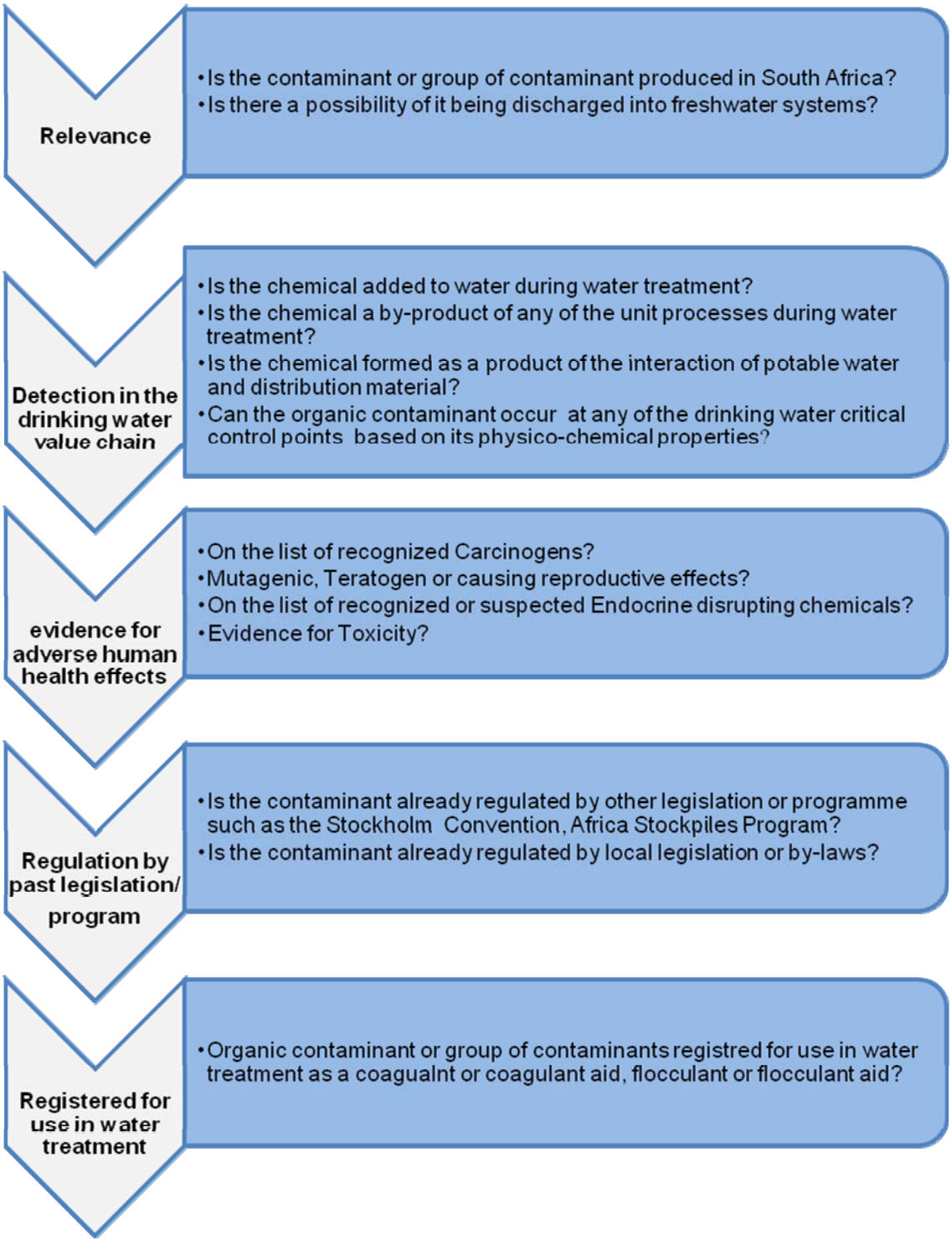

Figure 3.3 Other criteria for screening the preliminary list of organic contaminants of possible concern.

3.3.4 Step IV: Testing for organic contaminants in a prototype drinking water value chain, validation of the list of organic contaminants of concern by industry experts and relevant stakeholders.

During this step, organic contaminants on the preliminary list of organic contaminants of concern (PLOCC) obtained from step III must be assessed for occurrence in the drinking water value chain. Testing for organic contaminants in a prototype drinking water value chain should be done at this stage. This is achieved by determining the concentration levels by laboratory analysis, whereby comprehensive laboratory analyses of organic contaminants in biota (fish tissue), sediments and water samples are conducted. The aim of this is to determine which organic contaminants or group of organic contaminants occur in the drinking water value chain (Figure 3.2). For adequate results and information the following must be satisfied;

- At least all of the organic contaminants on the PLOCC should be assessed;
- The assessed organic contaminants must be representative of all functional groups of concern;
- Sample collection should cover all the critical control points along the drinking water value chain;
- The participating laboratories must be accredited for the various analysis. The methods used for the measurement of organic contaminants must also be accredited;
- Quality Assurance measures must be satisfactory and
- The data must be sufficient to allow adequate statistical analysis and verification.

Once the data has been collected, interpretation should be done. This is followed by a decision on whether the organic contaminant was positively identified or not in the drinking water value chain and whether it should pass onto the final list of organic contaminants of concern (FLOCC). Hence the outcome of this step is the Final list of organic contaminants of concern (FLOCC)

3.3.5 Step V: Establishment of Technical capability for the removal of organic contaminants through conventional water treatment, recommendations for the implementation of the FLOCC

Once the FLOCC has been arrived at, the decision to continue with the prioritization exercise should be done. This step like the preceding one should be completed in consultation with the relevant stakeholders especially the technical experts such as those involved with the various unit processes, manufacturing industry experts, organic chemists, water quality assurance personnel and those involved in the procurement of chemicals. To be cost

effective one could consider achieving the objectives of both steps in one workshop. The step is based on the following assumptions;

- Rural community based water utilities especially in developing countries still have poor infrastructure that do not meet the current challenges for organic contaminant removal. This can also be true for some urban based water utilities.
- The spread of vector based diseases such as malaria has resulted in the use of organic contaminants especially pesticides in public health programmes dedicated to control these diseases. However, the pesticide residues remain widespread in the environment and could be a risk to future generations. The WHO in its 3rd edition of the Guidelines for Drinking Water Quality identified those pesticides that are commonly used or being considered for vector control in drinking water sources and containers. [13] These are DDT and its metabolites, Diflubenzuron, Methroprene, Novaluron, Pirimiphos Methyl and Pyriproxyfen. The WHO proposes that it is important to achieve an appropriate balance between the intake of the pesticides from drinking water and the control of diseases–carrying insects. [7] The reason for this being the fact that the diseases spread by vectors are significant causes of morbidity and mortality. [13] On the other side evidence of the impact of these organic contaminants especially on the endocrine system on animals is no longer disputable. This information is crucial during this step and experts involved in these public health programmes would be needed to assist water utilities in decision-making.
- Although it is known that the chemical can be successfully removed by conventional treatment, it is prudent to prioritize it to assess that it does not occur in the drinking water value chain. This is true in cases where there is enough evidence on its potential adverse health effects. This will be possible for water utilities with appropriate infrastructure in place.
- Some water utilities might not have the capacity to remove the organic contaminants on the FLOCC in terms of the available unit processes, for example not using activated carbon processes like the Granular Activated Carbon (GAC) or Powdered Activated Carbon (PAC) as a minimum, and some organic contaminants can escape the process and be a potential risk to the consumer. This is a reality in most developing countries.

In the situation whereby the water utility has no capacity for organic contaminant removal, it will be prudent to adopt the FLOCC as the list of priority organic contaminants for monitoring in surface and groundwater. In this case, those laboratories that are accredited for organic analysis or with the capability for analysis like the situation in other universities and similar research organizations can be used by the water utility to analyse its water samples from

catchment to tap for analysis. The organic contaminants positively identified during these testing programs will be added to the "preliminary priority list of organic contaminants (PPLOC)" Figure 3.2.

3.3.6 Step VI: Prioritization of the organic contaminants on the final list of organic contaminants of concern (FLOCC)

It is well understood that the highest priority chemicals are those that have shown to cause human health effects as a consequence of exposure through drinking water. The high-priority chemical list can be modified if those chemicals are found not to be present, but a chemical not found in an initial investigation should not be forgotten. [30] Those chemicals that are found to be present, call for the "occurrence criteria, as in Step IV" in form of testing for the organic contaminants in environmental samples in the drinking water value chain. In the case of organic contaminants that have been shown to cause human health effects as a consequence of exposure through drinking water, evidence from toxicological studies, epidemiological studies and proprietary data can be used. Proprietary data can be sourced from the various health-related institutions such as hospitals, environmental justice organizations, manufacturing industries data on occupational health. Some information sources that could be used are presented in **Table 3.2**. The preliminary priority list of organic contaminants obtained from the preceding steps is subjected to the prioritization criteria described below. As in the above statement, the norm for prioritization is public health protection and the two pillars for the criteria is the occurrence of a contaminant in the drinking water value chain which increases the potential for exposure and the opportunity to cause adverse health effects.In order to accomplish this, the organic contaminants on the final list of organic contaminants of concern (FLOCC) are organized in a table as shown in Table 3.6. The contaminants are then prioritized using criteria reflective of the Drinking Water industry perspective. [Figure 3.5]

3.3.6.1 Step VI: Occurrence criterion in the drinking water value chain

Evidence for occurrence of the organic contaminant has been collected in four tiers in preceding steps, that is from the literature, water quality monograph development process, experts knowledge and judgement and testing for the occurrence of organic contaminants in the drinking water value chain. Once the data has been collected, intepretation should be done. This is followed by a decision on whether the organic contaminant was positively identified or not in the drinking water value chain. The responses are indicated as shown in Table 3.6 under the column "Found in the drinking water value chain?". The response is qualitatively made in form of "Y"-Yes or "N"-No.

Table 3.6: From the PPLOC to priority organic contaminants for monitoring in the drinking water value chain (*An example*)

Monograph Number	*Parameter*	Units	Standard/Guideline	Currently Analyzed for?	*Human Health Concern*									Remarks
					Persistent	Accumulative	Toxic	Carcinogen	Mutagen	Endocrine disruptor	Teratogenic	Found in the drinking Water value chain	Priority for analysis	
A. INDUSTRIAL CHEMICALS														
A1	Benzene	µg/l	10(WHO), 5(USEPA), 10(NZ), 1(AU)	Y	Y	Y	Y	Y	Y	-	Y	Y	S	Also causes taste and odour problems
A2	Benzo [a] pyrene	µg/l	0.2(US), 0.7(WHO), 0.7 (NZ), 0.01(EU), 0.01(AU)	Y	Y	Y	Y	Y	Y	Y	Y	Y	S	Most toxic Polynuclear aromatic hydrocarbon.
B1	2,4-Dichlorophenoxyacetic acid	µg/l	70(USEPA), 30(WHO), 40(NZ)	Y	N	N	Y	Y	N	Y	N	Y	*S*	Currently regulated herbicide
B2	Aldrin	µg/l	0.03(WHO), 0.04(NZ), 0.03(USEPA), 0.03(EU), 0.3(AU),0.7(Can)	Y	Y	N	Y	Y	Y	Su	N	Y	*S*	Immediately converted to Dieldrin in the aqueous environment.
-	Pendimethalin	µg/l	20(WHO), 20 (NZ), 300(AU)	N	Y	Y	Y	-	N	-	N	N	L	Liver toxicity
-	Linuron(herbicide)	µg/l	-	N	N	-	Y	Y	N	Y	N	-	L	Testicular hyperplasia
E5	Allyl chloride	µg/l	-	N	N	N	Y	Y	Y	-	-	Y	M	No criteria for regulation
E6	Diallyl ether	µg/l	-	N	N	N	Y	Y	-	-	-	Y	M	VOC, no drinking water criteria
-	*Pentachlorobenzene*	*µg/l*	-	*N*	*N*	*N*	*Y*	-	-	-	-	*Y*	*S*	*Liver and kidney toxicity*
-	*Trichlorobenzenes (Total)*	*µg/l*	*30(AU)*	*Y*	*N*	*N*	*Y*	-	-	-	-	*Y*	*S*	*See individual CBs*
-	*Polynuclear aromatic hydrocarbons*	*µg/l*	*0.10(EU)*	*Y*	*Y*	*Y*	*Y*	*Y*	-	*Y*	-	*Y*	*S*	*toxic effects arylhydrogen receptor mechanism*

Notes: **Y**-"Yes", **N**-"No", **Su**-"Suspected", ***S**-Analysis in the short term (1-2 years), **M**-Analysis in the medium term (3-5years), **L**-Analysis in the long term (5-10years)*

3.3.6.2 Step VI: Adverse human health criterion

The information gathered from the literature review and water quality monographs is used at this stage as it would be already available in Table 3.6. This information and the information obtained from the preceding section 3.3.6.1 is combined to assist in prioritizing the organic contaminants in four groups as indicated in Figure 3.4.

At this stage, the prioritization approach identifies;

- Contaminants that are demonstrated to cause adverse health effects and to occur in the drinking water [I in Figure 3.4, Table 3.6].
- Contaminants that are demonstrated to cause adverse health effects and have the potential of occurrence in drinking water [II in Figure 3.4, Table 3.6].
- Contaminants that are demonstrated to occur in drinking water and have the potential to cause adverse health effects [III in Figure 3.4, Table 3.6] and
- Contaminants that are demonstrated to have the potential to occur in drinking water and have the potential to cause adverse health effects [IV in Figure 3.4, Table 3.6]

The approach considers and uses as many of the available types of health effects and occurrence data identified in the data source evaluation as practical (Figure 3.4, Table 3.6).

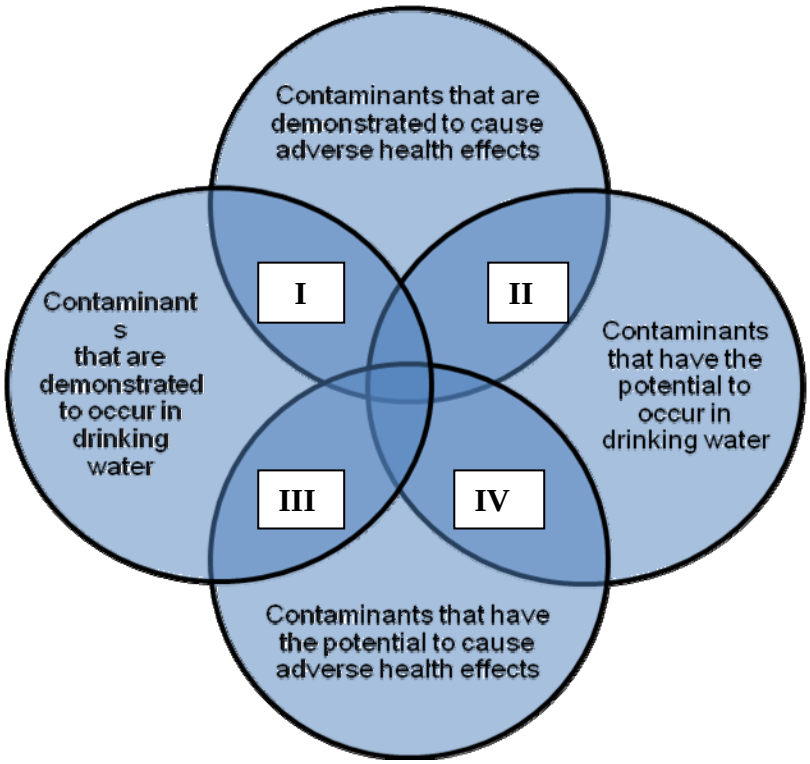

Figure 3.4: Prioritization criteria for drinking water contaminants-modified from the USEPA. [15]

The potential adverse health effects are re-affirmed as presented by the water quality monographs. Based on these two aspects a "priority for analysis" decision is made.[Table 3.6]

3.3.6.3 Step VI: Other criteria

This list is further subjected to analysis based on Drinking Water industry perspective and requirements. It is advisable that local conditions should define this process. The analysis covers aspects such as availability of standards/guidelines for regulation, potential to cause water quality problems, potential to stimulate customer perception of risk, removal efficiency and availability of expertise and capacity for analysis. [Figure 3.5]

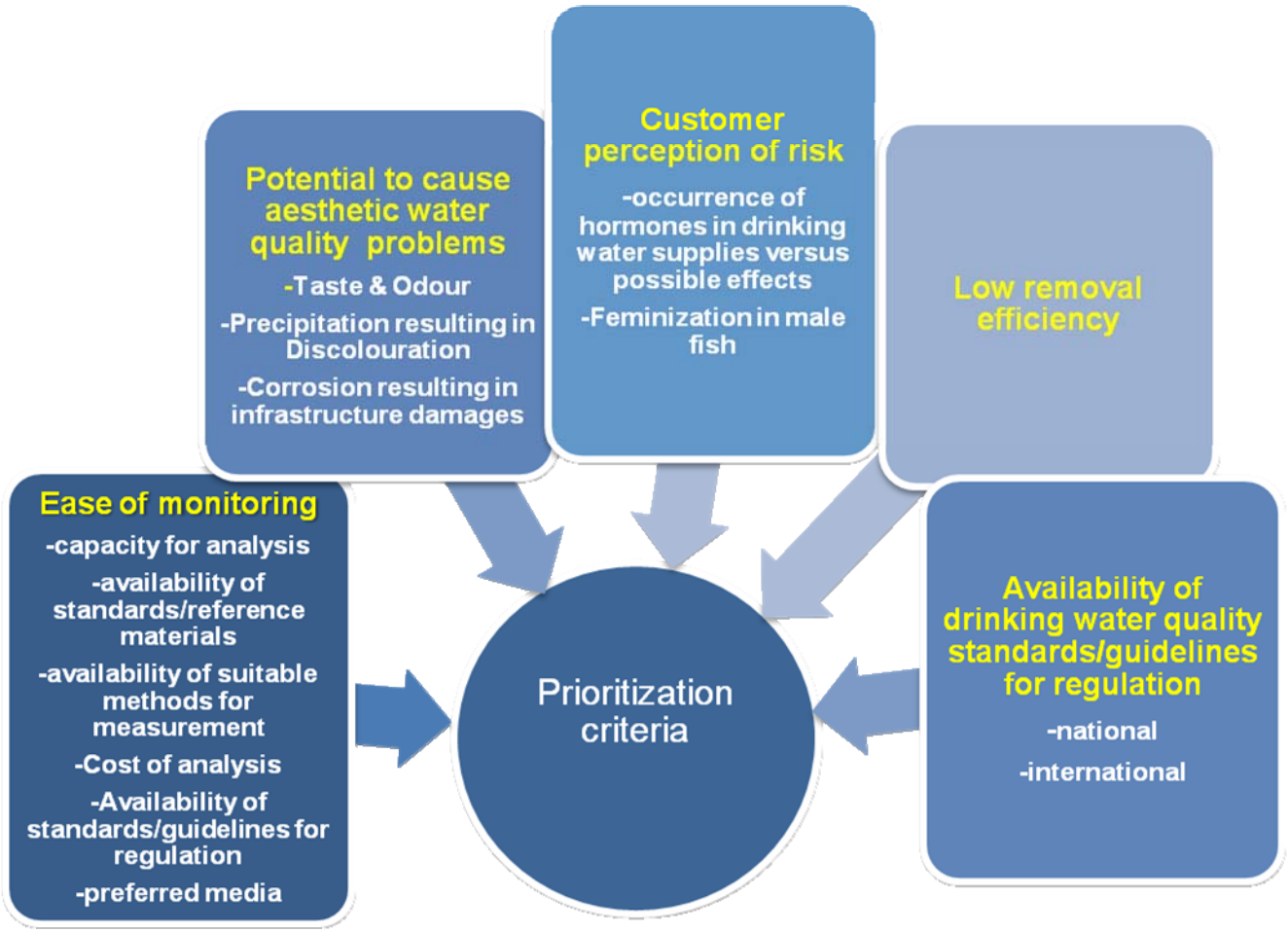

Figure 3.5: Prioritization criteria for the substances on the FLOCC

Based on the above criteria, [Figure 3.5] a semi-quantitative approach is used and three priority lists of organic contaminants are identified. [Table 3.6] The organic contaminants are prioritized into short-term (S), medium term (M) and long term (L) priority for analysis in the drinking water value chain. Those organic contaminants placed on the short-term priority list are adopted for immediate routine monitoring in the drinking water value chain:

- Short-term (S) substances falling within this category are listed in Table 3.6 and Figure 3.5. Organic constituents in this category are selected based on the following characteristics;
  -The wide range of potential human health concerns via the drinking water ingestion route;
  -The substance is known to cause water quality problems in the drinking water value chain such as the cause of offensive tastes and odours;
  -There is evidence that the occurrence of a substance or group increases customers perception of risk;
  -There are enough resources in place to support ease of monitoring;
  -Poor removal efficiency using conventional water treatment methods;
  -Availability of drinking water standards/guidelines to enable regulation;
  -Proof of occurrence in the drinking water value chain especially those contaminants formed during drinking water treatment, distribution, storage and use.
  At least four or more aspects must be satisfied.
- Medium term (M) substances falling within this category are listed in Table 3.6.
  The wide range of potential human health concerns via the drinking water ingestion route;
  -The substance is known to cause water quality problems in the drinking water value chain such as the cause of offensive tastes and odours;
  -No evidence that the occurrence of a substance or group increases customers perception of risk;
  -No resources in place to support ease of monitoring;
  -Moderate removal efficiency using conventional water treatment methods;
  -Non-availability of drinking water standards/guidelines to enable regulation;
  -Proof of occurrence in the drinking water value chain especially those contaminants formed during drinking water treatment, distribution, storage and use.
- Long term (L) substances falling within this category are listed in Table 3.6. Organic constituents in this category are selected based on the following characteristics;
  -Insufficient information on human health concerns via the drinking water ingestion route;

-Insufficient information on the impact of the organic contaminant on drinking water quality;

-No evidence that the occurrence of a substance or group increases customers perception of risk;

-No resources in place to support ease of monitoring;

-Removed from drinking water using conventional water treatment methods;

-Non-availability of drinking water standards/guidelines to enable regulation;

-Proof of occurrence in the drinking water value chain especially those contaminants formed during drinking water treatment, distribution, storage and use.

The outcome of this step is a preliminary priority list of organic contaminants (PPLOC) for monitoring in the drinking water value chain. However, further validation by Drinking water industry experts and relevant stakeholders still needs to be done.

3.3.7 Step VII: Validation of the preliminary priority list of organic contaminants (PPLOC) by Drinking Water industry experts and relevant stakeholders

The preliminary priority list of organic contaminants obtained from step VI must be presented to a group of experts from the Drinking Water Industry and relevant stakeholders for validation. This can be in form of a Workshop, meeting or use of questionnaires or a combination of these methods. The main aim of this step is to confirm if the organic contaminants on the PPLOC list should be adopted as a priority list for monitoring in the drinking water value chain. Industry specific information is crucial at this stage such as that used in Step VI, Figure 3.5. Benchmarking with other national and international bodies such as the WHO, USEPA, OECD and EU is once more necessary.

3.3.8 Review of priority list

The current status of research indicates that the release of organic contaminants into the aquatic environment is increasing. At the same time analytical methods that can detect these contaminants at lower levels than the current conventional measurement techniques such as Gas Chromatography Mass spectrometry (GC-MS) are being developed. [31] The other point to note is the increasing number of anthropogenic activities in catchments as well as the noticed effects of climate change which might result in the increase of organic contaminants released into source water resources. From these developments new organic contaminants that can be a priority for public health protection through appropriate drinking water quality management might be identified. For example, the EAWAG is currently developing prediction models to facilitate the identification of transformation products of pesticides, biocides and pharmaceuticals whose concentrations and effects make them relevant to water quality. [31] It will therefore be crucial to review the current priority list every five years given the need to

ensure that technical needs for successful measurement and quantification of organic contaminants of concern are in place. It will also be important to allow adequate consultation among all relevant stakeholders concerned with public health protection of the consumers as outlined in the protocol. [Figure 3.2]

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CHAPTER 4 THE VALIDATION OF THE SELECTION AND PRIORITIZATION PROTOCOL IN A PROTOTYPE DRINKING WATER VALUE CHAIN: A CASE STUDY OF THE RAND WATER BOARD

4.1 BACKGROUND

Rand Water is a bulk water supplier which provides treated water to more than 12 million people. Rand Water's area of supply includes a distribution network that is over 3 056 kilometres of large diameter pipeline, feeding 58 strategically located service reservoirs [Figure 4.1]. Its customers include metropolitan municipalities, local municipalities, mines and industries and it supplies, on average, 3 653 million litres of water to these customers daily. [1] Rand Water abstracts its source water from the Vaal Dam catchment. This catchment is mainly agricultural although other land-use activities such as coal mining, gold mining, fuel production and power generation, urban and industrial development are noticed. This could result in the release of organic contaminants into the catchment.

The potential impact of pesticides and other organic contaminants in the Vaal River catchment was noticed more than 20 years ago. A survey conducted by Bruwer et al. [1985] cited in Braune and Rodgers, [2] showed micro-organic contamination along the entire length of the Vaal River downstream of the Barrage. [2] The survey also indicated evidence of bio-accumulation of polychlorinated biphenyls (PCBs) and chlorinated pesticides in fish. [2] Van Steenderen et al. [1986] cited in Braune and Rodgers [2] reported a high degree of organic contamination in the Vaal River below the Barrage to Parys. [2] High phenolic compounds were found. These compounds can cause serious taste and odour problems, especially after chlorination. Van Steenderen et al. [3] investigated organic contamination between the Vaal Dam-Vaal River Barrage system.[3] The investigation of organic contaminants between the Grootdraai Dam and Parys resulted in 25 organic compounds being identified.[3] These included chlorinated benzenes, phenols, phthalates, saturated hydrocarbons, pesticides such as atrazine, γ-BHC, Cholesterol and polynuclear aromatic hydrocarbons such as Pyrene.

Rand Water in the early 80s did an extensive survey of all international organic criteria, compiled appropriate documents on the use of organic contaminants in its catchments and presented to a panel of experts at a Workshop funded by the company in order to establish usage in South Africa of compounds and the possibility of any detrimental health effects on Rand Water consumers. [4] It was from this study that it was noticed that the limiting factors have been the lack of accurate information about the extent of pollution, lack of capacity and expertise for analysis and the absence of local guidelines and standards for regulation of organic contaminants in drinking water. A recent study by Polder et al. 2008 [5] indicated that

higher concentrations of polybrominated diphenyl ethers (PBDEs) were measured in bird eggs from the Vaal River which is situated downstream of the most industrialized area in South Africa. [5] Some of the research needs identified for the Vaal River Catchment by Braune and Rodgers, 1987 [2] were the establishment of an organic pollutant monitoring system, factors affecting water quality in the Vaal Dam and the effects of future management options on water quality and the accumulation of pesticides in the aquatic food chain. [2]

The findings of the above mentioned study as well as the identified research needs and the global actions on persistent organic pollutants (POPs) and suspected or potential Endocrine Disrupting Chemicals (EDCs) have since served as a catalyst for Rand Water management to re-kindle the efforts to address concerns of possible drinking water contamination by organic contaminants. This view point was held by other role players in the water sector and relevant stakeholders such as the Department of Water Affairs (DWA), the Water Research Commission (WRC), other Water Boards, the Department of Agriculture, universities who started the dialogues and research in the area. It is because of this background, that Rand Water has been chosen for validation of the protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain.

4.2 APPLICATION OF THE PROTOCOL

4.2.1 STEP I: SELECTING THE "POOL OF ORGANIC CONTAMINANTS"

A list based approach was used in compiling the "pool of organic contaminants".[Figure 3.2 of the protocol] Information on naturally occurring organic contaminants, known classical and "emerging organic contaminants", organic contaminants deliberately added into the drinking water during its treatment including known water treatment residues [WTR], restricted, banned and locally used pesticides was collated. [Table 4.1] South Africa was used as an example for identifying the list of pesticides. Four manuals on used pesticides and management of pests were purchased from the national Department of Agriculture. [DoA] The PAN-UK database for South Africa's registered list of pesticides was used for comparison and confirmation. The lists of regulated organic contaminants, such as endocrine disrupting chemicals [EDCs] [Table 4.2], "the dirty dozen", [Table 4.3] and the EU list of priority substances for drinking water for human consumption. [Table 4.4] were also considered.

Residue limits in water, the list of "Recognized carcinogens" by the IARC, the EU list of priority pollutants (Table 4.4) and organic contaminants appearing in drinking water quality guidelines or standards such as the South African National Standard for drinking water (SANS 241), WHO guidelines for drinking water quality 3rd edition of 2004, Health Canada drinking water quality guidelines, the USEPA list of regulated organic contaminants on the drinking water quality standards, organic contaminants on the Australian drinking water quality guidelines and the New Zealand drinking water quality standards. Interviews were conducted with various organizations to identify organic contaminants being analyzed for. These were conducted with other Water utilities, the Department of Agriculture, its council, the Agricultural Research Council (ARC), the former Department of Environmental Affairs and Tourism (DEAT) and the Department of Water Affairs (DWA)'s Resource Quality Services (RQS) formerly known as the Institute for Water Quality Services (IWQS). The information gathered from the interviews was checked against the "pool of organic contaminants" or added accordingly.

An Excel spreadsheet was compiled out of the information provided in the preceding sections. The list of common names of active ingredients obtained from the four manuals from the national Department of Agriculture was added to the spreadsheet including all other sources. The list of organic contaminants on the WHO guideline document was used as a benchmark. The resultant list consisted of 850 organic contaminants. On observing the list, duplication of some organic contaminants was noticed. The other aspect was that of inorganic compounds appearing on the list and the listing of the plant extract names and food

additive. **The list was cleaned and the resultant "pool of contaminants" contained 600 compounds.** Some of the contaminants are presented on Table 4.6 and the rest in the attached CD-ROM.The organic contaminants assessed on the USEPA IRIS database are shown in green font on the list.

Table 4.1: Information sources for compiling the "pool of contaminants"

Organization	Information requested	Remarks
Other water utilities	Organic contaminants currently analyzed for in drinking water	BTEX, THMs, DOC, phenols
Department of Agriculture	Banned, restricted and frequently used pesticides in South Africa	A set of four manuals on pesticides used in South Africa for various purposes were obtained. [6-9]
Department of Environmental Affairs and Tourism	Africa Stockpiles Project implementation in South Africa	The dirty dozen [Table 4.3]
The Department of Water Affairs, National Toxicity Monitoring Programme	Toxicants monitored in national water resources	The dirty dozen [Table 4.3]
The WHO guidelines for drinking water quality, 3rd edition, 2004,	Organic contaminants of concern to public health	All listed organic contaminants ,[Table 4.5, CD-ROM]
The PAN-UK list of registered Pesticide for South Africa	List of currently used, banned, restricted pesticides	About 500 pesticides had been registered at the time of the study.[Table 3.2]
SANS 241:2006	List of organic parameters for analysis in drinking water	DOC, Phenols and THMs
Health Canada	List of organic parameters for analysis in drinking water	Listed organic contaminants of concern, [Table 4.5, CD-ROM]
New Zealand	List of organic parameters for analysis in drinking water	Listed organic contaminants of concern, [Table 4.5, CD-ROM]
IARC	List of organic contaminants "recognized as human carcinogens"	Listed organic contaminants of concern, [Table 4.5, CD-ROM]
USEPA, IRIS database	A list of organic compounds for which Chronic health hazard assessments for non-carcinogenic effects have been done	Listed organic contaminants of concern, [Table 4.5, CD-ROM]
EU Drinking Water Directive	List of organic contaminants for analysis in water used for human consumption	Table 4.4
EDCs for monitoring in drinking water (South Africa)	List of EDCs	WRC Project KV 143/05, see Table 4.2

Table 4.2: List of priority Endocrine disrupting Chemicals (EDCs) for monitoring in drinking water [10,11]

Compound	**Chemical Class**	**Relative potency to 17β-estradiol**
17β-estradiol Estriol Estrone 17α-Ethinylestradiol	Hormones	1 0.08-0.8 0.09-1 0.9-1.2
p-Nonylphenol Nonylphenol ethoxylates p-Octylphenol Octylphenol ethoxylates	Alkylphenols	$7x10^{-3}$-$1x10^{-5}$ $1x10^{-5}$ $1.5x10^{-3}$-$1x10^{-4}$ -
PCBs	Polychlorinated biphenyl dirty dozen	$1.x10^{-2}$-$1x10^{-4}$
DDT, DDE, DDD, Dieldrin, Aldrin, Endrin, α-Endosulfan, β-endosulfan, Endosulfan sulphate, Heptachlor, Heptachlor epoxide, Lindane (γ-BHC), Methoxychlor	Organochlorine pesticides	$1.x10^{-7}$
Chlorpyrifos, Azinphos methyl, Parathion	Organophosphorus pesticides	-
Deltamethrin	Pyrethroid, pesticide	
Atrazine, Simazine, Terbutylazine, 2,4-D, 2,4,5-T	Herbicides	$1x10^{-4}$
DEHP DBP Bisphenol A	Plasticiser Raw material for resins	$1x10^{-5}$ $1x10^{-5}$
Dioxins, Dibenzofurans	Dioxins/furans	-
Tributyltin, Cyhexatin	Organotin compounds	-
Vinclozolin	Fungicide	-

Table 4.3: The "Dirty dozen" as identified by the Stockholm Convention, May 2001 [41]

Compound or class of compounds	Comments
Aldrin	Insecticide used on crops such as corn, cotton also used for termite control.
Chlordane	Insecticide used on crops including vegetables, small grains, potatoes, sugarcane, sugar beets, fruits, nuts, citrus and cotton. Used on home lawn and garden pests. Also used extensively to control termites.
Dichlorodiphenyl trichloroethane (DDT)	Insecticide used on agricultural crops, primarily cotton and insects that carry diseases such as malaria and typhus.
Dieldrin	Insecticide used on crops such as corn, cotton also used for termite control.
Endrin	Insecticide used on crops such as cotton and grains, also used to control rodents.
Heptachlor	Insecticide used to control primarily against soil insects and termites. Also used against some crop pests and to combat malaria.
Hexachlorobenzene	Fungicide used for seed treatment. Also an industrial chemical used to make fireworks, ammunition, synthetic rubber, etc. Also unintentionally produced during combustion and the manufacture of certain chemicals. It is also an impurity in certain pesticides.
Mirex	Insecticide used to combat fire ants, termites, and meal bugs. Also used as a fire retardant in plastics, rubber, and electrical products.
Toxaphene	Insecticide used to control pests on crops and livestock and to kill unwanted fish in lakes.
Polychlorinated biphenyls(PCBs)	Used in electrical transformers and large capacitors as hydraulic and heat exchange fluids and as additives to paints and lubricants. Also in carbonless copy paper and in plastics. Unintentionally produced during combustion.
Polychlorinated dibenzo-p-dioxins (dioxins)	Unintentionally produced during most forms of combustion, including burning of municipal and medical waste and burning of backyard trash and industrial processes. Also can be found as trace contaminants in certain herbicides, wood preservatives and in PCB mixtures.
Polychlorinated dibenzo-p-furans (furans)	Unintentionally produced during most forms of combustion, including burning of municipal and medical wastes and burning of backyard trash and industrial processes. Also can be found as trace contaminants in certain herbicides, wood preservatives and in PCB mixtures.

Table 4.4 EU Drinking Water Directive (Council Directive 98/83/EC, 1998) list

Parameter	Remarks
Dissolved Organic Carbon,	Natural occurring contaminant
Acrylamide,	Water treatment residue
Benzene,	Industrial chemical
Benz[a]pyrene,	Industrial chemical (PAH)
2-dichloroethane	Disinfection by-product
Pesticides,	All Pesticides
Epichlorohydrin,	Water treatment residue
Polycyclic aromatic hydrocarbons	Industrial chemicals-Aromatic Hydrocarbons
Tetrachloroethene,	Industrial chemical
Trichloroethene,	Industrial chemical
Total trihalomethanes and	Disinfection by-products
Vinyl chloride	Industrial chemical

4.2.2 STEP II: VALIDATION OF THE "POOL OF CONTAMINANTS" BY INDUSTRY EXPERTS

Once the "pool of organic contaminants" was compiled a workshop [Table 4.5] was conducted to determine the organic contaminants of possible concern. This was a qualitative exercise where the guiding principle was the relevance of the organic contaminants and their public health significance to the drinking water. During the validation of the "pool of contaminants", similarities were noted and some organic contaminants were eliminated from the list based on the non-relevance to drinking water. The diversity of views and experience of the various experts was taken into consideration. The respondents which are listed according to the field field/s of expertise are shown in Table 4.5. It can be seen from the table that the group consisted of key experts relevant to public health protection through the delivery of safe drinking water. For continuity attendants of other validation workshops or meetings were drawn from this original list depending on their availability.

Some organic contaminants were adopted as of concern resulting in a "**Preliminary list of organic contaminants of possible concern (PLOCPC)" (Figure 3.2)** to be screened in Step III of the Protocol using various criteria. However, the experts suggested that the WHO guidelines for drinking water quality 3rd edition contained most of the organic contaminants of concern to drinking water and should be used as a benchmark. Taking into account the observations made on the "pool of organic contaminants" and experts views **this resulted in 328 organic contaminants of possible concern remaining on the list**. [**Table 4.6]** The PLOCPC was screened in Step III. [see attached CD-ROM]

Table 4.5: Number of responding experts per field of expertise

Field of Expertise	**Number of responding experts per field of expertise**	**Organization(s)**
Drinking water treatment, Water quality Assurance	13	Rand Water, Department of Water Affairs (DWA), Umgeni Water, Johannesburg Water, Ekurhuleni Metro
Organic Analysis in environmental samples	6	The Centre for Science and Information Research (CSIR), South African Bureau of Standards (SABS), Rand Water Analytical Services, Umgeni Water Analytical Services, the DWA's Resource Quality Services Unit.
Medical Background related to drinking water quality	1	Resource Quality Services
Toxicologists	2	Department of Water Affairs
Hydrologists	2	Department of Water Affairs
Protocol Development	3	Rand Water, Water Research Commission (WRC), Umgeni Water
Research institutions	10	WRC, CSIR and the Agricultural Research Council (ARC)
Pesticide information	3	WRC and ARC

Table 4.6: The "pool of organic contaminants" used for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain, [The complete list can be viewed in the attached CD-ROM]

#	Organic contaminant	CASRN	Other name	Classification
1	Acenaphthene	83-32-9	Dihydroacenaphthylene	Polynuclear Aromatic Hydrocarbon
2	Acenaphthylene	208-96-8	Cyclopenta[de]naphthalene	Polynuclear Aromatic Hydrocarbon
3	Acephate	30560-19-1	Orthene	Organophosphate foliar insecticide
4	Acetamiprid	135410-20-7	Neonicotinoid pesticide	Insecticide
5	Acetochlor	34256-82-1	Acetochlore	Chloroactanilide Herbicide
6	Acetone	67-64-1	Propanone	Solvent
7	Acetonitrile		Ethyl Nitrile	Disifection by-product
8	Acetophenone	98-86-2	Acetyl Benzene	Aromatic Ketone, industrial chemical
9	Acetyl chloride	75-36-5	Acetic acid, Chloride	Disinfection by-product
10	Acibenzolar-S-methyl	135158-54-2	Actigard	Fungicide, Benzodiathiazole
11	Acifluorfen, sodium	6276-59-9	Sodium, Acifluorfen	Herbicide, Diphenyl ether
12	Acrinathrin			
13	Acrylamide		Propenamide	Synthetic polymer residue
14	Acrylonitrile	107-13-1	Carbacryl	Plastic monomer
15	a-Endosulfan	115-29-7	Endosulphan	Organochlorine insecticide
16	Alachlor	15972-60-8	Metachlor	Chloroactanilide Herbicide
17	Alar			
18	Aldicarb	116-06-3	Carbamyl	Carbamide insecticide
19	Aldicarb sulfone	1646-88-4	Aldoxycarb	Carbamide insecticide
20	Aldicarb sulfoxide		Aldicarb Sulphoxide	Carbamide insecticide
21	Aldrin	309-00-2	Drinox	Organochlorine pesticide
22	alkylphenol ethoxylates (APE's)			Surfactants
23	alkylphenolic compounds			Surfactants
24	alkylphenolic polyethoxylates			Surfactants
25	Allyl chloride	107-05-1	3-Chloroprene	Water Treatment residue
26	Alpha-cypermethrin	52315-07-8	Cyperil	Pyrethroid

Table 4.7: The Preliminary list of organic contaminants of possible concern (PLOCPC), [The complete list can be viewed in the attached CD-ROM]

#	Organic contaminant	CASRN	Other name	Classification
1	Acetaldehyde	75-07-0	Ethanal, Ethyl aldehyde	naturula organic compound
2	Acetochlor	34256-82-1	Acetochlore	Chloroactanilide Herbicide
3	Acrylamide		Propenamide	Synthetic polymer residue
4	a-Endosulfan	115-29-7	Endosulphan	Organochlorine insecticide
5	Alachlor	15972-60-8	Metachlor	Chloroactanilide Herbicide
6	Aldicarb	116-06-3	Carbamyl	Carbamate pesticide
7	Aldicarb sulfone	1646-88-4	Aldoxycarb	Product of Aldicarb
8	Aldicarb sulfoxide		Aldicarb Sulphoxide	Product of Aldicarb
9	Aldrin	309-00-2	Drinox	Organochlorine pesticide
10	Allyl chloride	107-05-1	3-Chloropropene	Water treatment residue, Alkene
11	Alpha-cypermethrin	67375-30-8	Alphamethrin	Pyrethroid
12	alpha-Hexachlorocyclohexane (alpha-HCH)	319-84-6	Benzene hexachloride-Alpha isomer	Organochlorine pesticide residue
13	Ametryn	834-12-8	2-ethylamino-4-isopropylamino-6-methylthio-s-triazine	Triazine herbicide
14	Amitraz	33089-61-1	Amitraze	Antiparasitic drug
15	Anatoxin-a	64285-06-9	Ethanone	bicyclic amine alkaloid
16	Arochlor 1254	11097-69-1	Polychlorinated biphenyl 1254	Polychlorinated biphenyl
17	Arochlor 1260	85760-74-3	Polychlorinated biphenyl 1260	Polychlorinated biphenyl
18	aromatic hydrocarbons			
19	Atrazine	1912-24-9	2-aethylamino-4-chlor-6-isopropylamino-1,3,5-triazin	S-Triazine herbicide
20	Azinphos ethyl	86-50-0	Gusathion methyl	Organophosphorus pesticide
21	b-BHC	319-85-7	beta-Benzenehexachloride	Organochlorine pesticide
22	b-Endosulfan	33213-65-9	5-Norbornene-2,3-dimethanol	Organochlorine pesticide
23	Benfluralin	1861-40-1	*N*-butyl-*N*-ethyl-α,α,α-trifluoro-2,6-dinitro-*p*-toluidine	insecticide, Acaricide
24	Benomyl	84776-26-1	methyl N-[1-(butylcarbamoyl)benzimidazol-2-yl]carbamate	Fungicide

4.2.3 STEP III: SCREENING OF THE PRELIMINARY LIST OF ORGANIC CONTAMINANTS OF POSSIBLE CONCERN (PLOCPC)

The screening of the preliminary list of organic contaminants of possible concern to drinking water was performed at four different levels (Figure 3.2). This included the screening of the organic contaminants on the PLOCPC which involved conducting a literature survey as it was evident that there might be more contaminants of concern to the Drinking water industry. The list produced from the literature review was compared with the "Preliminary list of organic contaminants of possible concern (PLOCPC)" (Figure 3.2). Some organic contaminants can be eliminated at this stage based on the weight of evidence from the literature review. The compounds are arranged into a table according to their functional groups. It should be indicated at this stage if the organic contaminants are of health concern via the drinking water ingestion route. The fact that exposure to these contaminants can occur through other routes other than drinking water ingestion should be recognized. If there is any evidence from the literature review, it should be noted accordingly as this will assist in decision-making in future steps.

4.2.3.1 Step III: Literature survey on organic contaminants of concern to the Drinking water industry

The main aim of the literature review is to identify organic contaminants with the potential of occurring in source water, during water treatment, along the distribution networks and at the point of use. The main criteria guiding the review are occurrence and the potential for exposure to human beings through the drinking water ingestion route, dermal contact and inhalation during domestic water use. The focus is therefore on;

- Organic contaminants occurring in freshwater systems that could be used for drinking water production;
- Organic contaminants that can be detected in drinking water due to their use during water treatment such as synthetic organic polymers, their residues and/or disinfectants and their by-products;
- Organic contaminants that could occur in drinking water due to leaching from distribution material such as PVC pipes or as a result of reaction between the contact material and the water which can be of chemical or biological nature such as biofilms and
- Organic contaminants occurring at the point of use due to their physico-chemical properties, thereby increasing exposure to consumers through dermal contact and

inhalation. Such are the various Volatile organic compounds (VOCs) and Semi-volatile organic compounds (SVOCs).

As the population and demand for safe drinking water from domestic supplies increase, it is important to examine water quality and contaminant occurrence. This has resulted in recent research efforts being focused on organic contaminants. [12-35]The major outcome from this has been the detection of a number of more classic organic contaminants as well as the so called “emerging organic contaminants”. [36-40] Limited information is available on the fate of organic contaminants during water treatment, potable water distribution and at the point of use. [36, 37] Some studies have indicated that most organic wastewater contaminants are not completely removed during conventional wastewater and drinking water production processes. [36-40]This implies that such contaminants will be present in drinking water distributed to the consumers. The exposure of consumers to organic contaminants introduced during drinking water distribution either from materials of construction or by process needs to be assessed since consumers might have direct exposure. [13,33-39] It is therefore necessary to identify organic contaminants with the potential of entering into surface and groundwater sources, be introduced into the treatment process, survive the treatment process or be formed as impurities and/or by-products during the treatment process. This includes substances released into treated water due to leaching from distribution material such as reservoir linings, pipelines and/or released from household plumbing systems into the final drinking water. Consumers are also exposed to organic contaminants at the point of use through activities such as bathing and washing. [15] Hence, the review will cover the entire drinking water value chain.

Organic contaminants in source water resources

Source water resources on a global scale are at threat given the rate of industrialization. Organic contaminants that threaten source water quality include both naturally occurring organic compounds and synthetic organic compounds. Natural organic compounds include those that are from chemical and biological interactions in natural waters. Interactions and reactions occur resulting in the formation of new products, groups and mixtures of organic compounds. The processes most often involved in the breakdown of contaminants are photodegradation, aerobic and anaerobic action. All these processes can form a range of degradation products and consequently the environment may be exposed to a mixture of the parent compound and any resulting transformation products. The other processes include biochemical transformations which are not necessarily classified as degradation, for example the *in situ* methylation of heavy metals leading to the formation of toxic organometallic compounds.[42-43] Organic contaminants that are found in source water sources therefore

range from natural occurring compounds or mixtures, transformation products and synthetic compounds or mixtures of these thereof.

Naturally occurring organic contaminants

Natural organic compounds originate from the decay of plant and algae matter. [44-46] They include natural organic matter, [Table 4.8] humic substances, organometallics, algal toxins and their microbial metabolites. [44-47]

Table 4.8 Natural Organic Matter [NOM] Characterization [45]

TYPE OF NATURAL ORGANIC MATTER	CHARACTERIZATION
OC	Organic Carbon
OM	Organic Matter ≈ 1.7 OC
TOC(M)	Total organic carbon (matter), readily measured by a carbon analyser
DOC(M)	Dissolved Organic Carbon (matter)
NOC(M)	Natural Organic Carbon (matter), in most cases synonymous with TOC
POC(M)	Particulate Organic Carbon (matter) operationally distinguished from DOC by filtration through a 0.45μm nominal pore size filter
BOC(M)	Biodegradable organic carbon (matter)

Humic substances

Humic material (HM) is a form of environmental organic matter of plant or microbial origin. [44,46] The humic material is not made up of discrete, well defined molecules but is a class of substances that are produced and reside in soil and water, forming a major component of both the terrestrial (soil organic matter) and aquatic (natural organic matter) carbon pools: HM typically makes up to ≈ 50% of dissolved organic matter (DOM) in surface water, as well as much of organic sediment.[44-47] Because individual molecules cannot be identified, humic materials (also called humate or humus) is subdivided in an operational sense into the classes or categories.[44] These are Fulvic acid (FA), the fraction of humic matter that is soluble in aqueous solutions that span all pH values and Humic acid (HA) which is insoluble under acid conditions, typically at pH 2 but soluble at elevated pH conditions. Humin (Hu) is insoluble in water at all pH values. [44] Humic acids (HAs) are organic macromolecules with multiple properties and high structural complexity. They exist abundantly in soil, natural water and various terrestrial and aquatic environments.[44] Major HAs functional groups include carboxylic, phenolic, hydroxyl, carbonyl, amine, amide and aliphatic moieties, among others.[44] Due to this polyfunctionality, HAs are one of the most powerful chelating agents

among natural organic substances. [44]They are able to complex heavy metals, radionuclides, inorganic anions, halogens (organic acids aromatic compounds and pesticides among others. [46,47] These acids must be removed during the treatment process since they are responsible for turbidity and colour problems and act as disinfection by-products precursors.[44] Experience has shown that colour is an important concern for drinking water treatment plant operators since it is responsible for a significant number of consumer complaints about water quality. Hence the control is important for more than aesthetic purposes.

Organometallic compounds from NOM and naturally occurring metallic ions

Inorganic, biological and organic species in the aquatic environment live in continuous interaction. Organic matter in source water interacts with many inorganic metals such as Hg, As, Sn, Se to form organometallic compounds with different properties and toxicity.[48-50] For example inorganic tin undergoes alkylation in the aquatic environment to form compounds such as monomethyl tin (CH_3Sn^{3+}) and dimethyltin ($(CH_3)_2Sn^{2+}$).[48] The alkylation process is a biological one in that it takes place in the fish gut or via microorganisms in the water column.[48] The organotin product species are more toxic to aquatic biota than are the original inorganic tin compounds.[48] This toxicity is usually attributed to their ability to move across all membranes. Toxicity becomes greater as the number of organic groups increases in the series $RnSn^{(4-n)+}$ from n =1 to 3, where n is the number of organic groups, for example CH_3. [48]

The methylation of elemental mercury is another reaction of concern.[43,49-50] Dissolved organic matter (DOM) interacts very strongly with mercury, affecting its speciation, solubility, mobility and toxicity in the aquatic environment.[49] Strong binding of mercury by DOM is attributed to coordination of mercury at reduced sulphur sites within the organic matter, which are present at concentrations much higher than mercury concentrations found in most natural waters.[49] The build-up of MeHg is influenced by what forms of mercury are available in the water environment.[49-50] In anaerobic conditions sulphur reducing organisms may use inorganic mercury to make MeHg. Other significant anaerobic species include soluble $Hg(SH)_2$, or highly insoluble HgS. [44,50]

Cyanobacteria related organic contaminants of concern

In South Africa, as in many countries throughout the world, the proliferation of algae and cyanobacteria (blue-green algae) in surface waters such as reservoirs and rivers plays a significant role in the production of drinking water from such sources.[51] Cyanobacteria are one of the most diverse groups of gram-negative photosynthetic prokaryotes in terms of their

morphology, physiology and metabolism.[52] Due to their capacity for aerobic as well as anaerobic photosynthesis, a rapid growth of cyanobacteria in different habitat can take place. In eutrophic surface water, cyanobacteria are able to form intense blooms.[51-54] Nuisance algal blooms are most of the time associated with warm, summer months but it is not always the case.[52] The proliferation of algae and cyanobacteria in source water causes problems such as ineffective coagulation, flocculation and sedimentation, penetration of sand filters, clogging of sand filters, increase of organic loading of the water and the release of taste and odour causing compounds as well as cyanotoxins.[Table 4.8] Algae blooms can create very large quantities of organic matter in source water.[52] This will substantially increase the total organic carbon (TOC) content, may affect TOC compliance and subsequently, may require modifications of treatment. Increases in algal production can also lead to increases in disinfectant-by-product formation, taste and odour problems and cyanotoxin production [52]

Taste and odour problems

The taste and odour problems in drinking water have either directly or indirectly been linked to compounds such as Geosmin (trans-1,10-dimethyl-trans-9-decalol), 2-methylisoborneol (2-MIB), 2-isobutylmethoxy-pyrazine (2-IBMP), 2-isopropymethoxy-pyrazine (2-IPMP) and β-cyclocital.[51] Blue-green algae or diatom blooms are one of the most frequent causes of taste and odour problems encountered by a water system.[51] Some algae species produce taste and odour as a natural part of cell growth and division and as decaying vegetation. As fungi and bacteria decay or decompose the dead algae, substances are synthesized that cause the odour problems. [52] Examples of odour producers are *Oscillaria sp*., *Aphanizomen sp*. and odour producers include *Microcystis sp*. and *Anabaena sp.* [52] In addition, there are several other biological sources that are often overlooked, notably those which originate from terrestrial ecosystems, industrial waste treatment facilities, and drinking water treatment plants. [55] Many of the known producers are prokaryotes, which include both heterotrophs and photoautotrophs, and most drinking water research to date has focused on these taxa. [55]

Cyanotoxin production

Cyanobacteria have a number of special properties, and besides their ability for dinitrogen fixation using the enzyme nitrogenase many of them have the ability to form several toxic metabolites.[52-53,Table 4.9] Increasingly, harmful algal blooms (HABs) are being reported worldwide due to several factors primarily eutrophication.[Table 4.9]

Table 4.9:Name, producer organism and clinical symptoms for biotoxic cyanotoxins. [51,55-64]

NAME	PRODUCED BY	TOXICITY	CLINICAL SYMPTOMS
Alkaloids			
Anatoxin-a	*Anabaena, Planktothrix, Oscillatoria, Aphanizomenon*	Neurotoxin	Muscle weakness, respiratory distress, exaggerated abdominal breathing, hyperactivity, hypersalivation, numbness around the lips, paralysis
Homo anatoxin-a	*Anabaena, Planktothrix, Oscillatoria, Aphanizomenon*	Neurotoxin	Muscle weakness, respiratory distress, exaggerated abdominal breathing, hyperactivity, hypersalivation
Anatoxin –a(s)	*Anaebaena, Aphanizomenon*	Neurotoxin	Muscle weakness, respiratory distress, exaggerated abdominal breathing, hyperactivity, hyper salivation, numbness about the lips, paralysis
Saxitoxins	*Anaebaena, Aphanizomenon, Cylindrospermopsis, lyngbya, Planktothrix, Trichodesmium*	Paralytic Shellfish Poisons	Numbness around the lips, complete paralysis, death from respiratory distress
Cylindrospermopsin	*Aphanizomenon, Cylindrospermopsis, Phaphidiopsis, Umezakia*	Liver-toxins (hepatotoxins)	Abdominal pains, vomiting, swollen liver, liver failure, pathological damage to the kidneys, spleen, thymus and heart
Cyclic Peptides			
Nodularin	*Nodularia*	Hepatotoxin	Gastro-enteritis, fever, pains in muscles and joints, nausea, vomiting, diarrhoea, swollen liver, death by liver failure
Microcystins	*Synechococcus, Anaebaena, Aphanocapsa, Hapalosiphon, Microcystis Aeruginosa, Nostoc, Oscillatoria*	Hepatotoxins	Gastro-enteritis, fever, pains in muscles and joints, nausea, vomiting, blistering around mouth, diarrhoea, swollen liver, death by liver failure
Lipopolysaccharides			
Lipopolysaccharides	*All*	Acute effects	Allergic reactions, inflammation, irritation, gastroenteritis

Synthetic organic contaminants found in Source water resources

Synthetic organic contaminants have been found in source waters for many years. [65] Their numbers and varieties increase as our analytical capabilities increase.[65] The group of synthetic organic compounds encountered in this literature review includes different groups of polynuclear aromatic hydrocarbons [PAHs], [26,56,66-71] polychlorinated biphenyls [PCBs],[14,20,70,72-78]polychlorinated dibenzo-p-dioxins and dibenzofurans [PCDD/PCDF], [75,79,80] flame retardants such as polybrominated diphenyl ethers [PBDEs], [81] plasticizers,[45,56-58,75,82-83,85], organotins,[56,84,86] chlorophenols, [56,58,80,87] surfactants, [26,84,88-92] siloxanes, [93,94] per and polyfluorinated compounds [PFCs], [28,29,94] Benzotriazoles sometimes known as anticorrosives, [95,96] and engineered carbon based nanoparticles. [31,97,98] Major groups found in the literature were pesticides and their metabolites and pharmaceuticals and personal care products (PPCPs). The various groupings are presented in Figure 4.2.

Pharmaceuticals and personal care products (PPCPS)

Pharmaceuticals and personal care products, one of the emerging group of organic contaminantts has been extensively studied in the literature. [12,19,32,36-37,99-115] This term covers a diverse group of chemicals[107] which includes all drugs whether available by prescription or “over the counters” as well as nutraceuticals such as bioactive food supplements and consumer chemicals such as fragrances, sunscreen agents such as methylbenzylidene camphor, skin anti-ageing preparations like retinoids, diagnostic agents for example X-Ray contrast media. [109, Table 4.10] Whilst the environmental toxicology of PPCPs is not well understood, several effects cause concern, such as feminisation or masculinisation by hormones and xenoestrogens, synergistic toxicity from complex mixtures at low concentrations, potential creation of resistant strains in natural bacterial populations, and other potential concerns for human health.[110] It is important for water services providers to be able to evaluate the potential impact of PPCPs. [107,108] Groups of PPCPs such as analgesics, antibiotics, antiepileptics, ß-blockers and lipid regulators have been detected in water.[107,108] Examples include paracetamol, metformin, hydrochloride and ibuprofen.[107,108]

The most significant entry for pharmaceuticals into water bodies is the release of effluents containing the compounds from (WWTWs).[12] Other sources include run-off from intensive farming practices in which antibiotics are administered for use in therapy and as growth promoters in livestock, leachate from landfill sites, household waste (unwanted drugs) and waste from manufacturers. Major sources of PPCPs are Municipal, domestic and hospital sewage. [19,32,103] This is because the large portion of medication taken by patients

passes through their bodies unmodified and is excreted via urine and faeces to wastewater. [12,107,108] Removal from WWTWs or drinking water treatment plants depends on the drug's structure and treatment technology employed. [37,99-101,106] The fact that wastewater treatment does not completely remove some PPCPs is a cause for concern since they can enter the drinking water value chain either through surface or groundwater sources and are later not successfully removed during drinking water treatment.[12,37,109,111]

Table 4.10: Principal emerging PPCP compounds and their uses [32]

COMPOUND/ CLASS USE	**EXAMPLES OF CHEMICAL COMPOUNDS**
Pharmaceuticals	
Veterinary and human antibiotics	Trimethoprin, erytromycine, lincomycin, sulfamethaxole, chloramphenicol, amoxycillin
Analgesics and anti-inflammatory drugs	Ibuprofen, diclofenac, fenoprofen, acetaminophen, naproxen, acetylsalicylic acid, fluoxetine, ketoprofen, indometacine, paracetamol
Psychiatric drugs	Diazepam, carbamazepine, primidone, salbutamol
Lipid regulators	Clofibric acid, bezafibrate, fenofibric acid, etofibrate, gem fibrozol
B-Blockers	Metoprolol, propanolol, timolol, sotalol, atenolol
X-Ray contrasts	Iopromide, Lopamidol, diatrizoate
Steroids and hormones	Estradiol, estrone, estriol, diethylstilbestrol (DES)
Personal care Products (PCPs)	
Fragrances	Nitro, polycyclic and macrocyclic musks, phthalates
Sunscreen agents	Benzophenone, methylbenylidene
Insect repellents	N,N-diethyltoluamide
Antiseptics	Triclosan, Chlorophene

Pesticides

Like the PPCPs, pesticides have been widely researched. [14,20,72,78,84,116-145, Table 4.11] Pesticides occupy a unique position among other organic contaminants detected in the environment and in drinking water. This is probably due to their role and importance to the general public health. Pesticides are known as any substances or mixture of substances intended to prevent, destroy or mitigate any insects, rodents, fungi or weeds or any other forms of life declared to be the pests. [116]

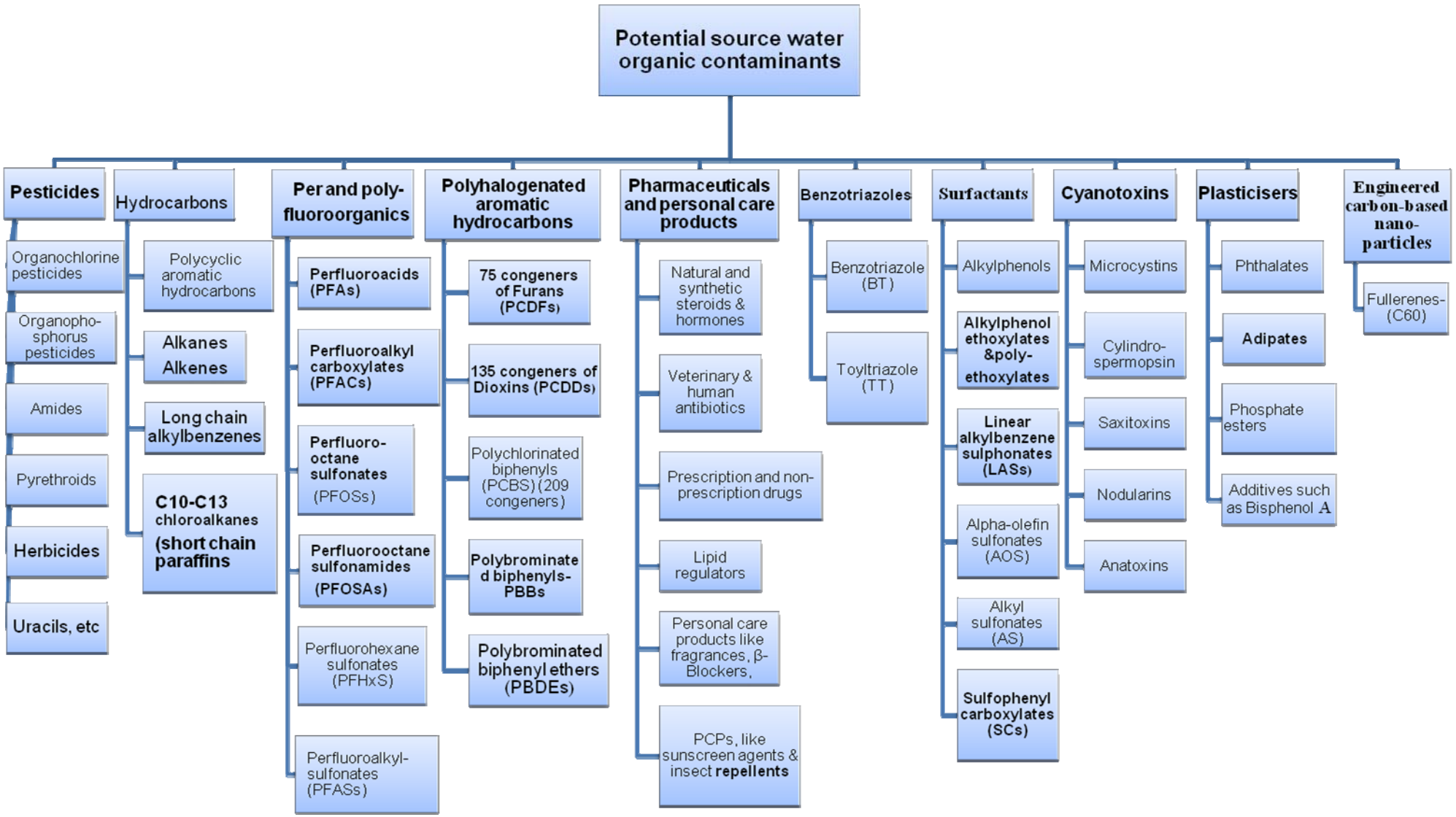


Figure 4.2 Potential source water organic contaminants found in the literature

Pesticide groups include among others, herbicides, insecticides, actinicides, fungicides, nematicides. [116] The largest commercial market lies with herbicides. [116] Pesticides comprise of different classes namely organochlorine pesticides such as DDT and its metabolites, hexachlorocyclohexane (HCH) and chlordane, organophosphorus pesticides such as azinphos methyl, malathion and chlorpyrifos, pyrethroids such as bifenthrin and cypermethrin, organotins such as cyhexatin and tributyltin, triazine herbicides such atrazine and simazine, oxime carbamates such as carbaryl and carbofuran, amidines such as amitraz, coumarin anticoagulants such as brodifacoum and nitromethanes such as chloropicrin.[116] Organochlorine pesticides are the most studied in the literature compared to other groups.[14,20,121,127-129,133-145] This might be due to the observed successes as a pre-historic group mainly in agriculture and vector control in public health programs. Although most organochlorine pesticides are either currently banned or restricted, they are still detected in various environmental matrices. This is due to their persistency and bioaccumulative nature.[127-129,133-145] Their ability to move through the atmosphere (long range air transportation allows them to be detected in oceans, rivers and lakes remote to their area of use or application.[130]

In substitution to organochlorine pesticides that are now prohibited because of their persistence in the environment and biomaginification along the food chain and toxicity to non-target organisms,[119] organophosphorus pesticides were introduced. Organophosphorus pesticides are used in agriculture for crop protection and orchard treatment, sheep dipping and in aquaculture for the control of sea lice[119]. Like organochlorine pesticides, members of this group exhibited the same undesirable properties leading to the introduction of other groups of pesticides perceived to be non-persistent and non-accumulative. [116,119] Pyrethroids and herbicides including other groups were introduced. [116,119] each pesticide group has its merits and demerits. Pyrethroids are characterized by their short half-lives in soil and water but high toxicity especially to target organisms.

Herbicides are currently the most used in agricultural activities compared to other groups as reflected by the literature.[78,84,117-118,125,126,139] In South Africa, the largest commercial market lies with herbicides especially the S-triazine group. [116, Table 4.11] A good example is Atrazine, a triazine herbicide that is widely used worldwide to control weeds in corn, sorghum, sugar cane, orchards, pastures and non-crop areas. [118,139] Subsequent to its extensive use, reports on soil, surface and groundwater contamination and adverse health effects have been published. [118,125,126,139,141]

Table 4.11: S-triazine herbicides and their major degradation products [139]

TRIAZINE HERBICIDE	DEGRADATION PRODUCTS
Atrazine	Deethylatrazine(DEA) Deisopropylatrazine (DIA) Hydroxyatrazine (HA) Didealkyl atrazine (DDA) Deethylhydroxyatrazine (DEHA) Deisopropylhydroxyatrazine (DIHA) Dide alkylhydroxyatrazine (DDHA)
Simazine	DIA Monodeethylsimazine Hydroxysimazine
Propazine	DEA Hydroxypropazine
Atraton	Deisopropylatraton
Terbutylazine (TBA)	Deethylterbutylazine
Metribuzin	Deamino metribuzin (DAM) Diketo metribuzin (DKM), Deaminodiketometribuzin (DADKM)

The detection of pesticides in South African source water resources, 2000-present

The use of pesticides poses a serious threat to the limited water resources of South Africa. The amounts which are not taken up by crop plants are often washed away by run-off into surface waters or leached through the soil, causing groundwater pollution. The problem of pesticide pollution is often intensified by inappropriate usage, disposal and monitoring in agriculture.[140] This literature review has been conducted for the identification of pesticides in the South African aquatic environment based on usage, pesticide properties and site characteristics. Evidence for extensive pesticide use and release to source water resources exist (Table 4.12). It is also evident that the biggest user is the agricultural industry and the main route into the drinking water value chain is mainly through run-off.

Maharaj [2005] investigated the problem of pesticide pollution in South Africa prior to 2005 [Table 4.12]. It is evident from the review that Chlorpyrifos, endosulfan, Azinphos-Methy, Atrazine, Simazine, Deltamethrin and Penconazole were the most encountered pesticides in the literature. [140, Table 4.12] Du Preez et al. [2005] evaluated seasonal exposures to triazines and other pesticides in surface waters in the Western Highveld corn producing region of South Africa. Atrazine and its metabolites deisopropylatrazine (DIA), Deethylatrazine (DEA) and Diaminochlorotriazine (DACT) were detected in corn growing

areas (CGA) while Terbutylazine (TBA) was detected in non corn growing areas (NCGA). Other herbicides such as Simazine and Acetochlor were infrequently detected. [141]

Dalvie et al. [2006] investigated the disposal of unwanted pesticides in Stellenbosch, South Africa. The study followed up a previous audit of unwanted and obsolete pesticides on farms in a rural district of South Africa six years after a National Retrieval Project (NRP) was undertaken.[142] 40 (56%) farms were in possession of obsolete pesticides of which 24 (59%) were farms that had unwanted stocks in the previous study. [142] There were more than 9tonnes of these pesticides, 50% more than in the previous study, including 20 chemicals that have been banned, withdrawn or restricted in South Africa or classified as WHO Class I toxicity. [142] These included pesticides no longer registered for use in South Africa such as Lindane, DDT, Dieldrin, MCPA, pesticides withdrawn or restricted such as Azinphos-Methyl, Chlordane, Chlorobenzilate, Dinoseb, Omethoate, Parathion, Vinclozolin, WHO Class I toxicity pesticides such as Chlorfenphos, Endosulfan, Fenamiphos, Methamidophos, Mevinphos, Parathion, Methomyl, Omethoate and non-Class I toxicity pesticides such as Chlorpyrifos, Endosulfan, Glyphosate and Paraquat. [142]

Recent studies [143-145] confirm widespread contamination of surface and groundwater sources by pesticides at low concentrations in South Africa. This confirms the existence of potential exposure of consumers as these source water resources are commonly used as sources for drinking water production. Barnhoorn et al. [2009] investigated the use and occurrence of DDT in the Limpopo province in northern South Africa. [143] DDT has been used since 1945 to control malaria transmission by *Anopheles funestus* and *Anopheles arabiensis* vectors in particular in the Vhembe District Municipality. DDT is used for indoor residual spraying (IRS).[143] Through IRS, DDT may reach the outdoor environment via dust and air and from possible spillages during application. [143] The samples contained p,p'-DDT, p.p'-DDD and p,p-DDE residues with the latter being the most ubiquitous and in the highest concentrations.

Table 4.12: Examples of organic contaminants found in some international freshwater systems as reflected by the literature

COUNTRY	FRESHWATER SYSTEM	ROUTES	ORGANIC CONTAMINANTS
India	Lakes Bhimtal, Sattal, Khurpatal, Naukuchiatal Nainital	Atmospheric long range transportation of pesticides followed by cold condensation, misuse of pesticides in agriculture	DDT and its metabolites o,p-DDT, p,-DDT, o,p-DDE, p,p-DDE as major constituents, Hexachlorocyclohexanes (HCHs) (δ-HCH, ß-HCH, γ-HCH(Lindane)[120,127]
South Africa	Rivers: Buffalo, Keiskama, Tyume Sandile Dam	Agricultural run-off,	DDT and its metabolites o,p-DDT, p,p´-DDT, 2,4´-DDE, 2,4´-DDD, Benzene-hexachloride (BHC), (α- BHC, δ-BHC, ß- BHC, HCB, Heptachlor, Aldrin, γ-Chlordane, Endosulfan, Dieldrin, Endrin, 2,4´-DDT, 4,4´-DDD, 4,4´-DDT[135,136]
South Africa	Vegetated wetland at the Lourens River (Western Cape)	spray drift-airborne Atmospheric deposition	Azinphos-methyl in water, Chlorpyrifos, Prothiofos, Endosulfan a, b and sulphate in sediment cores[140]
South Africa	Marine and freshwater samples in the Eastern Cape	Agricultural run-off	DDT, DDE, Heptachlor and Endosulfan[140]
South Africa	Crocodile River catchment in Mpumalanga/	Pesticide concentrations in fish tissues	BHC, Lindane,Dieldrin, Heptachlor and DDE[140]
South Africa	Surface water pollution levels in areas of KwaZulu-Natal	agricultural run-off	DDT and Deltamethrin[140]
South Africa	Lourens River at catchment scale	Agricultural run-off	Azinphos-methyl[140]
South Africa	Lourens River at catchment scale	Agricultural run-off and sediment samples	Azinphos-methyl, Chlorpyrifos and Endosulfan[140]
Burundi, Africa	Fish samples	Agricultural run-off	HCHs (γ-HCH predominant), Alachlor, o,p´DDE, α-Endosulfan, p,p´-DDE, o,p´DDD, Endrin, o,p´DDT, p,p´-DDD, p,p´-DDT, Endosulfan sulphate[131]
South Africa	Lourens River	Agricultural run-off	Endosulphans, Chlorpyrifos[134]

Table 4.12 contd

COUNTRY	FRESHWATER SYSTEM	ROUTES	ORGANIC CONTAMINANTS
Canada	Arctic and Subarctic lakes, Yukon River Basin	Atmospheric deposition to the snowpack and watershed, global distillation of POPs, enhanced gas phase deposition due to temperature effects, leachates from dumpsites.	HCHs (α-HCH, γ-HCH), Endosulfan, Dieldrin, Heptachlor epoxide, Total DDT [129]
Canada	Streams and rivers, e.g Fraser River	Agricultural run-off	DDT and its metabolites p,p´-DDT, p,p´-DDE, p,p´-DDD, various BHC (α- BHC, δ- BHC, ß- BHC, γ- BHC , Methoxychlor, Aldrin, α-Chlordane, γ-chlordane, dieldrin, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, HCHs[120,129]
South China	Pearl River estuary	Sources difficult to quantify, direct point source pollution, atmospheric deposition, non-point input of surrounding soils and sediments from both in and nearby the waterway.	HCHs, heptachlor, aldrin, heptachlor epoxide, endosulfan I, dieldrin, endrin, endosulfan II, endrin aldehyde, endosulfan sulphate, endrin ketone, methoxychlor, 4,4´-DDD, 4,4´-DDT, 4,4´-DDE[78]
EUROPE	European mountain lakes (Alps, Caledonian, etc)	LRAT, atmospheric deposition	HCHs, p,p´-DDT, p,p´-DDE, PCBs, HCB and endosulfan[133]
Thailand	Lake coastal waters	Atmospheric deposition, run-off from agricultural practices (although DDT use banned in 1983) Although usage of HCHs banned in 1980s, usage of γ-HCH still appear to be continuing.	HCHs, Cholrdanes, DDTs, HCB[14]
USA	Willamette River Basin, water, sediment	Run-off, atmospheric deposition	DDT and its metabolites[133
Hong Kong	Daya Bay China Inland water systems	Atmospheric deposition	HCHs, DDTs[74]

Organic contaminants from water treatment processes

A combination of chemical and physical processes is used to purify potable water, typically consisting of coagulation/ flocculation followed by sedimentation, carbonation/stabilization, filtration and disinfection. Disinfection can be accomplished using chlorination, ozonation or UV-Visible energy depending on main objective. Although the terms “coagulation” and “flocculation” are often used loosely and interchangeably, coagulation is, in fact, distinct from flocculation and is defined as the process that causes the neutralization of charges or a reduction of the repulsion forces between particles. [33] The overall electrical charge associated with particles and organic matter in water is usually negative. Consequently, positively charged coagulants are added to neutralize the electrical charge. [33] Flocculation is defined as the aggregation of particles into larger agglomerations called “flocs.” The coagulation step is virtually instantaneous, while the flocculation (transport) step requires some time for the flocs to develop. [33] Typically, flocs are developed by bubbling air into the water sample after coagulation to increase buoyancy of the flocs and bring the floc to the surface of the sample. [33] Effective coagulation/ flocculation can remove particles over a wide range of particle sizes. It has been found that particles as small as one micron in size can be removed.[33] Effective coagulation/ flocculation can remove most suspended particles, colloidal colour, bacteria (0.1-0.2 microns), *Giardia cysts* (5-15 microns), Cryptosporidium (4-7 microns), and most algae [33] Filtration improves particle removal over coagulation/ flocculation only in the size range from 0.5 to 1.0 micron.

While the addition of chemicals to source water during drinking water production is beneficial, the general concern is the formation of water treatment residues (WTRs). WTRs are by-products from the drinking water production. [146] Some of the WTRs have been found to be harmful to consumers. Hence, various options have to be used to optimise the coagulation/flocculation processes. WTRs from conventional water treatment processes consists mainly of the precipitated hydroxides of the treatment chemicals that are added to coagulate and flocculate dissolved and suspended material in the source water and also during the residue dewatering process.[146]

Some residues are preferred over others. Such has been the use of natural organic polymers as coagulant aids which gained momentum in developing countries. Chitosan (a residue of crustacean transformation) and *Moringa oleifera* (a tropical plant) are very efficient natural organic coagulants in water treatment. [147] *Moringa* may be useful for the production of drinking water in developing countries where other coagulants are expensive and operators are not well trained.[147] Other examples include extracts other than the dry seeds of *Moringa Oleifera* are extracts of Okra and Nirmali seeds, extracts of *Prosopis*

juliflora and *Cactus Laifaria* and modified chatoyant biopolymer. [148] Vegetable tannins which are polyphenolic products of plant origin have also been used. [148]

Natural organic polymers are preferred to metal salts because:

- They are effective in very low dosages as compared to metal salts
- Low dosages of polymers reduce the volume of sludge produced (because the volume of sludge is partly a function of chemical dose)
- Their effectiveness is less pH dependent that for metal salts
- Polymers improve the sludge dewatering process as compared to alum or iron salts and provide a high sludge density
- Polymers are generally more biodegradable than alum or iron salt sludges and therefore ease sludge digestion by micro-organisms
- They are non-corrosive and easy to handle
- Polymers do not pose problems in terms of residual metals contamination
- They have only a slight impact on pH and alkalinity[33,149]

The natural organic polymers are interesting because comparative to the use of synthetic organic polymers such as containing Acrylamide monomers, no human health danger from their use has been identified. [147]

Some WTRs of concern include those introduced by the use of synthetic organic polymers as coagulant or flocculants aids. [33,147, 151, Table 4.13] These structures may be polyelectrolytes, such as water-soluble flocculants or water insoluble ion exchange resins, or insoluble uncharged materials such as those used for plastic pipes and plastic trickling filter media. [152] Polydiallyldimethyl ammonium chloride (PDADMAC) and Epichlorohydrin-dimethylamine (epi-dma) are established coagulants in the treatment of drinking water. [150] Their efficiency can be seen in the fact that approximately 75% of water treatment works in South Africa have adopted these polyelectrolytes as part of their water treatment process.[150] However, polyelectrolyte products used in the water supply industry may contain in addition to polyelectrolyte, measurable amounts of certain contaminants.[153] These contaminants are essentially unreacted raw material from the polyelectrolyte, manufacturing process, for example monomer units, initiators and quenchers. A list is shown in Table 4.13. Another example includes polyacrylamide and its monomer Acrylamide. [154] Acrylamide can be acutely toxic. [75,154] Acrylamide is readily absorbed by ingestion and inhalation and through the skin, and then is widely distributed in body fluids. It is also a

cumulative neurotoxin, which can result in nerve damage from chronic oral exposure in humans and animals, with effects such as numbness and weakness in hands and legs. [75] Thus the USEPA has classified Acrylamide as a B2, a probable human carcinogen. [75]

Table 4.13: List of contaminants found in polyelectrolytes products [150]

CONTAMINANT	POLYELECTROLYTE
Diallyldimethylammonium Chloride	Polydadmac (PDADMAC)
Dimethylamine	Polydadmac (PDADMAC)/ Epi-dma
Allylchloride	Polydadmac (PDADMAC)
Diallylether	Polydadmac (PDADMAC)
5-Hexanal	Polydadmac (PDADMAC)
Epichlorohydrin	Epi-dma
Glycidol	Epi-dma
1,3-dichloro-2-propanol	Epi-dma
2,3-dichloro-1-propanol	Epi-dma
3-chloro-1,2-propanediol	Epi-dma
2-hydroxy-3-dimethylaminopropylchloride	Epi-dma
1,3-Bis(dimethylamino)-2-propanol	Epi-dma

Synthetic organic polymer use has resulted in other concerns other than introducing impurities in parent compounds resulting in the release of residual monomers and other organic contaminants of concern into water systems. [33,149-155]These include degradation of polyelectrolytes into other organic compounds of concern to human health, [33,149-155] serving as precursors for the formation of disinfection by-products, [33,149-155] and the formation of disinfection by-products which have high potential toxic effects to consumers than their parent compounds. [33,149-155,157,166] Disinfection by-products of concern such nitrosodimethylamine [NDMA] [33] and a range of VOCs [150,152] have been formed.

The polymer coagulant and its impurities might react with hypochlorite ions [OCl^-] in the drinking water purification process and subsequently form some undesired disinfectant by-products [DBPs] .[33] Three commercial polymers: Anionic polyacrylamide [PA], Cationic PolyDimethyl Diallyl Ammonium Chloride and non-ionic Polyacrylamide when used as coagulant aids in simulated water purification resulted in the formation of 23 DBPs. [35] These included; Benzene, Bromoform, Bromodichloromethane, Carbon tetrachloride, Chlorobenzene, Chloroform, Dibromochloromethane, Dichloromethane, 1,2 Dichlorobenzene, 1,4 Dichlorobenzene, 1,1 Dichloromethane, 1,2 Dichloroethane, 1,1 Dichloroethene, trans-1,2- dichloroethane, 1,2 – dichloropropane, cis 1,3- dichloropropylene,

trans- 1,3 dichloropropylene, Ethylbenzene; 1,1,2,2- tetrachloroethane, Toluene, 1,1,1-trichloroethane, 1,1,2- trichloroethane and 1,1,1- trichloroethene.[35]

Disinfection of drinking water for human consumption, potential organic contaminants

There is no doubt that chlorination has been successfully used for the control of waterborne infectious diseases for more than a century.[160] The disinfection of public water supplies through chemical and physical intervention strategies has resulted in a dramatic decline in outbreaks of waterborne diseases like typhoid fever and cholera.[158] Highly oxidising chemicals such as chlorine and ozone kill a variety of pathogenic micro-organisms during treatment and chlorine is applied in many countries as an additional safeguard in the distribution system.[158] However, identification of chlorination by-products [CBPs] and incidences of potential health hazards created a major issue on the balancing of the toxicodynamics of the chemical species and risk from pathogenic microbes in the supply of drinking water. [160] There have been epidemiological evidences of close relationship between its exposure and adverse outcomes particularly the cancers of vital organs in human beings.[28]

It has been confirmed that the chemical disinfection of water results in the formation of a wide variety and a large number of disinfection by-products [DBPs]. [158-164] DBPs have been identified in the drinking water value chain. [158-164] Oxidants such as chlorine Cl_2, Ozone [O_3], Chlorine dioxide ClO_2 and chloramines used as disinfectants, react with naturally occurring organic matter [NOM] to form DBPs.[159] The generation of disinfection by-products which have suspected adverse health effects on human health has been viewed as an important drawback of the use of these chemicals. [155-160] However, the DBP profiles can vary with treatment methods.[160] The number, chemical types and concentrations of DBPs formed depends on source water characteristics such as; type and concentration of disinfectant, application point in the treatment process, type and concentration of organic matter in the water, pH, temperature and contact time with the disinfectant. [168] Halogenated trihalomethanes [THMs] and haloacetic acids [HAAs] are two major classes of disinfection-by-products [DBPs] commonly found in waters disinfected with Chlorine. THMs (the combination of chloroform, bromodichloromethane, chlorodibromomethane and bromoform) and HAA5 (the five haloacetic acids, monochloro, dichloro-, trichloro-, monobromo-and dibromoacetic acids) are by-products of chlorination. Bromate is a by-product of both disinfection with ozone and chlorine. [168]

The challenge facing the water supply industry professionals is how to simultaneously minimise the risk from microbial pathogens and disinfection by-products. [162]DBPs are not an immediate threat to human health. [162] Their effects are significant if consumed over many years in exceedance to standards which may cause cancer [long term exposure 2ℓ for 70years].[162] Finding the right level of disinfection to control waterborne pathogens while minimising the lifetime risk of cancer caused by exposure to DBPs is the goal to be pursued in future regulations. [162] New DBPs are also emerging as organic contaminants of concern. [168] Such DBPs include brominated and iodinated compounds such as bromonitromethanes, iodotrihalomethanes, iodo-acids and brominated forms of MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) [Figure 4.3, 168] as well as nitrosodimethyl-amine (NDMA).

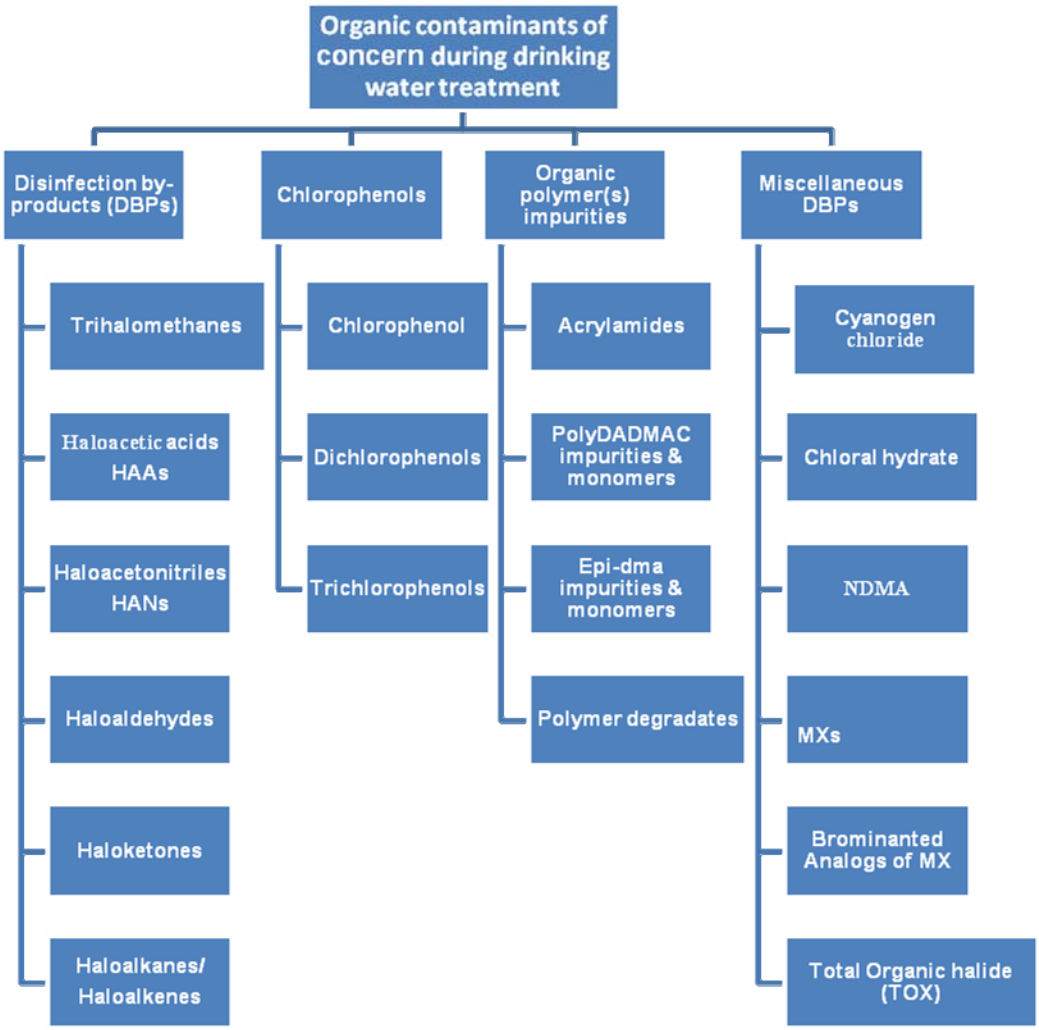


Figure 4.3: Organic contaminants from drinking water treatment chemicals

Organic contaminants from potable water distribution materials

The distribution system is a potential source of organic contamination of drinking water. Organic contaminants can enter supplies in several ways, that is, through leaching from plastic materials, application of renovation processes and permeation of certain plastic pipes and microbial activity in biofilms. [167] Some introduction of organic chemicals from distribution systems is inevitable at some level particularly in the early stages such with newly laid pipe or after a recent renovation. [167] Excessive leaching of organic substances from pipe materials, linings, joining and sealing materials, coatings and cement mortar pipe have occasionally been noted in the literature. [167] High density polyethylene pipes (HDPE), cross bonded polyethylene pipes (PEX) and polyvinylchloride (PVC) pipes for drinking water have been tested for leaching contaminants.[169] A range of esters, aldehydes, ketones, aromatic hydrocarbons and terpenoids were identified as migration products from HDPE pipes. [169] Phthalamides have been also found to leach from blue MDPE and this proved to be due to its presence as an impurity related to the blue pigment copper phthalocyanine. [169] A wide range of contaminants were found to leach into drinking water from GRP pipes including a range of contaminants such as phthalates and styrene. [169] Chemicals such as organotins and polynuclear aromatic hydrocarbons (PAHs) can enter the water supply as leachates. [169] Organotins can leach into drinking water from certain types of polyvinyl chloride pipes and PAHs particularly fluoranthene can leach from the older types of pipes which were lined with coal tar pitch. [169]

Permeation of Polyethylene (PE) pipes by organic chemicals has also been observed. [169] It has been demonstrated that blue MDPE pipes are readily permeated by non-polar chemicals such as toluene, slowly permeated by phenol, a more polar substance, but not permeated by more complex polar molecules such as the pesticides Paraquat, Malathion and Atrazine. [169] In additional experiments significant penetration of MDPE occurred with m-cresol, nitrobenzene, chlorobenzoic acid and cyclohexane.[169] Although attempts were made, accurate prediction of the rate of permeation by chemicals from physical/chemical data could not be made. [169] PE pipe is clearly vulnerable to permeation by certain chemicals which could lead to significant contamination of supplies, at least on a local basis. [169]

Leaching of organic compounds into water from reservoir/tank linings

Skjevrak et al. [2003] investigated the leaching of organic compounds from reservoir/tank linings. The one product examined, epoxy-resin (based coating) did demonstrate that a relatively high concentration of one of the ingredients used in the formulation could leach into water in the short term, although this level did rapidly reduce with time[169]. Although it is

difficult to use the results from the epoxy resin coating studied to predict the behaviour of other coatings, it does appear likely that some ingredients in any product will leach into water, particularly in the first few hours after application and following the first contact with water. [169]

Disinfection by-products formation

The disinfection process continues in the distribution network. THMs and other disinfection by-products will continue to form. THMs have shown seasonal variations on the concentrations in the distribution. [13] THM levels in summer and the wet season were on average about five times higher in winter, whereas average HAAs in spring were about four times higher than in winter.[13] THMs increased and stabilized in the extremities of the distribution system whereas HAAs decreased as water approaches the system extremities. This residence time of water is one important parameter in explaining the fate of both chlorinated disinfection by-products (CDBPs). [13]

Organic contaminants in natural biofilms in PVC pipes

Biofilms in pipes may trap in VOCs that can result in off-flavours (Table 4.14). Compounds frequently associated with cyanobacteria and algae such as ectocarpene, dictyopterene A and Ć, geosmin, beta-ionone and 6-methyl-5-hepten-2-one have been associated with this.[15] Microrganisms growing in biofilms form volatile amines, dimethydisulphide and 2-nonanone. -C8-compounds such as 1-octen-3-one and 3-octanone were believed to be from microfungi in the biofilm. [15] Biogenic volatile organic compounds responsible for offensive odours in freshwater are associated with many types of microorganisms. [15] Fresh water algae produce a variety of volatile organic compounds and bacterial degradation of organic material is known to produce odorous organic sulphides and volatile amines. [15] Actinomycetes, which are responsible for the production of well known odorous secondary metabolites such as geosmin and 2-methyl-isoborneol, are present in source water reservoirs as well as in the distribution systems. [15] Release of VOCs from natural biofilm present in the distribution network may cause odour episodes in the drinking water supply. The following compounds have been generated from the chlorination of natural biofilms; 2-Methylpropanal, 2-Butanone, Chloroform, 3-Methylbutanal, 3-Butene nitrile, Styrene, Dichlorobromomethane, Aliphatic amine, Isobutylnitrile, 1,1`-Oxy-bis-(4-chloro-butane), 1,2-dibromobutane, Bromoform, Benzaldehyde, Benzylnitrile, 2-Chloro-ethylbenzene, Benzylacetonitrile, 4-chloro-benzylchloride, 1,2-Dichloro-ethylbenzene, 1-Bromo-2,3-dimethyllindane, Butyldinitrile, Hexachlorocyclopentadiene, Chloromethylbenzenemethanol, Hexachloroethane, and 5-chloro-1-methyl-imidazole.[15]

Table 4.14: VOCs in natural biofilm established in HDPE pipes under flowing water conditions [15]

VOC	SUGGESTED ORIGIN
3- methylbutanal	Bacteria/algae/chlorination
Pentanal	Algae
4-Methyl-2-pentanone	-
Dimethyldisulphide	Bacteria/cyanobacteria
1-octene	-
n-octane	-
1-nonene	-
4-Methylpentanol	-
2-Heptanone	-
Heptanal	Algae
2-Ethyl-hexanal	-
1-Octene-3-one	Fungi
3-Octanone	Fungi/Algae/*Chrysophyceae*
6-Methyl-5-hepten-2-one	Algae/Cyanobacteria
2,4-Heptadienal	*Chrysophyceae/* Cyanobacteria
1,8-Cineol (eucalptol)	Algae
1-Octanol	Fungi/ *Chrysophyceae*
2-Nonanone	Bacteria *(Pseudomonas spp.)*
Dictyopterene A	Diatoms
5-Undecen-4-one	-
5-Ethyl-6-methyl-3-hepten-2-one	-
Ectocarpene	Diatoms
1-Nonanol	-
Dictyopterene Ć	Diatoms
p-Menthol	-
Camphor	Algae/ bacteria
Menthol	Cyanobacteria
2-Decenal	-
2,4-Decadienal	Algae/Cyanobacteria
Dodecanal	-
Geosmin	Algae/Cyanobacteria/ Actinomycetes
2,6 Di-tert-butyl-benzaquinone	Migrant from HDPE pipe
Tetradecanal	-
Hexadecanal	-
Heptadecene	-
B-Ionone	Algae/*crustacean*
Isobutyrate derivatives	Cyanobacteria (*Microcystis*)
Trimethylamine	Bacteria/Algae
Isobutylamine	Bacteria/cyanobacteria/algae
Isopentylamine	Bacteria/cyanobacteria/algae
2,4-Di-terbutylphenol	Migrant from HDPE pipe

From the preceding discussions it is evident that source waters used for drinking water production can be contaminated by a variety of individual or group of organic contaminants. Depending on their physico-chemical properties these organic contaminants distribute themselves among various environmental matrices, sediments, water or biota or preferably remain highly localized in one of them. Hydrophobic organic contaminants like the dirty dozen mainly remain in sediments and biota although they have been detected in the water column at very low concentrations, µg/l to ng/l. The main classes of organic contaminants of concern to source water quality identified above include natural occurring organic contaminants such as the algal toxins and their metabolites, synthetic organic contaminants such as pesticides, hydrocarbons, pharmaceuticals and personal care products, organic flame retardants, surfactants, polyhalogenated aromatic compounds such as dioxins and furans, polybrominated biphenyls (PBBs), polychlorinated biphenyls (PCBs), polyfluorinated organic compounds (PFOCs), plasticisers, siloxanes, organotins, carbon-based engineered nanoparticles and benzotriazoles (Figure 4.2). It is crucial for water utilities to understand the behaviour of these organic contaminants in their source water resources for planning and regulatory purposes. [165]

Potential organic contaminants that occur along the drinking water value chain as a result of deliberate use of other inorganic and organic chemicals have also been successfully characterized and identified (Table 4.13, Figure 4.3 and Table 4.14). Table 4.15 summarizes the list of identified organic contaminants which is the outcome of the literature review. This list will form part of the preliminary list of organic contaminants of concern (PLOCC) after the application of the Persistence, Bioaccumulation and Toxicity (PBT) criteria (Step III, Figure 3.2).

Table 4.15: The preliminary List of organic contaminants of concern based on the occurrence criterion (evidence from the literature)

Naturally occurring organic contaminants [18]		
Humic acids, Fluvic acids, organometallics such as Methyltin, Dimethyl tin, MeHg, Cyanotoxins such as anatoxin-a, Homoanatoxin-a, Anatoxin-a(S), saxitoxins, Cylindrospermopsin, Nodularin, microcystins and lipopolysaccharides. Geosmin (trans-1,10-dimethyl-trans-9-decalol), 2-isobutylmethoxy-pyrazine (2-IBMP), - 2-isopropymethoxy-pyrazine (2-IPMP), -β-cyclocital, -2-methylisoborneol (2-MIB)		
Industrial chemicals[63]		
16 PAHs PCBs PCDDs/PCDFs Brominated diphenyl ethers; - deca-BDE, octa-BDE and penta-BDE -Polybrominated biphenyls -bis-(2-ethylhexyl) adipate (DEHA) -Di- (2-ethylhexyl) phthalate (DEHP) -2-chloroethanol phosphate -tri-n-butylphosphate (TBP) -dimethylphthalate (DMP) -diethylphthalate (DEP) -butylbenzylpthalate (BBP) -di-n-butyl phthalate (DBP) -di-n-octylphthalate (DOP) -Bisphenol A - tributyltin (TBT) - MBT, DBT, DMT	-2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 2,3-Dichlorophenol 2,4-Dichlorophenol 2,5-Dichlorophenol 2,6-Dichlorophenol 3,4-Dichlorophenol 3,5-Dichlorophenol 2,3,4-Trichlorophenol -2,3,5-Trichlorophenol -2,3,6-Trichlorophenol -2,4,5-Trichlorophenol 2,4,6-Trichlorophenol -3,4,5-Trichlorophenol 2,3,4,5-Tetrachlorophenol -2,3,4,6-Tetrachlorophenol -2,3,5,6-Tetrachlorophenol -PCP	Linear alkylbenzene sulfonates (LAS) - alpha-olefin sulfonates (AOS) - alkyl sulfates (AS) -Alkylphenol polyethoxylates - Butylphenol (BP) nonylphenol (NP) octylphenol (OP) -nonylphenol ethoxylates (NPEOs) -octylphenol ethoxylates (OPEOs) octamethylcyclotetrasiloxane-D4 decamethylpentasiloxane-D5 perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) perfluorooctane sulfonamide (PFOSA) perfluorooctanoic acid (PFOA) perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA) and perfluorododecanoic acid (PFDoDA) benzotriazole (BT) -tolyltriazole (TT) -Fullerenes (C_{60})
PPCPs [46]		
Trimethoprin, erytromycine, lincomycin, sulfamethaxole, chloramphenicol, amoxicillin Ibuprofen, diclofenac, fenoprofen, acetaminophen, naproxen, acetylsalicylic acid, fluoxetine, ketoprofen,	indometacine, paracetamol Diazepam, carbamazepine, primidone, salbutamol Clofibric acid, bezafibrate, fenofibric acid, etofibrate, gem fibrozol, Nitro, timolol, sotalol, atenolol Estradiol, estrone, estriol, diethylstilbestrol (DES)	phthalates Benzophenone, methylbenylidene N,N-diethyltoluamide -Triclosan, Chlorophene Metoprolol, propanolol, Polycyclic & macrocyclic musks, Iopromide, Lopamidol, diatrizoate

Table 4.15 *continued*.

Pesticides [42]		
heptachlor epoxide, endosulfan II, endrin aldehyde, endosulfan sulphate, endrin ketone, DDT and metabolites hexachlorocyclohexane (HCH) Atrazine & metabolites, Simazine& metabolites, Propazine &metabolites	Dichlorvos, Malathion, Glyphosate, Omethoate, Thionazin, Atraton, Terbutylazine (TBA), Metribuzin,Dieldrin, Endrin, Methoxychlor, Mirex, o,o,o-triethylphosphorothioate, Methamidophos,HCB, heptachlor, aldrin, γ-chlordane, endosulfan,	Sulfotepp, Phorate, Dimethoate, Disulfoton, Parathion-methyl, Parathion, Isocarbophos, Isofenphos-methyl, Chlorpyrifos, dieldrin, Azinphos-Methyl Trichlorphos, Famphur, endrin,
Synthetic organic polymers and residues [16]		
Polydiallyl dimethyl ammonium chloride (POLYDADMAC), -epichlorohydrin-dimethylamine (epi-dma) -Dimethylamine -Allylchloride, -Diallylether	1,3-dichloro-2-propanol -2,3-dichloro-1-propanol 1,3-Bis(dimethylamino)-2-propanol 2-hydroxy-3-dimethylaminopropylchloride 3-chloro-1,2-propanediol	Epichlorohydrin, -Glycidol, -5-Hexanal, -Anionic polyacrylamide (PA), -Cationic PolyDimethyl Diallyl Ammonium Chloride, -non-ionic Polyacrylamide
VOCs and SVOCs[66]		
2-Methylpropanal, 2-Butanone, Chloroform, 3-Methylbutanal, 3-Butene nitrile, Dichlorobromomethane, Aliphatic amine, Isobutylnitrile, 1,1`-Oxy-bis-(4-chloro-butane), 1,2-dibromobutane, Styrene, Bromoform, 1-Octanol Benzaldehyde, Butyldinitrile, Benzylnitrile, 2-Chloro-ethylbenzene, Benzylacetonitrile, 4-chloro-benzylchloride, 1,2-Dichloro-ethylbenzene, 1-Bromo-2,3-dimethyllindane,	3- methylbutanal, Hexachloroethane, Pentanal, 4-Methyl-2-pentanone Dimethyldisulphide, 1-octene, n-octane 1-nonene 4-Methylpentanol 2-Heptanone Heptanal 2-Ethyl-hexanal 1-Octene-3-one 3-Octanone 6-Methyl-5-hepten-2-one Dictyopterene Ć p-Menthon, Camphor, Menthol 2-Decenal,5-chloro-1-methyl-imidazole, 2-Nonanone, Chloromethylbenzenemethanol, Ectocarpene, 1-Nonanol Hexachlorocyclopentadiene,	2,4-Decadienal Dodecanal, 1,8-Cineol (eucalptol) Geosmin 2,6 Di-tert-butyl-benzaquinone Tetradecanal Hexadecanal Heptadecene B-Ionone Isobutyrate derivatives Trimethylamine Isobutylamine Isopentylamine Dictyopterene A 5-Undecen-4-one 5-Ethyl-6-methyl-3-hepten-2-one 2,4-Di-terbutylphenol 2,4-Heptadienal

4.2.3.2 Step III: The persistence, bioaccumulation and toxicity [P, B, T] criteria (use of cut-off values organic contaminants obtained from the literature review

A database of properties characterizing the persistence, bioaccumulation and toxicity including other human health effects was created for the organic contaminants listed in Table 4.15. [CD-ROM] Information sources were consulted to obtain values for the physical properties and cut-off values characterizing the Persistence, Bioaccumulation and Toxicity attributes [Table 3.2, Table 3.3 and Table 3.4] of Chapter 3 of this document. Based on the cut-off values, it was decided whether to exclude the organic contaminant or to add it onto the preliminary list of organic contaminants of concern (PLOCC) (Figure 3.2). Values for each of the contaminants obtained from the above step were obtained from the literature and using a "Yes" or "No" decision making process a contaminant was characterized as "persistent" or "not persistent", accumulative or "not accumulative" and toxic or "not toxic". [Table 4.17] The same was done for other parameters.

Since not all the organic contaminants had readily available data on the fate and behaviour in the aquatic environment, human exposure effects, fate and behaviour in the human body, interactions with other chemicals in nature, measurement in environmental samples, removal methods from source water, drinking water quality guidelines or standards to enable regulation, it was necessary to develop water quality monographs at this stage. Water quality monographs were developed as an additional tool for screening the organic contaminants on the PLOCPC and those identified through the literature review.

4.2.3.3 Step III: Development of Water quality Monographs

The development of water quality monographs is used as a screening and information elucidation tool (Figure 3.2, Step III). An example of a completed water quality monograph is shown in Table 4.16. Completed water quality monographs were characterized by unique numbers (Table 4.17) and described in detail in the attached Compact Disk. It was observed that the PLOCPC contained some organic contaminants which lacked a lot of information, especially on the P, B, T criteria, removal from water during treatment, fate and behaviour in the environment and drinking water regulation criteria among others. The organic contaminants which were identified for water quality monograph development were automatically placed on the list of organic contaminants of concern (Table 4.16).

TABLE 4.16 MONOGRAPH A5: DI (2-ETHYLHEXYL) PHTHALATE (DEHP)

A. General Information

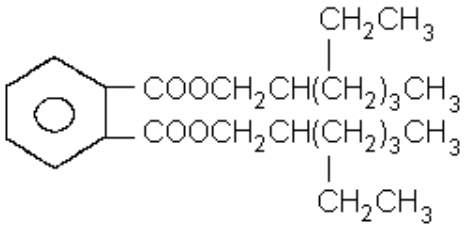
CASRN	117-81-7
Toxic	Yes
Mutagenic	Yes
Carcinogen	Yes
Endocrine Disruptor	Yes
Aesthetic	No
Priority pollutant	Yes
Accumulative	Yes
Persistent	Yes
Essential element	No
Teratogenic	Yes
R_fD	-
A.D.I/TDI	25µg/kg/day bw , UF = 100
L.O.A.E.L	666 mg/kg/day bw based on reduced fetal weight (oral, rats)
N.O.A.E.L	357 mg/kg/day bw based on reduced fetal body weight (oral in rats)
LD_{50} mg/kg (oral)	26000-4000mg/kg/day bw (acute oral toxicity) in rabbits
LD_{L0} mg/kg (oral)	-
Other names	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester; Phthalic acid, bis(2-ethylhexyl) ester; Bis(2-ethylhexyl) 1,2-benzenedicarboxylate; Bisoflex 81; Compound 889; Di(ethylhexyl) phthalate; Dioctyl phthalate; DEHP; DOP; Ethylhexyl Phthalate; Eviplast 80; Eviplast 81; Fleximel; Flexol DOP; Kodaflex DOP; Octoil; Octyl phthalate; Palatinol AH; Phthalic acid dioctyl ester; Pittsburgh PX-138; Sicol 150; Staflex DOP; Truflex DOP;etc

B. Occurrence

Di-(2-ethylhexyl) phthalate (DEHP) has been the most commonly used, and is still the plasticizer of choice for all PVC medical and surgical products. It is a manufactured chemical that is commonly added to plastics to make them flexible. DEHP is used as one of several plasticizers in polyvinyl chloride (PVC) resins for fabricating flexible vinyl products. It is present in many plastics, especially vinyl materials, which may contain up to 40% DEHP, although lower levels are common. DEHP is present in plastic products such as wall coverings, tablecloths, floor tiles, furniture upholstery, shower curtains, garden hoses, swimming pool liners, rainwear, baby pants, dolls, some toys, shoes, automobile upholstery and tops, packaging film and sheets, sheathing for wire and cable, medical tubing, and blood storage bags. These PVC resins have been used to manufacture teething rings, pacifiers, soft squeeze toys, balls, shower curtains, raincoats, adhesives, polymeric coatings, paperboard, de-foaming agents, enclosure for food containers, animal glue, surface lubricants, etc. It is also used for the manufacture of vinyl gloves used for medical examinations and surgery. As a non-plasticizer, di-(2-ethylhexyl) phthalate is used as a replacement for polychlorinated biphenyls (PCBs) in dielectric fluids for electric capacitors. It is also used as a solvent in erasable ink, an acaricide for use in orchards, an inert ingredient in pesticides, a component of cosmetic products and vacuum pump oil. Because of its widespread occurrence, DEHP is frequently detected in surface water, groundwater and

drinking water at levels up to ppb. It has also been detected in urban run-off at levels up to 39ppb and municipal and industrial landfills at concentrations between 0 to 150ppm.

C. Properties / Structure



DEHP is an organic compound of Molecular Formula: $C_{24}H_{38}O_4$, Molar Mass 390.56g/mol and appears as colourless oily liquid with a slight odour. It is insoluble in water, miscible with mineral oil and hexane and soluble in most organic solvents. Other properties includes, M.P -50°C, B.P 385°C, vapour pressure 1.32 mmHg @ 200°C, ρ = 0.9861g/cm^3 at 20°C, log K_{ow} = 4.89 and Henry's law constant = 1x10^{-5} atm.m^3/mol. Its high K_{ow} value show a strong tendency for this compound to partition to lipids of organisms especially small invertebrates.

D. Fate and Behaviour

Water solubility of DEHP is low but as in the case of airborne material the strong tendency to adsorb to particles results in an additional substantial amount of DEHP bound to suspended sediments in surface freshwater and in marine environments. When DEHP is released to water, it dissolves very slowly into underground water or surface waters that contact it. It takes many years before DEHP in buried or discarded materials disappears from the environment. DEHP is hydrolysed to monoesters including MEHP. It does not evaporate easily, and little will be present in the air even near sources of production. This chemical hydrolysis can have a half-life up to 100 years. However, under aerobic conditions DEHP is rapidly biodegradable. It is substantially or entirely degraded in microbial tests systems and the half-life in river water was found to be about one month.

When DEHP is released to soil, it usually attaches strongly to the soil and does not move very far away from where it was released. In soil, binding occurs to mineral and organic components. Its high octanol/water partition coefficient enhances binding to humic acids and other organic material. The measured sediment/water partition coefficient (Koc = 4.8 x 10^{-5}). Because DEHP does not evaporate easily, normally very little goes into the air. DEHP can also break down in the presence of other chemicals to produce mono (2-ethylhexyl) phthalate (MEHP) and 2-ethylhexanol. Many of the properties of MEHP are like those of DEHP, and therefore its fate in the environment is similar. In the presence of oxygen, DEHP in water and soil can be broken down by microorganisms to carbon dioxide and other simple chemicals. DEHP does not break down very easily when deep in the soil or at the bottom of lakes or rivers where there is little oxygen. It can be found in small amounts in fish and other animals, and some uptake by plants has been reported. It bio-accumulates in invertebrates and fish. DEHP in air will bind to dust particles and will be carried back down to earth through gravity and rain or snow.

E. Measurement

DEHP can be determined by gas chromatography with electron capture detection (GC-ECD). The detection limit using this method is 0.1ng/l. GC-FID has also been used for the determination of DEHP in water. The method detection with flame ionisation detection is 1µg/l. GC-MS has been successful in accurately measuring phthalates. The identity of the

compound can be confirmed by mass spectrometry with “single ion” monitoring especially when electron capture detection is used.

F. Human exposure

The major exposure route for DEHP is the ingestion of contaminated food. Human beings may also be exposed to DEHP through air, water, or skin contact with plastics that have DEHP in them. Food may also contain DEHP, but it is not certain how much. They may be exposed to DEHP through drinking water, but it is not known how common this is. If you drink water from a well located near a landfill or waste site, you may be exposed to higher-than-average levels of DEHP. At the levels found in the environment, DEHP is not expected to cause harmful effects in humans. Orally administered DEHP produced significant dose-related increases in liver tumour in rats and mice of both sexes. This was successfully extrapolated to human beings. Acute effects involve irritation of the eyes, the skin and the respiratory tract and or gastrointestinal tract. Chronic effects may cause dermatitis if contact with skin is prolonged. Repeated exposure to DEHP may affect the kidneys and liver and may cause numbness and tingling in the arms and legs.

1.2 G. Toxicology

The principal toxic effects of DEHP noted experimentally in mammals involve damage to the liver and in some cases the kidneys and secondly effects on the reproduction and development processes notably the production of testicular atrophy and a number of adverse developmental effects. Cancer type, hepatocellular carcinoma and adenomas have also been reported. It is also a teratogen and may damage the testes. Hence the primary target organs for DEHP toxicity have been shown to be the liver and testes. It is a B2 carcinogen.

1.3 H. Removal during Water Treatment

Driving force membrane processes seem to be most useful for treating water contaminated with DEHP and other phthalates. Reverse osmosis, nano-filtration and ultra filtration have also been applied to phthalate removal from water. Ozone-GAC has also been successfully used. The current BAT for removal of DEHP like DBP from drinking water is GAC.

I. National and International Drinking Water Criteria

Country/ Organisation	Criteria	µg/l DEHP
WHO	Guideline	8
USEPA	Standards (MCL)	6
AUSTRALIA	Guideline	10
CANADA	Guideline (MAC)	0.01
EU	Guideline value Max. admissible conc.	9
NEW ZEALAND	Standard	9
BRITISH COUNCIL	Fresh water aquatic life Drinking water	9
SOUTH AFRICA (DWAF)	Guideline Tolerable limit	8
RAND WATER	**Guideline**	**8**

J. General Discussion

DEHP is ubiquitous in the environment. It is persistent, bioaccumulative, toxic, carcinogenic, mutagenic and teratogenic. It is therefore recommended that the compound must be monitored throughout the drinking water value chain as an organic contaminant of concern.

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4.2.3.4 Step III: Other Criteria used for screening the PLOCPC

As reflected in Table 4.17 other criteria such as endocrine disruption, evidence of human health concern such as being carcinogenic, mutagenic, teratogen as per the literature review or proprietary data was used to screen the organic compounds on the PLOCPC list in addition to the "occurrence criteria"[Table 4.15]. Some organic contaminants might not have sufficient data to support the decision making process. "Other criteria" can therefore be used as presented in Figure 3.3 of Chapter 3. For example, questions as presented in Figure 3.3 can be asked and the answers could assist in deciding whether to list the organic contaminant as that of concern. The other criteria includes relevance of contaminant or group of organic contaminants to the Drinking Water industry, potential for being detected in any of the critical control points along the drinking water value chain, evidence for adverse human health effects, previous regulation such as the Stockholm Convention "dirty dozen" and being registered for use in drinking water treatment. More of the evidence emanating from these criteria would be obtained during the validation of the list of organic contaminants of concern to the drinking water industry [Figure 3.3, Step III of the Protocol].

Overall assessment

As observed from Table 4.17, 226 individual and groups of organic contaminants are represented by the PLOCC. It is evident that there was limited information on some organic contaminants to allow decision making based of the occurrence criteria and human health effects. This is true for compounds such as synthetic organic polymer residues; Allyl Chloride, Diallyl ether, 5-Hexanal and Glycidol, identified benzotriazoles, some plasticizers such as 2-Chloroethanol phosphate and tri-n-butylphosphate, some pesticides such as 3,4-dichloroaniline, 3,3',4,4'-tetrachloroazobenzene, Disulfuton, Isocarbophos and Hexachlorocyclohexane which has been proved to be not as important as its isomers.

Pesticides such as MCPB, 2,4-DB, Mecoprop, Dichlorprop, Fenoprop, 2,4,5-T were not frequently detected in the drinking water value chain. There is limited information for Atrazine metabolites although evidence suggests that they are suspected endocrine disruptors and some of the metabolites have been found to occur in surface waters which might be used as sources for drinking water production. It was however decided to keep the metabolites on the list.

Pharmaceuticals and personal care products [PPCPs] have limited information to satisfy the P,B,T criteria. However, most of them have been found to occur in source water resources. These include compounds such as Diclofenac, Ibuprofen, Amoxycilin, Chloramphenicol,

Sulfamethaxole, Lincomycin, Trimethoprin and Triclosan. These compounds were kept on the PLOCC due to other concerns such as the fact that they are continuosly added to the environment and as “emerging organic contaminants” a lot of research is currently going on to establish their public health significance in the aquatic environment. The outcome of this step was 226 organic contaminants on the preliminary list of organic contaminants of concern (PLOCC). [**Table 4.17] The rest of the table can be viewed in the attached CD-ROM.**

Monograph Number	Parameter	Human Health Concern									Remarks
		Persistent	Accumulative	Toxic	Carcinogen	Mutagen	Endocrine disruptor	Teratogenic	Found in the drinking Water value chain	Develop water quality monograph?	
A. INDUSTRIAL CHEMICALS											
A1	Benzene	Y	Y	Y	Y	Y	-	Y	Y	Y	Also causes taste and odour problems
-	*Chlorobenzene*	*N*	*N*	*Y*	*Y*	*N*	*N*	*N*	*Y*	*N*	*Liver or kidney problems*
-	*1,2-Dichlorobenzene*	*N*	*N*	*Y*	*Y*	*Y*	*N*	*Y*	*Y*	*N*	*Liver, kidney or circulatory system problems*
-	*1,2,4-Trichlorobenzene*	*N*	*N*	*Y*	-	-	-	-	*Y*	*N*	*Changes in adrenal glands*
-	*1,4-Dichlorobenzene*	*N*	*N*	*Y*	-	-	-	-	*Y*	*N*	*Yellow atrophy and cirrhosis of the liver*
-	*Pentachlorobenzene*	*N*	*N*	*Y*	-	-	-	-	*Y*	*N*	*Liver and kidney toxicity*
-	*Trichlorobenzenes (Total)*	*N*	*N*	*Y*	-	-	-	-	*Y*	*N*	*See individual CBs*
-	*Polynuclear aromatic hydrocarbons*	*Y*	*Y*	*Y*	*Y*	-	*Y*	-	*Y*	*N*	*Exert toxic effects through the arylhydrogen receptor mediated mechanism*
A2	Benzo [a] pyrene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Most toxic Polynuclear aromatic hydrocarbon.

4.2.4 STEP IV TESTING FOR ORGANIC CONTAMINANTS ON THE PLOCC, DETERMINATION OF CONCENTRATION LEVELS IN FISH, SEDIMENT AND WATER SAMPLES ALONG THE DRINKING WATER VALUE CHAIN.

The 226 organic contaminants on the preliminary list of organic contaminants of concern [PLOCC, Table 4.17] obtained from step III was assessed for occurrence in the drinking water value chain. This was achieved by determining the concentration, whereby comprehensive laboratory analyses of organic contaminants in biota [fish tissue], sediments and water samples were conducted. The aim of this was to determine which organic contaminants or group of organic contaminants occur in the drinking water value chain (Figure 3.2). Once the data had been collected, intepretation was done. This was followed by a decision on whether the organic contaminant was positively identified or not in the drinking water value chain and whether it should pass onto the final list of organic contaminants of concern (FLOCC). Hence the outcome of this step is the Final list of organic contaminants of concern (FLOCC)

4.2.4.1 OCCURRENCE OF ORGANIC CONTAMINANTS IN THE RAND WATER DRINKING WATER VALUE CHAIN: APPLICATION OF THE "OCCURRENCE CRITERION"

The organic contaminants on the PLOCC were assessed for occurrence in the Rand Water drinking water value chain.

4.2.4.1.1 Materials and Methods

The assessment of organic contaminants on the PLOCC was conducted along the drinking water value chain twice a year. This consisted of the low flow (dry season) and high flow (wet season) assessment.

Study Sites

Data for assessing the occurrence of organic contaminants in the Rand Water drinking water value chain were collected from the following sites:

- **SITE 1:Vaal Dam:** Vaal Dam 1–At the Vaal Dam, main Rand Water source water abstraction **[Figure 4.4]**
- **SITE 2: M-Canal-Raw water canal,** source water entering Zuikerbosch Drinking Water Production plant **[Figure 4.4]**
- **SITE 3: D-DB8**, **Potable water from** Zuikerbosch **Drinking water production plant,** 5km point after Chlorination.[**Figure 4.4]**
- **SITE 4: D-MAP_S1)**: Mapleton Booster station after Chloramination [**Figure 4.4]**
- **SITE 5: S1-Tap_Vosloo,**Tap water at Vosloorus Township along the S1 line from Mapleton **[Figure 4.4]**

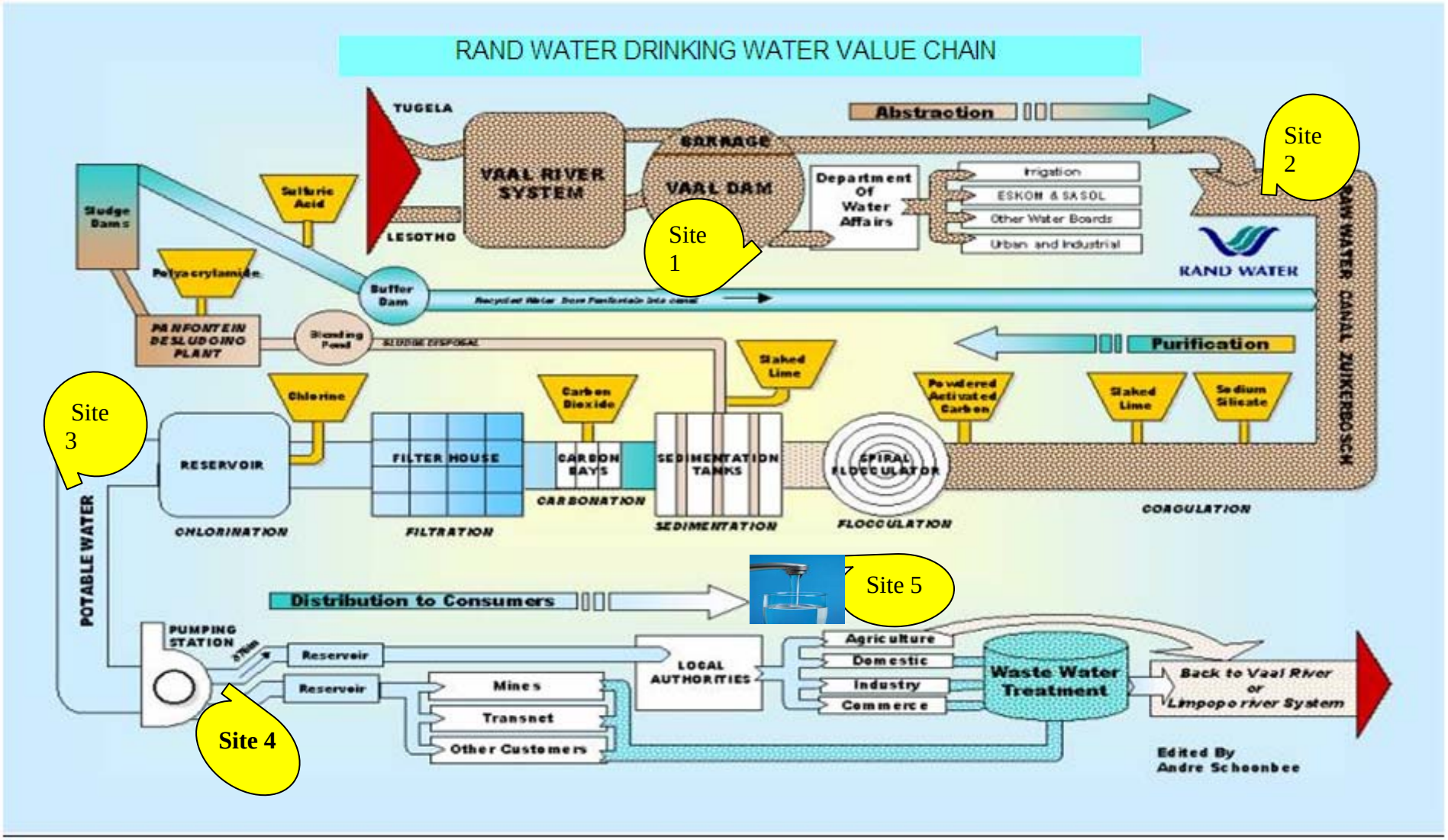

Figure 4.4 Sample site locations for the assessment of organic contaminants along the Rand Water drinking water value chain (*courtesy of A.Schoonbee*)

Field Sampling

Sample collection was conducted during the wet season (fast flow period of the year) in November/ December 2007 and during the dry season (low flow period of the year) in April/May 2007. Sediment, water and biota (fish) were selected from the source water (Vaal Dam: site C-VD1). From other sample points only water samples were collected. [Table 4.18]

TABLE 4.18: Summary of the specific matrix that was sampled and analyzed at each sample site

SAMPLING SITE	MATRIX					
	Sediment	Water	Biota: Fish			
			Muscle tissue	Liver tissue	Fat	Reproductive tissue (gonads)
SITE 1 **Source water (sample point VAAL DAM[C-VD1]**	X	X	X	X	X	X
SITE 2 **M-CANAL-Source Water**		X				
SITE 3 **D-DB8: Drinking Water after Chlorination**		X				
D-MAP_S1: Drinking water after Chloramination		X				
S1-Vosloo Tap-Drinkin water at the consumer tap.		X				

Fish samples

One fish species was collected from the Vaal Dam; namely, *Labeo umbratus* (moggel).This is a detritivoe, bottom feeder, on soft mud and detritus. Fish were collected by means of gill nets (*40mm to 150mm stretch mesh size*). Only female were used for the study due to the cost and the fact that gonads (eggs) of females are known to be good tissue for the accumulation of organics due to their fatty nature.

After capture the fish were transferred to a holding tank filled continuously with water from Site 1[Vaal Dam]. Before dissecting the fish, the fish was rinsed in clean water collected at the site. The fish were then killed by a hard blow on the head. Dissection was done on polythene dissection boards using high quality stainless steel dissection tools. Muscle tissue (skinless), gonads, liver and fat tissue were separated and packaged separately in extra heavy Aluminium foil, placed in a waterproof plastic bag and depending on the transportation time, kept on wet ice or frozen on dry ice as recommended by Du Preez et al. 2003. [171] In the laboratory three composite samples of each fish tissue were prepared to allow for replicate analysis. Composite samples were packaged individually in extra heavy Aluminium foil, placed in a waterproof plastic bag and kept frozen in a deep freeze as recommendations by Du Preez et al. 2003.[171] until analysis commenced.

Water samples

Samples were collected in triplicate from the five locations described above. The sample bottles were selected depending on the type of analysis. For example, for pesticide residue analysis, 2.5ℓ amber bottles were used. Water samples for volatile organic compounds (VOCs), Semi-volatile organic compounds (SVOCs) and Bisphenol A, were collected in 1ℓ glass bottles with Teflon lined caps. The samples were transported in cooler boxes (at 4˚C) to the respective laboratories and kept cool at 4˚C until analyzed, as recommended in laboratory method.

Sediment samples

Bottom sediment samples (approximately 10cm rab sample depth) from the Vaal Dam were collected in triplicate at the Vaal Dam (C-VD1) using an Edman grab. The sediment was placed in 125mℓ wide mouth glass jars with Teflon lined seal and delivered to the respective laboratories where they were kept at 4˚C until analyzed, as recommended in laboratory method.

Laboratory procedures

Two approaches namely, target and multi-residue analyses were used for the assessment of organic contaminants in fish, sediment and water samples. For maximum benefit, the organic contaminants on the PLOCC were arranged into functional groups. This made it possible for most of them to be screened using the multi-residue analysis approach. In the Multi-residue approach, a single extraction method was used to determine the most commonly encountered pesticides such as organochlorine pesticides (OCPs), organophosphorus pesticides (OPs) Polychlorinated biphenyls (PCBs) and pyrethroid groups of pesticides using a Gas

Chromatography with an electron capture detector (GC-ECD), flame photometry detector (GC-FPD), depending on the properties of the compounds. If pesticides are detected, the identity of the particular compound was confirmed using a GC-MS. It is important to note that not all pesticides will be detected using the multi-residue approach due to the nature and physical properties of certain compounds. These can only be detected and quantified using the target analysis approach.

In the target analysis approach, a method unique to a specific compound or group of compounds was used. For example, semi-volatile organics in both water and sediment were determined using a GC-MS method AM 186 based on the US EPA 8270, Benzene, toluene, ethylbenzene, xylene isomers commonly called the BTEX group were determined in water samples using the purge and trap GC-MS method GC 050, based on the US EPA 8260. The method is South African National Accreditation System (SANAS) Accredited for target compound analysis. This analysis was performed by the Centre for Science and Industrial Research (CSIR) organic analysis laboratory.

General Extraction procedures

Extractions were performed according to the internal procedures used by each participating laboratories (the Centre for Science, Information and Industrial Resarch (CSIR) Organic Chemistry I, the South African Bureau of Standards (SABS) and BioCrop and some internationally recognized methods such as those developed by the United States Environmental Protection Agency (USEPA). For example, The USEPA method 625 – Base/Neutral and Acids in Water was used for the extraction of Phenoxycarboxylic acids, 2,4-D, MCPA and Dichlorprop in water and sediment samples. For the extraction of the carbamate pesticides, Aldicarb, Aldicarb sulphoxide, Carbaryl, Carbofuran, Carbosulfan and Propoxur the method as described in the Official Methods of Analysis of AOAC International was used. The extraction procedure outlined in the South African Bureau of Standards (SABS) in house method no. 021/2001 Multi Residue Method for the Determination of Organochlorine and Synthetic Pyrethroid Pesticide Residues in Animal Tissue was used for the extraction of organic contaminants in fish tissue.

Assessment of organic contaminants in Fish tissue

On analysis, the samples were passed through a meat mincer. Single determinations on representative portions of the well-mixed samples were carried out using South African Bureau

of Standards (SABS) in-house method no. 021/2001 Multi-residue method for the determination of Organochlorine and synthetic pyrethroid pesticide residues in animal tissue. This method was used to determine the concentration levels of organic contaminants. Organochlorine pesticides, organophosphorus pesticides, synthetic pyrethroids and PCB congeners were determined using this method for each fish tissue. Triplicate analysis was done for each composite sample.

Assessment of organic contaminants in Sediment and Water samples

Organochlorine pesticides, organophosphorus pesticides, synthetic pyrethroids, PCB congeners, triazines, chloracetamides were analyzed using the method as described in official Methods of Analysis of AOAC International-16th Edition Vol 1. Phenoxyacetic acids, 2,4-D and MCPA were analyzed using SABS in-house Method no. 018/2000 viz Determination of 2,4-D Residues in various citrus and relevant matrices. To analyze for Dichlorprop, method CFP1 1991 Method for determining residues of Dichlorprop in citrus fruits was used. The EPA Method 625 Base/Neutral and Acids in water were used for extraction in both cases. Carbamate pesticides (Aldicarb, Aldicarb sulphone, Aldicarb sulphoxide, Carbaryl, Carbofuran, Carbosufan and Propoxur) were analyzed using Method no. AM127.

For the determination of selected volatile compounds on the PLOCC, in sediment samples such as Benzene, Toluene, Ethylbenzene, m,p-Xylene and o-Xylene (BTEX) group an in-house Headspace GC-MS Method AM191, based on USEPA methods 5021 and 8260 was used. This is a target compound analysis. Bisphenol A was determined using a CSIR in-house GC-MS Method. Semi-volatile organic compounds were determined using an the CSIR in-house GC-MS method AM 186 (based on USEPA method 8270).

Quality Assurance

This was performed according to the internal procedures used by each participating laboratory. The limit of detection (LOD) of the organic contaminants was determined as the concentration of analyses in a sample that gives rise to a peak with a signal–to-noise ratio (S/N) of 3. In some instances, the lowest limit of detection (LLOD) was used. The limit of quantification (LOQ) was also detected for some organic contaminants as shown in tables below based on the method in this case GC-MS performance and on laboratory background levels, which were determined by analyzing the procedural blanks. The LOQ were established at three times the standard deviation of the procedural blank level. The methods were optimized and validated using control water, sediment and fish samples spiked at 2µg/l, 0.2mgkg and 0.03mg/kg respectively. [Table

4.19] Recovery determinations consisted of adding these known amounts of the relevant organic contaminant or pesticide residue to portions of an untreated control sample and analysing these concurrently with the samples. Recovery percentage (%) of most organic contaminants from fish tissue, water and sediment samples were generally good. [Table 4.19] However, low recoveries from sediment samples were observed for organochlorine pesticides o,p-DDT, p,p'-DDT and Heptachlor. [Table 4.19] The organophosphates Dichlorvos and Sulfotep showed low recoveries from both sediment and fish samples. General low percentage (%) recovery values were obtained for the organophosphorus pesticides from fish samples. These included Dichlorvos, Sulfotep, Diazinon, Chlorpyrifos-Methyl, Pirimifos-Methyl, Parathion, Fenthion, Chlorpyrifos, Chlorfenvinphos and Profenophos. In all the five sites, triplicate samples were collected during each survey, to evaluate the reproducibility of the overall methods.

Statistical procedures and data processing

The sample size was 495 random-samples from 5 sites in the area of study. The study involved the collection of samples from 5 sites described in preceding sections, 3 matrices (fish, water and sediment) at the DAM site only**;**

11 functional groups of organic contaminants (type of chemicals) per site

3 replicate samples per group

The statistical model for the experiment is given as follows;

$$Y_{ijkl} = \mu + A_i + B_j + C_k + D_l + A_iB_j + A_iC_k + B_jC_k + A_iB_jC_k + \varepsilon$$

Where;

μ	denotes the overall or common effect
A_i	denotes the effect of sites; i = 1, 2, = number of sites.
B_j	denotes the effect of matrices; j = 1, 2, 3 = number of matrices per site
C_k	denotes the effect of groups; k = 1,…., 11 = number of groups per matrix
D_l	denotes the effect of samples; l = 1, 2, 3= number of samples per group
ε	denotes the error term

Total number of rows = 5 x 3 x 11 x 3 = 495 hence, the number of samples = 495

The statistical model was duplicated for calculating sample size for other sites along the drinking water value chain.

The objective of data analysis was to find out whether or not there was a significant difference among 5 sites, among the 3 matrices per site for the first two sample sites, among the 11 groups per matrix and to assess the effect of samples for significance. This is a typical generalized linear modeling procedure in statistics. The statistical model used is the univariate repeated measures analysis of variance (ANOVA). The model is univariate as there is only one outcome variable of interest (the concentration of each organic compound obtained from each sample). Data entry and analysis was done in the statistical package STATA version 10. Generalized linear Models were used for extensive data analysis. Standard diagnostic procedures for generalized linear models were used to assess the adequacy of the fitted model.

Table 4.19: Recovery percentage (%) determination results

Organic contaminant/ Pesticide residue	**% Recovery**		
	Fish (*0.03mg/kg*)	**Sediment (*0.01mg/kg*)**	**Water (2µg/l)**
Trifluralin	na	120+	120+
2,4-D	na	<50	120
MCPA	na	<50	97
Dichlorprop	na	101	86
Aldicarb	na	69	108
Aldicarb sulphone	na	97	68
Aldicarb sulphoxide	na	100	120+
Carbaryl	na	103	120
Carbofuran	na	120+	108
Carbosulfan	na	120+	108
Propoxur	na	106	107
p,p'-DDT	120+	<50	79

na- not assessed

Table 4.19 cont.: Recovery percentage (%) determination results

Organic contaminant/ Pesticide residue	Recovery %		
	Fish (*0.03mg/kg*)	Sediment (*0.01mg/kg*)	Water (2µg/l)
α-BHC	103	82	82
γ-BHC	105	70	84
Heptachlor	107	53	85
Aldrin	74	87	82
Heptachlor epoxide	105	86	84
β-Endosulfan	103	84	81
Endosulfan sulphate	81	79	81
Dieldrin	107	88	82
p,p'-DDE	109	87	83
Endrin	120+	84	86
p,p'-DDD	102	93	85
o,p'-DDT	120+	<50	80
Methoxychlor	106	90	81
Dichlorvos	56	54	89
Mevinphos	82	50	98
Sulfotep	53	86	91
Diazinon	59	89	91
Pirimifos-Methyl	60	87	86
Chlorpyrifos-Methyl	48	88	91
Fenitrothion	63	88	95
Parathion	47	85	95
Malathion	53	86	95
Fenthion	52	88	93
Chlorpyrifos	61	92	92
Chlorfenvinphos	67	87	93
Profenophos	44	94	93
Cypermethrin	119	92	79
Deltamethrin	120+	96	79
Cyhalothrin	113	89	81
Cyfluthrin	120+	91	79
PCB-291	92	79	69
PCB-293	97	79	73
PCB-294	114	80	78
PCB-297	74	81	78
PCB-296	91	81	79
PCB-298	82	83	78
Simazine	na	69	114
Atrazine	na	87	116
Tertbutylazine	na	98	115
Acetochlor	na	121	116
Alachlor	na	114	114
S-Metolachlor	na	111	120+

4.2.4.1.2 RESULTS OF TESTING FOR ORGANIC CONTAMINANTS ALONG THE RAND WATER DRINKING WATER VALUE CHAIN

The results of testing for organic contaminants in biota (fish), water and sediment samples collected along the Rand Water drinking water value chain are shown in Tables 4.20-4.29. A decision on whether the organic contaminant was positively identified or not in the drinking water value chain was made. The responses are indicated in Table 4.31 under the column "Found in the drinking water value chain?". The response is made in form of "Y"-Yes or "N"-No. Metolachlor was detected in all water samples from the Vaal Dam to the tap while apparent residues of Atrazine, Simazine and Terbutylazine were detected at levels below the detection limits during the wet season. Other contaminants positively identified along the Rand Water drinking water value chain include the disinfection by-products Chloroform, Bromodichloromethane, Dibromochloromethane and cyanotoxins products 2-Methylisoborneol and Geosmin. All contaminants which were positively identified occurred at concentration lower than the recommended drinking water quality guideline or standard when compared with the WHO drinking water guidelines [CD-ROM] which does not constitute a health hazard. The rest of the organic contaminants were either detected below the detection limit or could not be quantified due to analytical limitations and hence indicated a not detected (nd) result.

Apparent residues of Aldicarb and its metabolites were detected at a level of 0.02µg/kg in sediment samples from the Vaal Dam. Heptachlor was detected in the fat tissue of fish samples, Dieldrin in fat tissue and gonads and p,p'-DDE in fat and gonads during the low flow season (dry period). During the high flow season, p,p'-DDE was detected in all four fish tissues while Deltamethrin a pyrethroid was detected in muscle tissue. The results were subjected to statistical analysis as described in preceding sections.

Table 4.20: Results of the assessment of volatile organic contaminants (VOCs) and semivolatile organic contaminants (SVOCs) in water samples

CASRN	Volatile & Semi-Volatile Organic contaminants	Water-Low and High Flow seasons						
		Method	MDL (µg/ℓ)	Site 1: Vaal Dam (µg/ℓ)	Site 2: M-Canal Raw (µg/ℓ)	Site 3: D-DB8 (µg/ℓ)	Site 4: Map-B8-S1 (µg/ℓ)	Site 5: Tap, Vooslorus (µg/ℓ)
71-43-2	Benzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
108-88-3	Toluene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
100-41-4	Ethylbenzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
108-38-3 & 106-42-3	m,p-Xylene	Purge&Trap GC-MS	2	<2	<2	<2	<2	<2
95-47-6	o-Xylene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
108-90-7	Chlorobenzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
106-46-7	1,4-Dichlorobenzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
95-50-1	1,2-Dichlorobenzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
120-82-1	1,2,4-Trichlorobenzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
87-61-6	1,2,3-Trichlorobenzene	Purge&Trap GC-MS	1	<1	<1	<1	<1	<1
108-95-2	Phenol	GC-MS	4	nd	nd	nd	nd	nd
95-48-7	2-Methylphenol	GC-MS	1	nd	nd	nd	nd	nd
106-44-5	4-Methylphenol	GC-MS	2	nd	nd	nd	nd	nd
105-67-9	2,4-Dimethylphenol	GC-MS	1	nd	nd	nd	nd	nd
95-57-8	2-Chlorophenol	GC-MS	2	nd	nd	nd	nd	nd
59-50-7	4-Chloro-3-methylphenol	GC-MS	1	nd	nd	nd	nd	nd
120-83-2	2,4-Dichlorophenol	GC-MS	2	nd	nd	nd	nd	nd
88-06-2	2,4,6-Trichlorophenol	GC-MS	1	nd	nd	nd	nd	nd
95-95-4	2,4,5-Trichlorophenol	GC-MS	1	nd	nd	nd	nd	nd
87-86-5	Pentachlorophenol	GC-MS	2	nd	nd	nd	nd	nd
91-20-3	Naphthalene	GC-MS	2	nd	nd	nd	nd	nd
208-96-8	Acenaphyhylene	GC-MS	1	nd	nd	nd	nd	nd
83-32-9	Acenaphthene	GC-MS	1	nd	nd	nd	nd	nd

CASRN	Volatile & Semi-Volatile Organic contaminants	Water-Low and High flow seasons						
		Method	MDL (µg/ℓ)	Site 1: Vaal Dam (µg/ℓ)	Site 2: M-Canal Raw (µg/ℓ)	Site 3: D-DB8 (µg/ℓ)	Site 4: Map-B8-S1 (µg/ℓ)	Site 5: Tap, Vooslorus (µg/ℓ)
86-73-7	Fluorene	GC-MS	1	nd	nd	nd	nd	nd
85-01-8	Phenathrene	GC-MS	1	nd	nd	nd	nd	nd
120-12-7	Anthracene	GC-MS	1	nd	nd	nd	nd	nd
206-44-0	Fluoranthene	GC-MS	1	nd	nd	nd	nd	nd
129-00-0	Pyrene	GC-MS	1	nd	nd	nd	nd	nd
56-55-3	Benz[a]anthracene	GC-MS	1	nd	nd	nd	nd	nd
218-01-9	Chrysene	GC-MS	1	nd	nd	nd	nd	nd
205-99-2 & 207-08-9	Benzo[b] + [k] fluoranthene	GC-MS	1	nd	nd	nd	nd	nd
50-32-8	Benz0[a]pyrene	GC-MS	1	nd	nd	nd	nd	nd
193-39-5	Indeno[1,2,3-cd]pyrene	GC-MS	1	nd	nd	nd	nd	nd
53-70-3	Dibez[a,h]anthracene	GC-MS	1	nd	nd	nd	nd	nd
191-24-2	Benzo[g,h,i]perylene	GC-MS	1	nd	nd	nd	nd	nd
131-11-3	Dimethylphthalate	GC-MS	1	nd	nd	nd	nd	nd
84-66-2	Diethylphthalate	GC-MS	4	nd	nd	nd	nd	nd
84-74-2	Di-n-Butylpthalate	GC-MS	5	nd	nd	nd	nd	nd
85-68-7	Butylbenzylphthalate	GC-MS	1	nd	nd	nd	nd	nd
117-81-7	Bis(2-Ethylhexyl)phthalate	GC-MS	5	nd	nd	nd	nd	nd
117-84-0	Di-n-Octylphthalate	GC-MS	1	nd	nd	nd	nd	nd
80-05-7	Bisphenol A	GC-MS	15	nd	nd	nd	nd	nd

Table 4.20 cont.

**The results for the low flow and high flow seasons were the same for all determinants*

Table 4.21: Results of the assessment of selected pesticide groups and PCBs in water-Low flow season

Class of Organic contaminants	Assessed Organic contaminant /metabolite	Water-Low Flow Season						
		Method	MDL (µg/ℓ)	Site 1: Vaal Dam (µg/ℓ)	Site 2: M-Canal Raw (µg/ℓ)	Site 3: D-DB8 (µg/ℓ)	Site 4: Map-B8-S1 (µg/ℓ)	Site 5: Tap, Vooslorus (µg/ℓ)
Organochlorine pesticides	α-BHC	AOAC international 16th Edition Volume 1.	0.5	nd	nd	nd	nd	nd
	γ-BHC			nd	nd	nd	nd	nd
	Heptachlor			nd	nd	nd	nd	nd
	Aldrin			nd	nd	nd	nd	nd
	Heptachlor epoxide			nd	nd	nd	nd	nd
	β-Endosulfan			nd	nd	nd	nd	nd
	Endosulfan sulphate			nd	nd	nd	nd	nd
	Dieldrin			nd	nd	nd	nd	nd
	p,p'-DDE			nd	nd	nd	nd	nd
	Endrin			nd	nd	nd	nd	nd
	p,p'-DDD			nd	nd	nd	nd	nd
	o,p'-DDT			nd	nd	nd	nd	nd
	Methoxychlor			nd	nd	nd	nd	nd
Organophophorus pesticides	Dichlorvos	AOAC international 16th Edition Volume 1	0.5	nd	nd	nd	nd	nd
	Mevinphos			nd	nd	nd	nd	nd
	Sulfotep			nd	nd	nd	nd	nd
	Diazinon			nd	nd	nd	nd	nd
	Pirimifos-Methyl			nd	nd	nd	nd	nd
	Chlorpyifos-Methyl			nd	nd	nd	nd	nd
	Fenitrothion			nd	nd	nd	nd	nd
	Parathion			nd	nd	nd	nd	nd
	Malathion			nd	nd	nd	nd	nd
	Fenthion			nd	nd	nd	nd	nd
	Chlorpyrifos			nd	nd	nd	nd	nd
	Chlorfenvinphos			nd	nd	nd	nd	nd
	Profenophos			nd	nd	nd	nd	nd

Table: 4.21 cont.

Class of Organic contaminants	Assessed Organic contaminant/ metabolite	Water-Low Flow Season						
		Method	MDL (µg/ℓ)	Site 1: Vaal Dam (µg/ℓ)	Site 2: M-Canal Raw (µg/ℓ)	Site 3: D-DB8 (µg/ℓ)	Site 4: Map-B8-S1 (µg/ℓ)	Site 5: Tap, Vooslorus(µg/ℓ)
Synthetic Pyrethroids	Cypermethrin Deltamethrin Cyhalothrin Cyfluthrin	AOAC 16th Ed. Volume 1	0.5	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd
Polychlorinated Biphenyls	PCB-291 PCB-293 PCB-294 PCB-297 PCB-296 PCB-298	AOAC 16th Ed. Volume 1	0.5	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd
Triazine Herbicides	Simazine Atrazine Tertbutylazine	AOAC 16th Ed. Volume 1	0.3	nd nd nd	nd nd nd	nd nd nd	nd nd nd	nd nd nd
Chloroacetamides	Acetochlor Alachlor S-Metolachlor Trifluralin	AOAC 16th Ed. Volume 1	0.3	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd
Phenoxycarboxilic Acids	2,4-D MCPA Dichlorprop	SABS Method no. 018/2000	0.2	nd nd nd	nd nd nd	nd nd nd	nd nd nd	nd nd nd
Carbamate pesticides	Aldicarb Aldicarb sulphone Aldicarb sulphoxide Carbaryl Carbofuran Carbosulfan Propoxur	Method no. AM 127	3.0	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd 3.0

Table 4.22: Results of the assessment of selected pesticide groups and PCBs in water-High flow season

Class of Organic contaminants	Assessed Organic contaminant /metabolite	Water-High Flow Season: Method	LLOQ (µg/ℓ)	Site 1: Vaal Dam (µg/ℓ)	Site 2: M-Canal Raw (µg/ℓ)	Site 3: D-DB8 (µg/ℓ)	Site 4: Map-B8-S1 (µg/ℓ)	Site 5: Tap, Vooslorus (µg/ℓ)
Organochlorine pesticides	α-BHC	AOAC international 16th Edition Volume 1.	0.3	nd	nd	nd	nd	nd
	γ-BHC			nd	nd	nd	nd	nd
	Heptachlor			nd	nd	nd	nd	nd
	Aldrin			nd	nd	nd	nd	nd
	Heptachlor epoxide			nd	nd	nd	nd	nd
	β-Endosulfan			nd	nd	nd	nd	nd
	Endosulfan sulphate			nd	nd	nd	nd	nd
	Dieldrin			nd	nd	nd	nd	nd
	p,p'-DDE			nd	nd	nd	nd	nd
	Endrin			nd	nd	nd	nd	nd
	p,p'-DDD			nd	nd	nd	nd	nd
	o,p'-DDT			nd	nd	nd	nd	nd
	Methoxychlor			nd	nd	nd	nd	nd
Organophophorus pesticides	Dichlorvos	AOAC international 16th Edition Volume 1	0.3	nd	nd	nd	nd	nd
	Mevinphos			nd	nd	nd	nd	nd
	Sulfotep			nd	nd	nd	nd	nd
	Diazinon			nd	nd	nd	nd	nd
	Pirimifos-Methyl			nd	nd	nd	nd	nd
	Chlorpyifos-Methyl			nd	nd	nd	nd	nd
	Fenitrothion			nd	nd	nd	nd	nd
	Parathion			nd	nd	nd	nd	nd
	Malathion			nd	nd	nd	nd	nd
	Fenthion			nd	nd	nd	nd	nd
	Chlorpyrifos			nd	nd	nd	nd	nd
	Chlorfenvinphos			nd	nd	nd	nd	nd
	Profenophos			nd	nd	nd	nd	nd

LLOQ-Lowest limit of Quantification

Table: 4.22 cont

Class of Organic contaminants	Assessed Organic contaminant/ metabolite	Water-High Flow Season						
		Method	LLOQ (µg/ℓ)	Site 1: Vaal Dam (µg/ℓ)	Site 2: M-Canal Raw (µg/ℓ)	Site 3: D-DB8 (µg/ℓ)	Site 4: Map-B8-S1 (µg/ℓ)	Site 5: Tap, Vooslorus (µg/ℓ)
Synthetic Pyrethroids	Cypermethrin Deltamethrin Cyhalothrin Cyfluthrin	AOAC 16th Ed. Volume 1	0.3	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd
Polychlorinated Biphenyls	PCB-291 PCB-293 PCB-294 PCB-297 PCB-296 PCB-298	AOAC 16th Ed. Volume 1	0.3	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd
Triazine Herbicides	Simazine Atrazine Tertbutylazine	AOAC 16th Ed. Volume 1	0.3	<0.3 <0.3 <0.3	<0.3 <0.3 <0.3	<0.3 <0.3 <0.3	<0.3 <0.3 <0.3	<0.3 <0.3 <0.3
Chloroacetamides	Acetochlor Alachlor S-Metolachlor Trifluralin	AOAC 16th Ed. Volume 1	0.3	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd	nd nd nd nd
Phenoxycarboxilic Acids	2,4-D MCPA Dichlorprop	SABS Method no. 018/2000	0.2	nd nd nd	nd nd nd	nd nd nd	nd nd nd	nd nd nd
Carbamate pesticides	Aldicarb Aldicarb sulphone Aldicarb sulphoxide Carbaryl Carbofuran Carbosulfan Propoxur	Method no. AM 127	0.05	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd 0.4-0.5 0.4-0.5 nd	nd nd nd nd nd nd nd	nd nd nd nd 0.4-0.5 0.4-0.5 3.0

Propoxur- a carbamate derivative

Table 4.23: Results of the assessment of selected organic contaminants in water (Low flow season)

Organic contaminant (special Target analysis using Biocrop Lab Method no. 3.7.01.1 GC-MS	**LOD (µg/ℓ)**	**LOQ (µg/ℓ)**	**Site 1: Vaal Dam (µg/ℓ)**	**Site 2: M-Canal Raw (µg/ℓ)**	**Site 3: D-DB8 (µg/ℓ)**	**Site 4: Map-B8-S1 (µg/ℓ)**	**Site 5: Tap, Vooslorus (µg/ℓ)**
Endrin	0.108	0.359	<0.108	<0.108	<0.108	<0.108	<0.108
Acephate	0.139	0.465	<0.139	<0.139	<0.139	<0.139	<0.139
Dimethoate	0.090	0.301	<0.090	<0.090	<0.090	<0.090	<0.090
Methadithion	0.098	0.327	<0.098	<0.098	<0.098	<0.098	<0.098
Terbufos	0.175	0.583	<0.175	<0.175	<0.175	<0.175	<0.175
Cypermethrin I	0.120	0.399	<0.120	<0.120	<0.120	<0.120	<0.120
Cypermethrin II	0.099	0.331	<0.099	<0.099	<0.099	<0.099	<0.099
Cypermethrin III	0.085	0.285	<0.085	<0.085	<0.085	<0.085	<0.085
Cypermethrin IV	0.097	0.323	<0.097	<0.097	<0.097	<0.097	<0.097
Cyfluthrin I	0.099	0.332	<0.099	<0.099	<0.099	<0.099	<0.099
Cyfluthrin II	0.095	0.315	<0.095	<0.095	<0.095	<0.095	<0.095
Cyfluthrin III	0.087	0.290	<0.087	<0.087	<0.087	<0.087	<0.087
Cyfluthrin IV	0.011	0.036	<0.011	<0.011	<0.011	<0.011	<0.011
Deltamethrin	0.108	0.359	<0.108	<0.108	<0.108	<0.108	<0.108
Esfenvalerate	0.067	0.224	<0.067	<0.067	<0.067	<0.067	<0.067
Fenvalerate	0.132	0.440	<0.132	<0.132	<0.132	<0.132	<0.132
Permethrin I	0.061	0.202	<0.061	<0.061	<0.061	<0.061	<0.061
Permethrin II	0.006	0.021	<0.006	<0.006	<0.006	<0.006	<0.006
Cyhalothrin	0.071	0.237	<0.071	<0.071	<0.071	<0.071	<0.071
Trans-Chlordane	0.140	0.465	<0.140	<0.140	<0.140	<0.140	<0.140
Cis-Chlordane	0.132	0.441	<0.132	<0.132	<0.132	<0.132	<0.132
PCB 153	-	-	nd	nd	nd	nd	nd
Metalochlor	0.168	0.560	0.073	0.073	0.076	0.083	0.078
HBC	0.095	0.316	<0.095	<0.095	<0.095	<0.095	<0.095
Heptachlor epoxide	0.081	0.269	<0.081	<0.081	<0.081	<0.081	<0.081
p,p'-DDE	0.101	0.338	<0.101	<0.101	<0.101	<0.101	<0.101
p,p'-DDD	0.074	0.245	<0.074	<0.074	<0.074	<0.074	<0.074
p,p'-DDT	0.078	0.262	<0.078	<0.078	<0.078	<0.078	<0.078

Table 4.24: Results of the assessment of selected organic contaminants in water (High flow season)

Organic contaminant (special Target analysis using Biocrop Lab Method no. 3.7.01.1 GC-MS	**LOD (µg/ℓ)**	**LOQ (µg/ℓ)**	**Site 1: Vaal Dam (µg/ℓ)**	**Site 2: M-Canal Raw (µg/ℓ)**	**Site 3: D-DB8 (µg/ℓ)**	**Site 4: Map-B8-S1 (µg/ℓ)**	**Site 5: Tap, Vooslorus (µg/ℓ)**
Endrin	0.108	0.359	<0.108	<0.108	<0.108	<0.108	<0.108
Acephate	0.139	0.465	<0.139	<0.139	<0.139	<0.139	<0.139
Dimethoate	0.090	0.301	<0.090	<0.090	<0.090	<0.090	<0.090
Methadithion	0.098	0.327	<0.098	<0.098	<0.098	<0.098	<0.098
Terbufos	0.175	0.583	<0.175	<0.175	<0.175	<0.175	<0.175
Cypermethrin I	0.120	0.399	<0.120	<0.120	<0.120	<0.120	<0.120
Cypermethrin II	0.099	0.331	<0.099	<0.099	<0.099	<0.099	<0.099
Cypermethrin III	0.085	0.285	<0.085	<0.085	<0.085	<0.085	<0.085
Cypermethrin IV	0.097	0.323	<0.097	<0.097	<0.097	<0.097	<0.097
Cyfluthrin I	0.099	0.332	<0.099	<0.099	<0.099	<0.099	<0.099
Cyfluthrin II	0.095	0.315	<0.095	<0.095	<0.095	<0.095	<0.095
Cyfluthrin III	0.087	0.290	<0.087	<0.087	<0.087	<0.087	<0.087
Cyfluthrin IV	0.011	0.036	<0.011	<0.011	<0.011	<0.011	<0.011
Deltamethrin	0.108	0.359	<0.108	<0.108	<0.108	<0.108	<0.108
Esfenvalerate	0.067	0.224	<0.067	<0.067	<0.067	<0.067	<0.067
Fenvalerate	0.132	0.440	<0.132	<0.132	<0.132	<0.132	<0.132
Permethrin I	0.061	0.202	<0.061	<0.061	<0.061	<0.061	<0.061
Permethrin II	0.006	0.021	<0.006	<0.006	<0.006	<0.006	<0.006
Cyhalothrin	0.071	0.237	<0.071	<0.071	<0.071	<0.071	<0.071
Trans-Chlordane	0.140	0.465	0.044	<0.140	<0.140	<0.140	<0.140
Cis-Chlordane	0.132	0.441	0.042	<0.132	<0.132	<0.132	<0.132
PCB 153	-	-	nd	nd	nd	nd	nd
Metalochlor	0.168	0.560	0.016	0.073	0.076	0.083	0.078
HBC	0.095	0.316	<0.055	<0.095	<0.095	<0.095	<0.095
Heptachlor	0.081	0.269	0.027	<0.081	<0.081	<0.081	<0.081
epoxide	0.101	0.338	0.025	<0.101	<0.101	<0.101	<0.101
p,p'-DDE	0.074	0.245	0.023	<0.074	<0.074	<0.074	<0.074
p,p'-DDD	0.078	0.262	0.024	<0.078	<0.078	<0.078	<0.078
p,p'-DDT							

Table 4.25: Results of the analysis of VOCs and SVOCs in sediment samples

Volatile and Semi-volatile organic contaminants	Sediment -CSIR lab (low & High flow season		
	Method	MDL (µg/kg)	Site 1: Vaal Dam (µg/kg)
Benzene	Headspace GC-MS	10	<10
Toluene	Headspace GC-MS	10	<10
Ethylbenzene	Headspace GC-MS	10	<10
m,p-Xylene	Headspace GC-MS	20	<20
o-Xylene	Headspace GC-MS	10	<10
Chlorobenzene	Headspace GC-MS	10	<10
1,4-Dichlorobenzene	Headspace GC-MS	10	<10
1,2-Dichlorobenzene	Headspace GC-MS	10	<10
1,2,4-Trichlorobenzene	Headspace GC-MS	10	<10
1,2,3-Trichlorobenzene	Headspace GC-MS	10	<10
Phenol	GC-MS	130	nd
2-Methylphenol	GC-MS	170	nd
4-Methylphenol	GC-MS	130	nd
2,4-Dimethylphenol	GC-MS	160	nd
2-Chlorophenol	GC-MS	160	nd
4-Chloro-3-methylphenol	GC-MS	100	nd
2,4-Dichlorophenol	GC-MS	170	nd
2,4,6-Trichlorophenol	GC-MS	90	nd
2,4,5-Trichlorophenol	GC-MS	90	nd
Pentachlorophenol	GC-MS	170	nd
Naphthalene	GC-MS	150	nd
Acenaphyhylene	GC-MS	90	nd
Acenaphthene	GC-MS	110	nd
Fluorene	GC-MS	90	nd
Phenathrene	GC-MS	70	nd
Anthracene	GC-MS	70	nd
Fluoranthene	GC-MS	70	nd
Pyrene	GC-MS	70	nd
Benz[a]anthracene	GC-MS	60	nd
Chrysene	GC-MS	60	nd
Benzo[b] + [k] fluoranthene	GC-MS	90	nd
Benz0[a]pyrene	GC-MS	70	nd
Indeno[1,2,3-cd]pyrene	GC-MS	80	nd
Dibenz[a,h]anthracene	GC-MS	60	nd
Benzo[g,h,i]perylene	GC-MS	50	nd
Dimethylphthalate	GC-MS	90	nd
Diethylphthalate	GC-MS	100	nd
Di-n-Butylpthalate	GC-MS	100	nd
Butylbenzylphthalate	GC-MS	100	nd
Bis(2-Ethylhexyl)phthalate	GC-MS	280	nd
Di-n-Octylphthalate	GC-MS	100	nd
Bisphenol A	GC-MS	330	<330

Table 4.26: Results of the analysis of selected pesticides groups and PCBs in sediment samples

Class of Organic contaminants	Assessed Organic contaminant/ metabolite	Sediment –Low and High Flow Seasons		
		Method	LLOQ (µg/kg)	Site 1: Vaal Dam(µg/kg)
Organochlorine pesticides	α-BHC γ-BHC Heptachlor Aldrin Heptachlor epoxide β-Endosulfan Endosulfan sulphate Dieldrin p,p'-DDE Endrin p,p'-DDD o,p'-DDT Methoxychlor	AOAC international 16th Edition Volume 1.-SABS	10	nd nd nd nd nd nd nd nd nd nd nd nd nd nd nd
Organophophorus pesticides	Dichlorvos Mevinphos Sulfotep Diazinon Pirimifos-Methyl Chlorpyifos-Methyl Fenitrothion Parathion Malathion Fenthion Chlorpyrifos Chlorfenvinphos Profenophos	AOAC international 16th Ed. Volume 1-SABS	10	nd nd nd nd nd nd nd nd nd nd nd nd nd nd nd
Synthetic Pyrethroids	Cypermethrin Deltamethrin Cyhalothrin Cyfluthrin	AOAC international 16th Ed. Volume 1	10	nd nd nd nd
Polychlorinated Biphenyls	PCB-291 PCB-293 PCB-294 PCB-297 PCB-296 PCB-298	AOAC international 16th Ed. Volume 1	10	nd nd nd nd nd nd
Triazine Herbicides	Simazine Atrazine Tertbutylazine	AOAC international 16th Ed. Volume 1	5	nd nd nd

Table: 4.26 cont.

Class of Organic contaminants	Assessed Organic contaminant/ metabolite	Method	LLOQ (µg/kg)	Site 1: Vaal Dam (µg/kg)
Chloroacetamides	Acetochlor Alachlor S-Metolachlor Trifluralin	AOAC international 16th Ed. Volume 1	5	nd nd nd nd
Phenoxycarboxilic Acids	2,4-D MCPA Dichlorprop	SABS Method no. 018/2000	5	nd nd nd
Carbamate pesticides	Aldicarb Aldicarb sulphone Aldicarb sulphoxide Carbaryl Carbofuran Carbosulfan Propoxur	Method no. AM 127	0.05	nd nd nd nd nd nd nd nd 0.02

Table: 4.27 Results of Target Analysis for selected pesticide groups and PCBs in sediments

Organic contaminant	LOD (µg/kg)	Site 1: Vaal Dam (µg/kg)	Organic contaminant	LOD (µg/kg)	Site 1: Vaal Dam (µg/kg)
Endrin	30.60	<30.60	Esfenvalerate	28.20	<28.20
Acephate	30.00	<30.00	Fenvalerate	29.40	<29.40
Dimethoate	24.00	<24.00	Permethrin I	29.40	<29.40
Methadithion	32.40	<32.40	Permethrin II	29.40	<29.40
Terbufos	46.80	<46.80	Cyhalothrin	30.00	<30.00
Cypermethrin I	29.40	<29.40	*Trans*-Chlordane	35.40	<35.40
Cypermethrin II	29.40	<29.40	*Cis*-Chlordane	35.40	<35.40
Cypermethrin III	29.40	<29.40	PCB 153	-	nd
Cypermethrin IV	29.40	<29.40	Metalochlor	67.80	<67.80
Cyfluthrin I	33.00	<33.00	HBC	32.40	<32-40
Cyfluthrin II	33.00	<33.00	Heptachlor epoxide	37.20	<37.20
Cyfluthrin III	33.00	<33.00	p,p'-DDE	34.20	0.70
Cyfluthrin IV	33.00	<33.00	p,p'-DDD	33.60	<33.60
Deltamethrin	37.80	<37.80	p,p'-DDT	39.00	<39.00

Table 4.28: Results of Multi-residue determination of selected pesticide groups and PCBs in fish tissue

Class of Organic contaminants	Assessed Organic contaminant/ metabolite	Fish–Low Flow Season-Vaal Dam SABS Method no.0212001				
		LLOD (µg/kg	Fat tissue (µg/kg)	Gonads (µg/kg)	Muscle tissue (µg/kg)	Liver (µg/kg)
Organochlorine pesticides	α-BHC		nd	nd	nd	nd
	γ-BHC		nd	nd	nd	nd
	Heptachlor		<20.00	nd	nd	nd
	Aldrin		nd	nd	nd	nd
	Heptachlor epoxide		nd	nd	nd	nd
	β-Endosulfan		nd	nd	nd	nd
	Endosulfan sulphate		nd	nd	nd	nd
	Dieldrin	20.00	40.00	nd	nd	nd
	p,p'-DDE		30.00	nd	nd	nd
	Endrin		nd	nd	nd	nd
	p,p'-DDD		nd	nd	nd	nd
	o,p'-DDT		nd	nd	nd	nd
	Methoxychlor		nd	nd	nd	nd
Organophophorus pesticides	Dichlorvos		nd	nd	nd	nd
	Mevinphos		nd	nd	nd	nd
	Sulfotep		nd	nd	nd	nd
	Diazinon		nd	nd	nd	nd
	Pirimifos-Methyl		nd	nd	nd	nd
	Chlorpyifos-Methyl	20.00	nd	nd	nd	nd
	Fenitrothion		nd	nd	nd	nd
	Parathion		nd	nd	nd	nd
	Malathion		nd	nd	nd	nd
	Fenthion		nd	nd	nd	nd
	Chlorpyrifos		nd	nd	nd	nd
	Chlorfenvinphos		nd	nd	nd	nd
	Profenophos		nd	nd	nd	nd
Synthetic Pyrethroids	Cypermethrin		nd	nd	nd	nd
	Deltamethrin	20.00	nd	nd	40.00	nd
	Cyhalothrin		nd	nd	nd	nd
	Cyfluthrin		nd	nd	nd	nd
Polychlorinated Biphenyls	PCB-291		nd	nd	nd	nd
	PCB-293		nd	nd	nd	nd
	PCB-294	20.00	nd	nd	nd	nd
	PCB-297		nd	nd	nd	nd
	PCB-296		nd	nd	nd	nd
	PCB-298		nd	nd	nd	nd

N.B-None of the organic contaminants or pesticide residues were detected in fish tissue during the high flow season

Table 4.29: Multi-residue method results for the determination of selected organic contaminants in fish tissue

Assessed Organic contaminant/ metabolite	Fish–Low Flow Season-Vaal Dam using Method no. 3.7.01.1 Biocrop Lab				
	LOD (µg/kg)	Fat tissue (µg/kg)	Gonads (µg/kg)	Muscle tissue (µg/kg)	Liver (µg/kg)
Endrin	102.00	<102.00	<102.00	<102.00	<102.00
Acephate	100.00	<100.00	<100.00	<100.00	<100.00
Dimethoate	80.00	<80.00	<80.00	<80.00	<80.00
Methadithion	108.00	<108.00	<108.00	<108.00	<108.00
Terbufos	156.00	<156.00	<156.00	<156.00	<156.00
Cypermethrin I	98.00	<98.00	<98.00	<98.00	<98.00
Cypermethrin II	98.00	<98.00	<98.00	<98.00	<98.00
Cypermethrin III	98.00	<98.00	<98.00	<98.00	<98.00
Cypermethrin IV	98.00	<98.00	<98.00	<98.00	<98.00
Cyfluthrin I	110.00	<110.00	<110.00	<110.00	<110.00
Cyfluthrin II	110.00	<110.00	<110.00	<110.00	<110.00
Cyfluthrin III	110.00	<110.00	<110.00	<110.00	<110.00
Cyfluthrin IV	110.00	<110.00	<110.00	<110.00	<110.00
Deltamethrin	126.00	<126.00	<126.00	<126.00	<126.00
Esfenvalerate	94.00	<94.00	<94.00	<94.00	<94.00
Fenvalerate	98.00	<98.00	<98.00	<98.00	<98.00
Permethrin I	98.00	<98.00	<98.00	<98.00	<98.00
Permethrin II	98.00	<98.00	<98.00	<98.00	<98.00
Cyhalothrin	100.00	<100.00	<100.00	<100.00	<100.00
Trans-Chlordane	-	-	-	-	-
Cis-Chlordane	-	-	-	-	-
PCB 153	116.00	<116.00	<116.00	<116.00	<116.00
Metalochlor	-	-	-	-	-
HBC	108.00	<108.00	<108.00	<108.00	<108.00
Heptachlor epoxide	-	-	-	-	-
p,p'-DDE	-	-	-	-	-
p,p'-DDD	-	-	-	-	-
p,p'-DDT	-	-	-	-	-

N.B-None of the organic contaminants or pesticide residues were detected in fish tissue during the high flow season.

The interpretation of results at the 5% level of significance

The two main effects (sites and contaminants), as well as the interaction effect between sites and contaminants) were tested. In addition to this, the significance of association between the various levels of sites and contaminants needs was also tested. The analysis of all sets of results indicated that there is a significant difference among functional groups at the 5% level (P=0.000 < 0.05) and a significant difference among contaminants at the 5% level (P=0.000 < 0.05). However, the results indicated that there is no difference among sites at the 5% level (P=0.996 > 0.05). The interaction effect between functional groups and contaminants is significant at the 5% level (P=0.000 < 0.05) and the interaction effect between functional groups and sites is insignificant at the 5% level (P=0.997 > 0.05). The results confirm that the levels at which the contaminants were detected were low when compared to WHO drinking water quality guidelines,[56,CD-ROM] which shows that there is no need to be concerned from a health risk perspective. The main aim of this exercise was to determine if any of the organic contaminants occurred in the drinking water value chain as per the occurrence criterion (Figure 3.2, Step IV). Those contaminants identified were added or confirmed to be added onto the Final list of organic contaminants (FLOCC) as shown in Table 4.19. However, the final list of organic contaminants of concern was finalized after taking consideration of all screening criteria including the results of the assessment in the drinking water value chain. This was accomplished at a validation workshop.

4.2.4.1.3 Step IV: The validation of the FLOCC by Drinking Water industry experts

The main aim of this step was to confirm the need to prioritize the organic contaminant or group of organic contaminants for monitoring in the drinking water value chain and to confirm the final list of organic contaminants of concern (FLOCC)**.** [Table 4.17] The list of organic contaminants was presented to a group of experts from the Drinking Water industry and relevant stakeholders for validation. The group of experts was drawn from the group that was presented in Table 4.5 for continuity. The workshop was informed of the results of the testing exercise, which is the assessment of PLOCC organic contaminants in the drinking water value chain. This workshop comprised of experts from the Water industry, agricultural sector, medical field, hydrologists, toxicologists, organic chemistry technical experts, chemical engineers, researchers and representatives from the national standards generation bureau.[Table 4.5] At this workshop it was agreed that most of the organic contaminants on the PLOCC were already on the WHO drinking water quality guideline document [56, CD-ROM] and this document receives extensive international rolling revision. Factors such as relevance to the South African Drinking water industry, potential for being detected in any of the critical control points along the drinking water value chain, evidence for adverse human health effects, previous regulation such as the Stockholm Convention “dirty dozen” and being

registred for use in drinking water treatment. [Figure 3.3, Step III of the Protocol]. Those organic contaminants that were detected in any matrix of interest during the assessment for occurrence in the drinking water value chain were moved directly onto the FLOCC.[Table 4.30]

The following aspects were also considered in identifying compounds for the FLOCC. It was agreed that:

- Benzo[a] Pyrene is the most toxic of all the 16 recognized PAHs, hence it will not be necessary to analyse for all 16 but to use BaP as an indicator for assessing contaminantion by PAHs.
- Benzene is a known human carcinogen. It is already being analyzed for in the BTEX group for protection against organoleptic properties such as taste and odour and to safeguard consumer complaints. If benzene is appropriately controlled in the drinking water value chain, chlorinated benzenes are going to be minimized especially those forming after chlorination.
- Glycol ethers have been associated with the cause of taste and odours in surface waters. It was decided to adopt the group as of concern.
- Plasticizers such as Bisphenol A, Di-n-butylphthalate, and Di-(2- ethylhexyl)phthalate and detergent metabolites Octylphenol and Nonylphenol are known for their estrogen mimicking effects as evidenced from previous local research.
- The “dirty dozen” list on the PLOCC was adopted as the list of organic contaminants of concern. Hence it was automatically transferred on the FLOCC.
- It was decided move all organochlorine pesticides with enough information on occurrence and potential adverse health effects as shown by the literature and the assessment exercise onto the FLOCC.
- Some parent organic contaminants such as Hexachlorocyclohexane (HCH) have no significance to drinking water but its isomers such as β-HCH, δ-HCH, γ-HCH have been found to cause endocrine disruption effects, liver tumours and are persistent in the environment. The same applies to triazine herbicides such as Atrazine and Simazine which degrade into more stable metabolites of more human health concern. It will be prudent to move these organic contaminants to the FLOCC.
- Benzene and its chlorinated products were moved onto the FLOCC due to taste and odour concerns.
- Synthetic polymer residues, especially those that are known be in use in some water treatment plants were also moved onto the FLOCC.
- Disinfection by-products which have been positively identified during the assessment in the drinking water value chain and those that are currently regulated were also moved onto the FLOCC.

- Polychlorinated biphenyls are currently being regulated in South Africa under the Africa Stockpiles Project. It was agreed that the group consists of a lot of congeners. Only those contaminants that have been detected and whose standards are available be added onto the FLOCC. Another proposal was the analysis of PCB-153 as an indicator of the group since standards for this congener are available.
- Pharmaceuticals and personal care products which were detected in aquatic environments were moved onto the FLOCC due to their perceived risks.

From the preceding step, it is evident that some of the organic contaminants on the PLOCC were excluded from the process. One hundred and twenty (120) organic contaminants including some metabolites where relevant were identified for the FLOCC. [Table 4.30]

Table 4.30: The final list of organic contaminants of concern (FLOCC)

Industrial Chemicals[31]	Pesticides[32]	Disinfection by-products [DBPs][18]	Polymer residues[13]	Cyanotoxins[10]	PPCPs & Hormones
Benzene	2,4-Dichlorophenoxyacetic acid [2,4-D]	Chloroform*	Acrylamide	Geosmin*	Triclosan
Chlorobenzene	Fenoprop	Bromodichloromethane*	Epichlorohydrin	2-MIB*	Trimethropin
1,2-Dichlorobenzene	MCPA	Dibromochloromethane*	Diallyldimethylammonium Chloride	Anatoxin-a	Erythromycine
1,2,4-Trichlorobenzene	Aldrin*	Formaldehyde	Dimethylamine	Homoanatoxin-a	Lincomycin
1,4-Dichlorobenzene	Atrazine & metabolites*	Trichloroacetaldehyde	Allyl Choride	Anatoxin-a(S)	Sulfametaxole
Pentachlorobenzene	Dieldrin*	Monochloroacetic acid	Diallyl Chloride	Microcystins	Amoxycillin
2-Chlorophenol	Chlorpyrifos	Trichloroacetic acid	5-Hexanal	Saxtoxins	Ibuprofen
2,4-Dichlorophenol	Cyhexatin	Dichloroacetic acid	Glycidol	Cylindrospermopsin	Diclofenac
2,4,6-Dichlorophenol	DDT*	Bromoacetic acid	1,3-Dichloro-2-propanol	Nodularin	Fenoprofen
Pentachlorophenol	DDD	Dibromoacetic acid	2,3-Dichloro-1-propanol	β-Methylaminoalanine	Naproxen
Di-2-(ethylhexyl)phthalate	DDE*	Bromochloroacetic acid	3-Chloro-1,2-propanediol		Acetaminophen
Di-n-Butylphthalate	Diquat	Dichloroacetonitrile	2-Hydroxy-3-dimethylaminopropyl Chloride		Acetylsalicylic acid
Di-2-(ethylhexyladipate (DEHA)	Endosulfan	Trichloroacetonitrile	1,3-Bis (dimethylamino)-2-propanol		Fluoxetine
2,3,7,8-Tetrachlorodiphenyldioxin	Endosulfan Sulphate	Bromoacetonitrile			Paracetamol
Nitrilotriacetic acid (NTA)	β-Endosulfan	Chloroacetonitrile			Clofibric acid
Benzo[a]Pyrene	Endrin	Bromoacetonitrile			Bezafibrate
Bisphenol A	Heptachlor*	Dibromoacetonitrile			Fenofibric acid
Ethylbenzene	Heptachlor Epoxide	Nitrosodimethylamine			Carbamazepine
Ethylene Glycol monethylether	Lindane	THMs*			Cotinine
Ethylene Glycol methyl ether acetate	Methoxychlor				β-Coprostanol
Ethylene Glycol monobutyl ether acetate	Paraquat				Primidone
p-Octylphenol	Simazine*				Gemifibrozil
p-Nonylphenol	Terbutylazine*				17β-Estradiol
Polychlorinated biphenyls	Acetochlor				Estriol
Aroclor 1016	Metolachlor*				Estrone
Aroclor 1254	Aldicarb*				17α-Ethinylestradiol
Aroclor 1260	Deltamethrin*				
Toluene	Vinclozolin				
Xylene isomers	Cyanazine				
Dibutyltin	Hexachlorobenzene [HCB]				
Dimethyltin	HCH isomers				
Tributyltin	Cypermethrin				

*-Detected in Rand Water drinking water value chain

4.2.5 Step V: Establishment of Technical capability for the removal of organic contaminants through conventional water treatment, recommendations for the implementation of the FLOCC

This step like the preceding one was completed in consultation with the relevant stakeholders especially the technical experts such as those involved with the various unit processes, manufacturing industry experts, organic chemists, water quality assurance personnel and those involved in the procurement of chemicals. [Table 4.5] The following aspects were considered;

- Rural community based water utilities especially in developing countries still have poor infrastructure that do not meet the current challenges for organic contaminant removal. This can also be true for some urban based water utilities.
- The spread of vector based diseases such as malaria has resulted in the use of organic contaminants especially pesticides in public health programmes dedicated to control these diseases. However, the pesticide residues remain widespread in the environment and could be a risk to future generations. It will be crucial for these pesticides to be monitored in surface and groundwater resources in order to protect consumers.
- Some water utilities might not have the capacity to remove the organic contaminants on the FLOCC in terms of the available unit processes, for example not using activated carbon processes like the Granular Activated Carbon (GAC) or Powdered Activated Carbon (PAC) as a minimum, and some organic contaminants can escape the process and be a potential risk to the consumer. This is a reality in most developing countries. The Rand Water drinking water treatment process is shown in Figure 4.4.

Based on these observations it was recommended that rural community based utilities and those that do not have the capacity to remove selected groups of organic contaminants should test for organic contaminants in their drinking water value chains. In this case, those laboratories that are accredited for organic analysis or with the capability for analysis like are the situation in other universities and similar research organizations can be used by the water utility to analyse its water samples from catchment to tap for analysis. The organic contaminants positively identified in such programmes will be added to the preliminary priority list of organic contaminants (PPLOC). In South Africa, such evidence could be gathered from national published documents such as Water Research Commission (WRC) completed projects and published articles on Water SA. The most frequently detected

organic contaminants were DDT and its metabolites especially in rural communities of KwaZulu Natal and the Limpopo provinces.

4.2.6 STEP VI Prioritization of the organic contaminants on the final list of organic contaminants (FLOCC)

The one hundred and twenty (120) organic contaminants on the FLOCC list were prioritized using the criteria presented in Step VI of the protocol. It was agreed that the highest priority chemicals are those that have shown to cause human health effects as a consequence of exposure through drinking water. According to the World Health Organization, [170] the high-priority chemical list can be modified if those chemicals are found not to be present, but a chemical not found in an initial investigation should not be forgotten. As a result, the prioritization criteria was applied to the FLOCC but observations made in other steps were used to take a final decision on whether to eliminate an organic contaminant from the preliminary priority list of organic contaminants or add it on the list.

4.2.6.1 Step VI: Occurrence criterion

Evidence for occurrence of the organic contaminant was collected in four tiers in preceding steps, that is from the literature, water quality monograph development process, experts knowledge and judgement and testing for the occurrence of organic contaminants in the drinking water value chain. Once the data has been collected, intepretation should be done. This was followed by a decision on whether the organic contaminant was positively identified or not in the drinking water value chain. The responses are indicated as shown in Table 4.31 under the column “Found in the drinking water value chain?”. The response is qualitatively made in form of “Y”-Yes or “N”-No.

4.2.6.2 Step VI: Adverse human health effect criterion

The information gathered from the literature review and water quality monographs was used at this stage as it would be already available in Table 4.17. This information and the information obtained from the preceding section 4.2.6.1 is combined to assist in prioritizing the organic contaminants in four groups as indicated in Figure 3.4.

At this stage, the prioritization approach identifies;

- Contaminants that are demonstrated to cause adverse health effects and to occur in the drinking water [I in Figure 3.4, Table 4.31].
- Contaminants that are demonstrated to cause adverse health effects and have the potential of occurrence in drinking water [II in Figure 3.4, Table 4.31].

- Contaminants that are demonstrated to occur in drinking water and have the potential to cause adverse health effects [III in Figure 3.4, Table 4.31] and
- Contaminants that are demonstrated to have the potential to occur in drinking water and have the potential to cause adverse health effects [IV in Figure 3.4, Table 4.31]

The approach considers and uses as many of the available types of health effects and occurrence data identified in the data source evaluation as practical (Figure 3.4, Table 4.31).

4.2.6.3 Step VI: Other criteria

This list is further subjected to analysis based on Drinking Water industry perspective and requirements. It is advisable that local conditions should define this process. The analysis covers aspects such as availability of standards/guidelines for regulation, potential to cause water quality problems, potential to stimulate customer perception of risk, removal efficiency and availability of expertise and capacity for analysis. [Figure 3.5 Chapter 3 of Protocol] Based on these criteria, a semi-quantitative approach is used and three priority lists of organic contaminants are identified. [Table 4.31] The organic contaminants are prioritized into short-term [S], medium term [M] and long term [L] priority for analysis in the drinking water value chain. Those organic contaminants placed on the short-term priority list are adopted for immediate routine monitoring in the drinking water value chain.

- Short-term [S] substances falling within this category are listed in Table 4.31 and Figure 3.5. Organic constituents in this category are selected based on the following characteristics;
  -The wide range of potential human health concerns via the drinking water ingestion route;
  -The substance is known to cause water quality problems in the drinking water value chain such as the cause of offensive tastes and odours;
  -There is evidence that the occurrence of a substance or group increases customers perception of risk;
  -There are enough resources in place to support ease of monitoring;
  -Poor removal efficiency using conventional water treatment methods;
  -Availability of drinking water standards/guidelines to enable regulation;
  -Proof of occurrence in the drinking water value chain especially those contaminants formed during drinking water treatment, distribution, storage and use.
  At least four or more aspects must be satisfied.
- Medium term (M) substances falling within this category are listed in Table 4.31.
  The wide range of potential human health concerns via the drinking water ingestion route;

-The substance is known to cause water quality problems in the drinking water value chain such as the cause of offensive tastes and odours;

-No evidence that the occurrence of a substance or group increases customers perception of risk;

-No resources in place to support ease of monitoring;

-Moderate removal efficiency using conventional water treatment methods;

-Non-availability of drinking water standards/guidelines to enable regulation;

-Proof of occurrence in the drinking water value chain especially those contaminants formed during drinking water treatment, distribution, storage and use.

- Long term (L) substances falling within this category are listed in Table 4.31. Organic constituents in this category are selected based on the following characteristics;

  -Insufficient information on human health concerns via the drinking water ingestion route;

  -Insufficient information on the impact of the organic contaminant on drinking water quality;

  -No evidence that the occurrence of a substance or group increases customers perception of risk;

  -No resources in place to support ease of monitoring;

  -Removed from drinking water using conventional water treatment methods;

  -Non-availability of drinking water standards/guidelines to enable regulation;

  -Proof of occurrence in the drinking water value chain especially those contaminants formed during drinking water treatment, distribution, storage and use.

On completion of preceding steps, three categories of organic constituents of importance to the water utility and its customers were established. [Table 4.31] **The outcome of this step was a preliminary priority list of organic contaminants [PPLOC] for monitoring in the drinking water value chain.** [Table 4.31]

Table 4.31: The Preliminary Priority List of Organic Contaminants (PPLOC) for monitoring in the drinking water value chain (*Complete table in CD_ROM*)

Monograph Number	*Parameter*	Units	Standard/Guideline	Currently Analyzed for?	*Human Health Concern*									Remarks
					Persistent	Accumulative	Toxic	Carcinogen	Mutagen	Endocrine disruptor	Teratogenic	Found in the drinking Water value chain	Priority for analysis	
A. INDUSTRIAL CHEMICALS														
A1	Benzene	µg/l	10(WHO), 5(USEPA), 10(NZ), 1(AU)	Y	Y	Y	Y	Y	Y	-	Y	Y	S	Also causes taste and odour problems
A2	Benzo [a] pyrene	µg/l	0.2(US), 0.7(WHO), 0.7 (NZ), 0.01(EU), 0.01(AU)	Y	Y	Y	Y	Y	Y	Y	Y	Y	S	Most toxic Polynuclear aromatic hydrocarbon.
B1	2,4-Dichlorophenoxyacetic acid	µg/l	70(USEPA), 30(WHO), 40(NZ)	Y	N	N	Y	Y	N	Y	N	Y	*S*	Currently regulated herbicide
B2	Aldrin	µg/l	0.03(WHO), 0.04(NZ), 0.03(USEPA), 0.03(EU), 0.3(AU),0.7(Can)	Y	Y	N	Y	Y	Y	Su	N	Y	*S*	Immediately converted to Dieldrin in the aqueous environment.
-	Pendimethalin	µg/l	20(WHO), 20 (NZ), 300(AU)	N	Y	Y	Y	-	N	-	N	N	L	Liver toxicity
-	Linuron(herbicide)	µg/l	-	N	N	-	Y	Y	N	Y	N	-	L	Testicular hyperplasia
E5	Allyl chloride	µg/l	-	N	N	N	Y	Y	Y	-	-	N/A	M	No criteria for regulation
E6	Diallyl ether	µg/l	-	N	N	N	Y	Y	-	-	-	N/A	M	VOC, no drinking water criteria
-	*Pentachlorobenzene*	*µg/l*	-	*?*	*N*	*N*	*Y*	-	-	-	-	*N/A*	*S*	*Liver and kidney toxicity*
-	*Trichlorobenzenes (Total)*	*µg/l*	*30(AU)*	*Y*	*N*	*N*	*Y*	-	-	-	-	*N/A*	*S*	*See individual CBs*
-	*Polynuclear aromatic hydrocarbons*	*µg/l*	*0.10(EU)*	*Y*	*Y*	*Y*	*Y*	*Y*	-	*Y*	-	*N/A*	*S*	*toxic effects arylhydrogen receptor mechanism*

Notes: **Y**-"Yes", **N**-"No", **Su**-"Suspected", ***S**-Analysis in the short term (1-2 years), **M**-Analysis in the medium term (3-5years), **L**-Analysis in the long term (5-10years),*
N/A-Not assessed

4.2.7 Step VII Validation of the priority list of organic contaminants by Drinking water industry experts and relevant stakeholders

The preliminary priority list of organic contaminants obtained from step VI [Table 4.31] was presented to a group of experts from the Drinking Water Industry and relevant stakeholders for validation. [Table 4.5] At this workshop, industry specific criteria and analytical challenges were identified as other aspects affecting organic analysis by water utilities. All contaminants with priority "S" for analysis were moved onto the priority list of organic contaminants. [**Table 4.32**] Benchmarking with other national and international bodies such as the WHO, USEPA, OECD and EU [CD-ROM] was done at this stage. However, local conditions and relevancy were given more emphasis.The outcome of this step was a list of 100 priority organic contaminants for monitoring in the drinking water value chain. This includes key metabolites and isomers for organochlorine pesticides such as DDT, Chlordane, Hexachlorocyclohexane (HCH), acetamide herbicides such as Metolachlor and Acetoclor and metabolites of S-Triazine herbicides. **The outcome of this step was a Priority list of organic contaminants (PLOC)** [**Table 4.32**]

Table 4.32: The Priority list of Organic contaminants (PL(ing water value chain

Industrial Chemicals[29]	Pesticides[37]	products [DBPs][13]	Polymer residues[7]	Cyanotoxins[9]	Hormones[5]
Benzene Chlorobenzene 1,2-Dichlorobenzene 1,2,4-Trichlorobenzene 1,4-Dichlorobenzene Pentachlorobenzene 2-Chlorophenol 2,4-Dichlorophenol 2,4,6-Dichlorophenol Pentachlorophenol Di-2-(ethylhexyl)phthalate Di-n-Butylphthalate Di-2-(ethylhexyladipate (DEHA) 2,3,7,8-Tetrachlorodiphenyldioxin Nitrilotriacetic acid (NTA) Benzo[a]Pyrene Bisphenol A Ethylbenzene p-Octylphenol p-Nonylphenol Polychlorinated biphenyls Aroclor 1016 Aroclor 1248 Aroclor 1254 Aroclor 1260 Toluene Xylene isomers Dibutyltin Dimethyltin Tributyltin	2,4-Dichlorophenoxyacetic acid [2,4-D] 2,4,5-TP Fenoprop MCPA Aldrin* Atrazine & metabolites* Dieldrin* Chlorpyrifos Cyhexatin DDT* DDD DDE* Diquat Endosulfan Endosulfan Sulphate β-Endosulfan Endrin Heptachlor* Heptachlor Epoxide Lindane Methoxychlor Paraquat Simazine* Terbutylazine* Acetochlor ethanesulfonic acid Acetochlor oxanilic acid Acetoclor Metolachlor* Metolachlor ethane sulfonic acid Metolachlor oxanilic acid Aldicarb* Deltamethrin* Vinclozolin Chlordane Cis,Trans-isomers Hexachlorobenzene [HCB] HCH isomers Cypermethrin	Chloroform* Bromodichloromethane* Dibromochloromethane* Formaldehyde Trichloroacetaldehyde Monochloroacetic acid Trichloroacetic acid Dichloroacetic acid Bromoacetic acid Dibromoacetic acid Bromochloroacetic acid Nitrosodimethylamine THMs*	Acrylamide Epichlorohydrin Diallyldimethylammonium Chloride Dimethylamine 1,3-Dichloro-2-propanol 2,3-Dichloro-1-propanol 3-Chloro-1,2-propanediol	Geosmin* 2-MIB* Anatoxin-a Homoanatoxin-a Anatoxin-a(S) Microcystin-LR Saxtoxin Cylindrospermopsin Nodularin	17β-Estradiol Estriol Estrone 17α-Ethinylestradiol Diethylstilbestrol (DES),

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CHAPTER 5 GENERAL DISCUSSIONS AND CONCLUSIONS

5.1 INTRODUCTION

The occurrence of organic contaminants in drinking water and its sources is a growing concern for the Drinking Water industry and its consumers. Because of the large amount of organic contaminants, prioritizing of these contaminants is necessary to get a clear overview of the problem and dedicate limited resources to priority organic contaminants. The paucity of information on the potential organic contaminants that threaten source waters that could be used for drinking water production as well as approaches used to select and prioritize them for monitoring in the drinking water value chain prompted the need for the development of a generic protocol to address these challenges. The generic protocol is presented in Figure 3.2 of Chapter 3 and is presented here for discussion. The protocol and its major components which form part of Objective 2 of this study are discussed in detail in the following sections. The protocol was validated in a prototype drinking water value chain in Chapter 4. This validation exercise addresses Objectives 3 and 4 of the study. The findings of the validation exercise will guide the discussion and conclusions will be drawn up from these experiences. The role of stakeholder participation and expert judgment in shaping the protocol is also discussed. The various criteria used in the protocol was drawn up from the perspective of the Drinking Water industry and validated using the Drinking Water industry experts and relevant stakeholders to ensure its applicability and sustainability for use.

5.2 The discussion of the results of the assessment of the components of the protocol

The aim of this study was to develop a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain. A process based on the previous research findings and conceptual models was followed. [Figure 3.1] Such are described in Chapter 2 and the three phases are emphasized in the USEPA and OSPAR Commission methodologies.[1,2] The protocol model developed in this study is described in Chapter 3 [Figure 3.2] and validated in Chapter 4. This Chapter discusses the evaluation of the protocol in a selected drinking water value chain, the views and inputs of the various experts and challenges faced during its implementation.

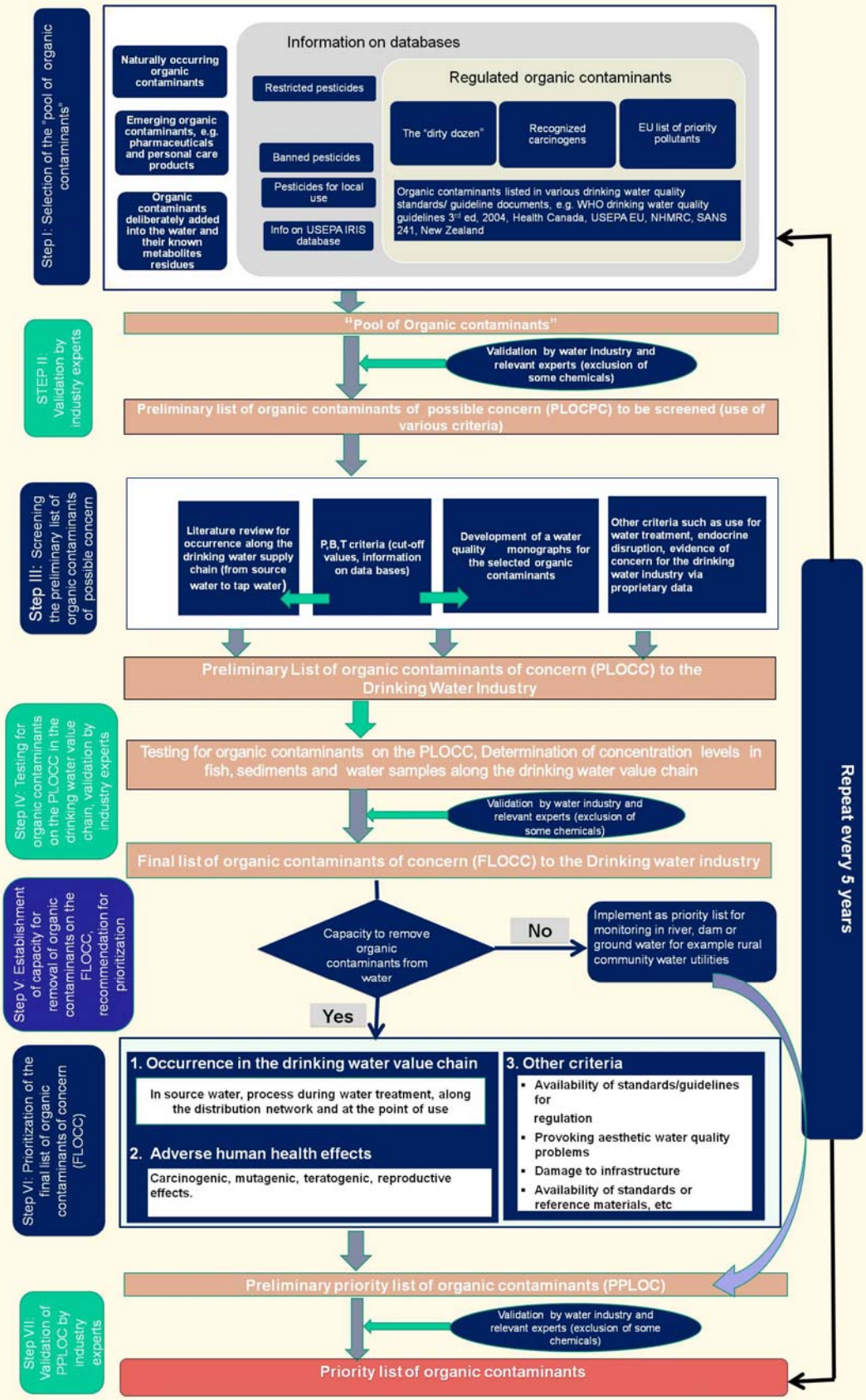

Figure 3.2 A generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain.

5.2.1 Selection of the "Pool of organic contaminants"

The exercise begins with the identification of potential drinking water organic contaminants prior to any attempts to screen or sort them. These cover a range of organic contaminants that the consumers can be exposed to via the drinking water ingestion route, dermal contact during recreational activities including other relevant water uses and the inhalation route. This forms the first step of the protocol. This step is a challenging step as it requires a lot of insight into the subject matter, which is the understanding of the types of organic contaminants that appear on the list as new ones are imported from other existing lists. It is well known that chemical substances including organic compounds are known by different names. The list of names for an organic contaminant can be long. The extracted information below shows the complexity of the problem. The names by which Di-2-(ethylhexyl) phthalate [DEHP] a compound that has been listed as one of the priority organic contaminants in this study are listed below. [Table 5.1]

Table 5.1 Other names for Di-2-(ethylhexyl) phthalate (DEHP)

1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester; Phthalic acid, bis(2-ethylhexyl) ester; Bis(2-ethylhexyl) 1,2-benzenedicarboxylate; Bisoflex 81; Compound 889; Di(ethylhexyl) phthalate; Dioctyl phthalate; DEHP; DOP; Ethylhexyl Phthalate; Eviplast 80; Eviplast 81; Fleximel; Flexol DOP; Kodaflex DOP; Octoil; Octyl phthalate; Palatinol AH; Phthalic acid dioctyl ester; Pittsburgh PX-138; Sicol 150; Staflex DOP; Truflex DOP; Vestinol AH; Vinicizer 80; Witcizer 312; 1,2-Benzenedicarboxylic acid, bis(ethylhexyl) ester; 2-Ethylhexyl phthalate; o-Benzenedicarboxylic acid, dioctyl ester; Dioctyl-o-benzenedicarboxylate; Bis-(2-ethylhexyl)ester kyseliny ftalove; DAF 68; Di(2-ethylhexyl)orthophthalate; Ergoplast fdo; Good-rite gp 264; Hatcol dop; Mollan O; Nuoplaz dop; Platinol ah; Platinol dop; Rcra waste number U028; Reomol dop; Reomol D 79P; Ergoplast FDO-S; Bis(2-ethylhexyl) o-phthalate; DOF

It is crucial for the person compiling this list to accurately identify the organic contaminants otherwise an inaccurate list can be used. An attempt was made to clean the list of all the unnecessary and irrelevant compounds or groupings which appeared after the amalgamation of the respective lists such as inorganic pesticides, plant extracts, inorganic essential oils, human medicinal estrogens, chlorinated benzenes, diesel engine exhaust, dialkyltins, foaming agents, solvents, hydrolyzed proteins just to mention a few examples. For the protocol to work individual organic contaminants or groups of contaminants that can be accurately quantified or an indicator chosen for them should be used. Examples that fall in this category are Polynuclear aromatic hydrocarbons, Polychlorinated biphenyls, Halogenated aromatic compounds, typified by the polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and diphenylethers (PCDEs), are industrial compounds or byproducts which have been widely identified in the environment and in chemical-waste dumpsites. Halogenated aromatics are invariably present in diverse analytes as highly complex mixtures of isomers and congeners and this complicates the hazard and risk assessment of these compounds. Several studies have confirmed the common receptor-mediated mechanism

of action of toxic halogenated aromatics and this has resulted in the development of structure-activity relationships for this class of chemicals. [8] The most toxic halogenated aromatic is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and based on *in vivo* and *in vitro* studies the relative toxicities of individual halogenated aromatics have been determined relative to TCDD [i.e., toxic equivalents]. [8] As a result such a compound can be used to represent the group of contaminants on the "pool of organic contaminants" and not "dioxin-like organic compounds" or "polychlorinated or polybrominated aromatic organic compounds".

5.2.2 Step II: Validation of the "pool of organic contaminants" by industry experts

Once the "pool of contaminants" was compiled a workshop was conducted to determine the organic contaminants of possible concern. This was a qualitative exercise where the guiding principle was the relevance of the organic contaminants and their public health significance to the drinking water. During this step, similarities were noted and some organic contaminants were eliminated from the list based on the non-relevance to drinking water and the diversity of views and experience of the various experts. These included observations such as organic contaminants that have never been detected in the drinking water value chain due to their short half-lives in the aquatic environment or general environment such as the pyrethroid group of pesticides of which the majority are characterized by high acute toxicity and short half lives.

For the validation of the protocol, no changes to what is proposed on the model was made except for the fact that at the workshop, attendees felt that most organic contaminants were already presented in the WHO guidelines for drinking water quality document, the 3rd edition published in 2004. It was therefore agreed that the list will form part of the working document to be used in Step II of the protocol. The reasons given were the fact that the document is produced by experts across the world and undergoes a rolling revision to update the information. This emphasized the role of expert judgment in decision-making. The process followed was transparent and key stakeholders were given the opportunity to comment on the method that was used to compile the "pool of organic contaminants". It was recognized however, that most emerging contaminants such as the Pharmaceuticals and personal care products [PPCPs] and surfactants were not listed on the WHO list. Organic contaminants on the WHO list were adopted for inclusion in the "Preliminary list of organic contaminants of possible concern (PLOCPC)" as agreed in the preceding Step. [Figure 3.2] **This resulted in 328 organic contaminants of possible concern remaining on the list. The PLOCPC was screened in Step III. [attached CD-ROM].**

5.2.3 Step III: Screening the preliminary list of organic contaminants of possible concern (PLOCPC)

The lack of information on the extent of occurrence of organic contaminants in the drinking water value chain necessitated further literature review in order to fill the information gaps outlined in Table 4.16. At this stage, water quality monographs were developed for selected organic contaminants. This part of the screening exercise proved to be valuable as it identified additional information that was used for decision-making on whether to keep the contaminant on the list of organic contaminants of concern or pass it on to the preliminary list of organic contaminants of concern. [PLOCC] The major challenge of this STEP was the diversity and bulkiness of information to synthesize the evidence from.

It was evident from the literature review that many organic contaminants could be found in the drinking water value chain especially in source water resources used for drinking water production. Main groups are summarized in Figure 4.2 of Chapter 4. The challenge was in accurately identifying them. The Persistence, Bioaccumulation and Toxicity criteria was used as attributes for the occurrence and health effects criteria. This guided the literature survey and the outcomes are reflected in the respective water quality monographs (see attached Part Two of this document-"Water quality monographs for selected organic contaminants"). However, the collating of water quality monographs was also not easy given the fact that the information needs were tailor made for the Drinking Water industry as directed by the Template presented in Table 4.16 of Chapter 4. Information sites given in Table 3.2 respond to a particular aspect which might not answer even 1% of the information needed to complete the synthesized water quality monograph. For example the IARC database only answers on the carcinogenicity of compounds and the USEPA IRIS database on the critical health effects over a long period of being exposed to a particular contaminant.

During the screening exercise, it was recognized that the task was complex requiring classification judgments in a context where data was uncertain or missing hence the adoption of the qualitative approach and use of tailor made criteria proposed by the experts and other relevant stakeholders during the workshops (Figure 3.3). Due to data gaps and uncertainties, evaluating contaminants using varying occurrence and health effects data entailed making assumptions based on weight of evidence. The focus of the contaminant selection process was on the protection of public health.

5.2.4 Step IV: Testing for organic contaminants on the PLOCC in the drinking water value chain followed by the validation by Drinking Water industry experts

To assess the occurrence of organic contaminants in the drinking water value chain, samples were collected from source water (the Vaal Dam) to the consumer tap.

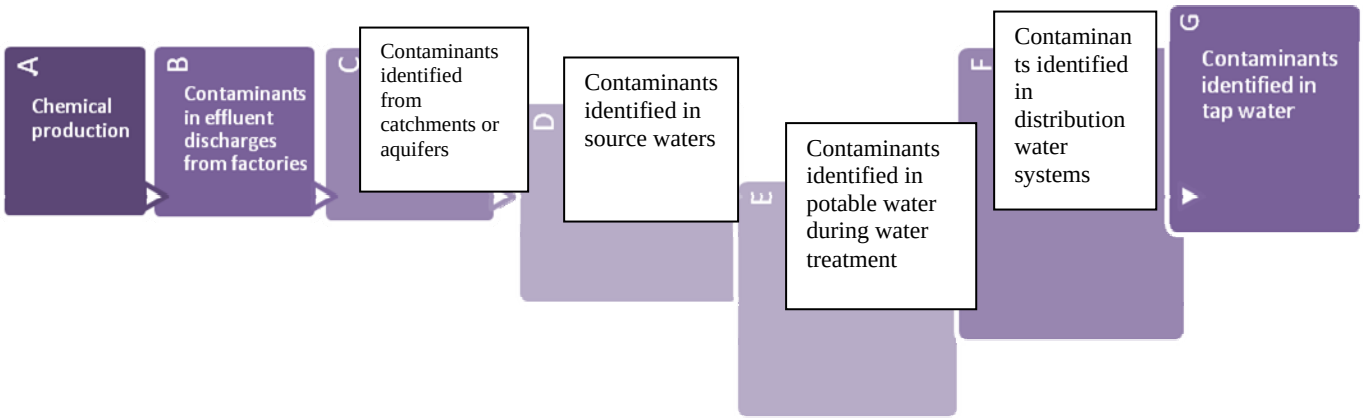

Figure 5.1 Points along the drinking water value chain where contaminants can be identified (modified from the recommendations of the National Research Committee (NRC) to the USEPA).

The arrangement in Figure 5.1 agrees with the current study design for the validation of the protocol “testing for organic contaminants in the drinking water value chain” which forms part of the occurrence criteria.

A ⟶ C will indicate potential occurrence while;

D ⟶ G will indicate demonstrated occurrence in the drinking water value chain hence the placement of the organic contaminant on the priority list of organic contaminants for monitoring in the drinking water value chain.

This arrangement extended the screening process especially the occurrence criterion resulting in a four tier process. The first tier being the verification through the literature survey, followed by the development of water quality monographs, expert input and finally the assessment of concentration levels of organic contaminants in the matrix of interest along the drinking water value chain. For industrial organic contaminants, the potential for occurrence in the drinking water value chain may be estimated using a combination of production volume information and water solubility. Those of concern will show high production volumes and high water solubility

indicating high possibility of recharge. However, getting this data has proved to be difficulty, hence the use of qualitative approaches. Based on the above analyses, a contaminant which was positively identified in any part of the drinking water value chain during the testing exercise will therefore be placed on the priority list.

The assessment of organic contaminants for the occurrence criterion was performed using both multi-residue analysis and target compound analysis. However, most results were either below the limit of Detection (LOD), below the Method Reporting Limit (MRL) or non-detected ("nd"). This became a major challenge in data interpretation and application of the occurrence criterion. Measurements below the detection limit raise the degree of uncertainty as this happens as a result of a number of factors. For example, it cannot be reliably asserted that they are statistically different from zero. This is a cause for concern since most organic contaminants on the preliminary priority list occurred at levels lower than the detection limit or were reported as "not detected". This constitutes a limitation in implementing the occurrence criterion (Step III of the Protocol). However, due to their properties, it will be advisable to continue monitoring for these organic contaminants especially in source water. This is due to the fact that organic contaminants are found in the water column at very low concentrations.[3] It has also been observed that investigations or assessments of organic contaminants related to chronic low level exposures or related situations often face the difficult task of dealing with levels of contamination that are difficult to detect and/or quantify. [4] This insight led to the assessment of the criterion as discussed in preceding sections in order to make sure that there was enough evidence to support the decision making process.

.Corl et al. [2002] suggests the following options;

- Nondetect = value for the method reporting limit (MRL), a most conservative assumption for a risk assessment, because it will tend to bias data on the high side. When this approach is used, there is a high degree of confidence that the analyte is probably present, but at a level that is at or just below the MRL.
- Nondetect = value of 0, indicating that the analyte is absent. This assumption is a nonconservative approach because it potentially will bias data on the low side. Assigning a value of 0 may be acceptable if it is highly unlikely that the analyte is present in the sample. An example would be the case for background samples where there is no history of the target analyte being detected.
- Nondetect = "no value" given. This is different than providing a value of "0" in as much as "0" value does having meaning if a statistical analysis of the data is performed. The "no value" approach is also a nonconservative approach.

- Nonndetect = value that is 1/2MRL. This is “middle-of-the-road- approach” where it is possible that the analyte would be detected in the sampling location and it “could be” as high as 1/2MRL.
- Nondetect = value that is the percentage of not detects (NDs) in a data set multiplied by the MRL. This is a statistical approach that takes into consideration the number of ND reports in relation to the overall number of data points in the data set. As an example if there are 25% of the data were NDs. Therefore 25% of the MRL would be the value given to the ND data.

The proposed solution to this will be the development of analytical tools that could detect the organic contaminants at these lower concentration levels at which they occur in environmental samples and along the drinking water value chain.

Another limitation for the implementation of the occurrence criterion is the assurance that the non detection of a parent compound means its absence in the matrix of interest as it is possible that the compound might have been degraded into its metabolites that are either more or less persistent or toxic. In reality, if the parent compound breaks down quickly into its metabolites, it will definitely be detected at lower levels in the matrix of interest or not detected at all. For example, in this study Dieldrin was detected in fish fat tissue and gonads other than Aldrin during the dry season. This is because Dieldrin occurs as a metabolite of the unstable Aldrin which is immediately converted to Dieldrin once in the environment. Aldrin is immediately converted to Dieldrin as soon as it is discharged to the environment. Dieldrin is therefore more stable than its parent compound and it can bio-accumulate in fish. A similar observation was made for DDT. p,p'-DDE was detected in fat and gonads during the low flow season. [dry period] The detection of p,p'-DDE in most fish tissue is an indicator that the most persistent and bio-accumulative DDT metabolite is p,p'-DDE. Hence, the absence of DDT in any of the samples does not suggest its 100% removal during treatment but rather that when it reaches the environment it breaks down into more stable metabolites which are more bio-available than the parent compound.

The behaviour of S-Triazine herbicides in the drinking water value chain also indicated the importance of considering degradation products when managing organic contaminants in the drinking water value chain. S-Triazine herbicides have been found to form stable degradation products under both aerobic and anaerobic conditions in the environment. [Table 5.2] Transformation products of organic contaminants have the potential to be similarly or even more mobile, persistent or toxic than their parent compounds. These should therefore be

included in the assessment of water quality, sediment and biota in order to safeguard human health. [5]

Apparent residues of Atrazine, Simazine and Terbutylazine occurred at levels below the detection limit in water samples along the drinking water value chain during the wet season. Atrazine was detected in most samples except sediment and fish in both seasons. The challenge is that none of the known metabolites or degradation products was analyzed for in this study. However, evidence from the literature showed that Atrazine, Simazine and Propazine metabolites Deethylatrazine (DEA), Deisopropylatrazine (DIA) and Deethylhydroxyatrazine (DEHA) are stable in the aquatic environment. [7] It will therefore be prudent to consider analyzing for the degradation products in water including the parent compounds. Atrazine has been found to have a half-life time of 30-90 days in the environment. [7] The detection of apparent residues of these herbicides in the drinking water value chain is an indication that they do persist in the aquatic environment especially source water and need to be analyzed for. Screening for organic contaminants in the drinking water value chain will only be of value if the physico-chemical properties characterizing their fate and behaviour in the drinking water value chain are well understood in order to choose the appropriate time for their sampling and accurate detection methodology.

Table 5.2: S-Triazine Herbicides and their degradation products [7]

TRIAZINE HERBICIDE	**DEGRADATION PRODUCTS**
Atrazine	Deethylatrazine(DEA) Deisopropylatrazine (DIA) Hydroxyatrazine (HA) Didealkyl atrazine (DDA) Deethylhydroxyatrazine (DEHA) Deisopropylhydroxyatrazine (DIHA) Dide alkylhydroxyatrazine (DDHA)
Simazine	DIA Monodeethylsimazine Hydroxysimazine
Propazine	DEA Hydroxypropazine
Atraton	Deisopropylatraton
Terbutylazine (TBA)	Deethylterbutylazine
Metribuzin	Deamino metribuzin (DAM) Diketo metribuzin (DKM) Deaminodiketometribuzin (DADKM)

5.2.4.1 Compiling the final list of organic contaminants of concern (FLOCC)

This step is the most important as decision are made based on the evidence collected from Steps I, II, III and IV of the protocol. The decision is mainly based on the occurrence criterion, potential human health effects and other criteria as presented in Figure 3.3 of the protocol. The role of expert judgment was significant at this stage.

5.2.5 Establishing the capacity for the removal of organic contaminants on the FLOCC. Recommendations for water utilities without capacity

This step like the preceding one was completed in consultation with the relevant stakeholders especially the technical experts such as those involved with the various unit processes, manufacturing industry experts, organic chemists, water quality assurance personnel and those involved in the procurement of chemicals. It was established that the Rand Water drinking water treatment process has the capacity to remove most organic contaminants. The conventional processes consists of seven stages namely coagulation, flocculation, sedimentation, stabilization, filtration, disinfection followed by chloramination at booster sites. [Figure 4.4 of Chapter 4] GAC filtration is used as per requirement. Experience has shown that GAC filtration is efficient in removing most hydrophobic organic contaminants such as PAHs with high log Kow and low solubility. But in contrast, the hydrophilic compounds with low log Kow and high solubility such as most pharmaceuticals and pesticides are partially or not removed. This has been indicated by their detection at relatively low concentrations in finished-water samples. Disinfection using Chlorine has been found to be successful in removing organic contaminants by oxidation. For example Bisphenol A, Nonylphenol and other PAHs have been successfully removed by chlorination. However, the concerns emanate from the products of their degradation, which occur in form of disinfection-by-products. [DBPs] It was considered therefore recommended to proceed to the prioritization step given that the water utility had capacity to remove most organic contaminants of concern.

5.2.6 Prioritization of the substances on the final list of organic contaminants of concern (FLOCC)

This step is the most difficult of all steps presented for the protocol. During this step, it has to be decided, which of the organic contaminants is of priority for the protection of public health. Some researchers have proposed the use of prototype classification approaches such as using neural networks as proposed by the USEPA methodology discussed in section 2.2 of Chapter 2. In this study, the “occurrence criteria” as described in Figure 3.4 and the evidence of occurrence in environmental samples collected along the drinking water value chain and expert judgment was considered adequate for an organic contaminant to be placed on a “priority list of organic contaminants for monitoring in the drinking water value chain. For health effects, the

USEPA used severity and potency as attributes while prevalence, magnitude and persistence –mobility is used for the occurrence attributes**.** Given the complexity and time needed to assess these attributes for example, in the case of severity assessment, one needs to evaluate the disability adjusted life years lost from exposure to a contaminant which might further be complicated by confounding factors and complexity of experimental design when using human subjects. It was decided that for the prioritization process, criteria reflective of the Drinking Water industry needs and for use by the industry should be adopted. [Figure 5.2] The approach was successful.

5.2.6.1 Occurrence and adverse human health effects criteria

The organic contaminants that were prioritized based on this criterion were mainly industrial pollutants produced or used in large volumes and with a high recharge to the environment, hence instead of using the parameter “bio-accumulative”, the term “accumulative was used during the development of water quality monographs. Very persistent compounds will also accumulate easily in the environment and can possibly be found in high concentrations in the source waters used for drinking water production. These high concentrations can result in potential human health risk. [9] Under the potential to cause human health effects, the toxicological potency of the selected organic contaminants is considered. This information was obtained by consulting existing databases as outlined in Table 3.2 of the protocol. Adverse human health effects such as endocrine disruption, carcinogenicity, teratogenicity, mutagenicity, reproductive toxicity or other forms of toxicity were assessed. The International Agency for Research on Cancer (IARC) database provided the carcinogenicity information while the USEPA IRIS database provided the non-cancer chronic related human risk assessment. Evidence was collected for each individual organic contaminant or group of organic contaminants.

Organic contaminants that fall into this category include surfactants, pesticides, pharmaceuticals and personal care products [PPCPs], plasticizers, petroleum products and polychlorinated dioxin-like compounds. Table 3.1 of Chapter 3 gives an estimation of the magnitude of this problem. Table 4.12 of Chapter 4 listed those organic contaminants that were positively identified in the drinking water value chain. S-Triazine herbicides especially Atrazine, DDT and its metabolites, Heptachlor and its epoxide, Dieldrin, Endosulfan and its isomers, Hexachlorocyclohexane isomers and Lindane were detected in most surface water systems worldwide. In South Africa, the mostly detected pesticides according to the literature and validation exercise include DDT and its metabolites and S-triazine herbicides like Atrazine, Simazine and Terbutylazine. Some old pesticides are still found in surface water systems. These include Endosulfan and its metabolites, HCH isomers, Aldicarb, Heptachlor and

Chlordane. Bisphenol A is an industrial compound manufactured in large quantities, most production being used as a monomer for the production of polycarbonate and epoxy resins. [9] Because of its ubiquitous nature and of its endocrine effects, it is an important organic contaminant. It has been shown to have an estrogenic effect on human health breast cancer cells. [9] Hence, it was prioritized in this study for monitoring in the drinking water value chain.

The Alkylphenols and Alkylphenol ethoxylates [APEOs] and the phthalate esters are other classes of important industrial organic contaminants. The most important APEO is Nonylphenolpolyethoxylate [NPEO] with worldwide production of more than 400 000 tons/year. [9] Hence, Nonylphenol and Octylphenol which have been found in most surface water systems receiving wastewater effluents are important organic contaminants from this family of industrial chemicals. These compounds especially their para isomers have been found to show estrogenic effects at very low concentrations.

Phthalates like Di-2(ethyhexyl) phthalate [DEHP] and Di-n-butylphthalate [DBP] are the most important with a cumulative yearly production of some million tons worldwide. [9] They have been found to express anti-androgenic effects. [9] Polychlorinated biphenyls [PCBs] which are industrially produced synthetic oils, especially used in transformers and are excellent example of the Persistent Organic Pollutants [POPs] PCBs can demonstrate estrogenic behaviour and during unintended combustion, they can be transformed into even more toxic dioxins. The interviews conducted at the former Department of Environmental Affairs and Tourism [DEAT] in South Africa, indicated that PCBs were being regulated under the Africa Stockpiles Project and old transformers based on these compounds were being phased out. Some experimental evidence shows that non-dioxin–like aryl hydrocarbon receptor agonists/antagonists are able to impact the overall toxic potency of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and related compounds, and this needs to be investigated further. [8] The derived toxic equivalents can be used for hazard and risk assessment of halogenated aromatic mixtures; moreover, for more complex mixtures containing congeners for which no standards are available (e.g., bromo/chloro mixtures), several *in vitro* or *in vivo* assays can be utilized for hazard or risk assessment.

5.2.6.2 Other criterion

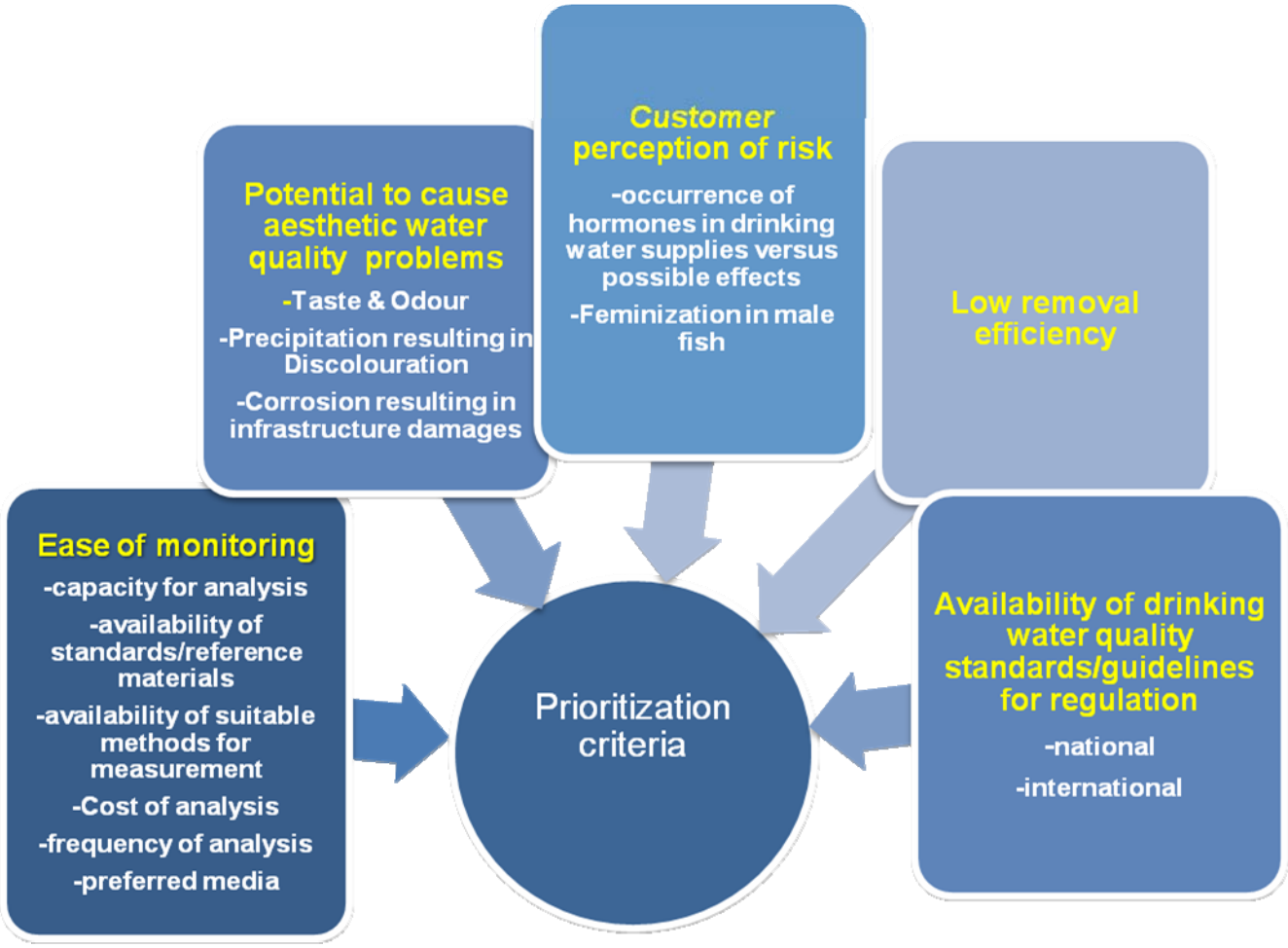

Figure 5.2 Other criteria used for the prioritization of organic contaminants

Availability of standards for regulating a contaminant

Although standards for safe drinking water are mostly guidelines developed by health organizations like the World Health Organization [WHO], Health Canada and the United States Environmental Protection Agency [USEPA] they a play a significant role in regulation of contaminants with a perceived risk or proven risk for public health protection. The availability of

a standard or guideline for drinking water quality was enough proof that the contaminant needs to be prioritized. However, to do this, other aspects of relevance needed to be considered. Actual statutory standards or guidelines are not available for most organic contaminants. This is the case in most developing countries. Hence benchmarking with these organizations especially the WHO is considered the best practice.

Customer perception of risk [Figure 5.2]

Unlike professional toxicologists and scientists or medical doctors, consumers depend on reliable sources such as media for their public health protection. Reality has shown that with technological advancement customers have become more informed than ever. A good example, are developments in the field of "emerging organic contaminants" which is gaining research momentum at a fast rate. From the literature review it was evident that like the pesticides, PPCPs were the highly researched group of contaminants. Several pharmaceutically active compounds have been detected in surface water systems. Their presence in the drinking water value chain has caused serious public concern due to their perceived risks. Mostly effects from natural and synthetic hormones such as endocrine disrupting effects even at low concentrations and suspected synergistic effects of different hormones have been noted hence their addition to the priority list in this study. The hormones have been found to cause feminization in male fish at concentrations as low as 1ng/ℓ. [9]

Potential to cause aesthetic water quality problems [Figure 5.2]

Water quality is the physical, chemical and biological characteristics of water. It is most frequently used by reference to a set of standards against which compliance can be assessed. The most common standards used to assess water quality relate to drinking water quality. The norm for setting these standards is public health protection through guaranteeing the safety of consumers. Once the quality is impaired and the water cannot be used for its intended purpose or purposes it constitutes a water quality problem. Water quality problems that are crucial to the water services provision business are organoleptic properties. The majority of customers that drink the water provided by water utilities have no insight into the chemical and biological characteristic of the water but can judge its safety using its appearance, taste and odour. This is regarded highest on the drinking water quality provision agenda as inadequate satisfaction of these qualities can force customers to use unsafe water sources or use home treatment devices which can render water unsafe for its intended use especially the children, immuno-compromised and the elderly. As a result, organic contaminants that contribute to taste and odour problems such as the BTEX group, chlorophenols, Geosmin, 2-Methylisrnoneol and other cyanobacteria related toxins were considered as priority organic contaminants for having the potential to cause taste and odour problems in water as well as their potential adverse health effects.

Low removal efficiency [Figure 5.2]

Activated carbon filtration is an excellent treatment step for polar organic molecules. However, most water utilities cannot afford full operation on these filters or have them at all in their drinking water value chain. Evidence from the literature and validation exercise showed that some organic contaminants depending on their physico-chemical properties are not removed or are partially removed by conventional water treatment methods. The contaminants of concern in this case include cyanobacteria related compounds such as Geosmin and 2-MIB, PPCPs, some pesticides, disinfection by-products such as N-nitrosodimethylamine [NDMA] and detergents metabolites such as Nitrilotriacetic acid (NTA). The latter organic contaminants are very small and polar. They are also very mobile in the environment and difficult to remove using conventional water treatment methods even by those with activated carbon filtration resulting in them escaping the system and being detected in drinking water. Nanofiltration has been proposed for their removal. [9] The other concern about NDMA is that it is a member of a family of extremely potent carcinogens, the N-Nitrosoamines. The study by Stackelberg et al. [2007] [10] indicated that combined water treatments [clarification, disinfection and GAC filtration] were effective at degrading or removing many organic compounds from source water supplies to concentrations below analytical detection. However, the concern is inadequate knowledge of the effects of these compounds at those low levels.

Ease of monitoring [Figure 5.2]

Although an organic contaminant or group of organic contaminants can be identified as a priority organic contaminant for monitoring in the drinking water value chain, it is crucial that the ease of monitoring in terms of the following elements be satisfied. It was noted however, that this can be a national or regional challenge which has to be addressed by each utility depending on available resources. The aspects to consider include assessing the capacity for analysis, the availability of standards/reference materials, the availability of suitable methods for measurement, the cost of analysis, possibility of increasing or decreasing the frequency of analysis depending on the availability of resources and preferred media for optimal coverage of contaminants of concern.

5.3 General conclusions

The aim of this study was to develop a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain. This aim has been fully achieved both on a theoretical and practical level. The initial step was a critical evaluation of the literature for approaches used for selecting and prioritization of organic variables of priority to the drinking water industry. This objective was successfully conducted resulting in a simple

model. A generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain has been successfully developed and validated in a prototype drinking water value chain. This covers objectives 2 and 3 of this study. The area in which the protocol was tested is one of the biggest water utilities in Africa and the assessment covered the whole drinking water value chain from catchment to tap.

The protocol has been successfully implemented in the Rand Water value chain. Organic contaminants monitoring is currently in place. Sampling is done twice a year during the high and low flow episodes. An annual report has been published since 2008 and progress reports presented to Top Management and relevant stakeholders.

The occurrence, potential exposure and human health effects criteria play a major role in selecting and prioritizing organic contaminants for monitoring in the drinking water value chain. Industry specific criteria such as existence of drinking water quality guidelines or standards, availability of capacity for analysis, extent of use of certain organic contaminants in local catchments, relevance of a particular contaminant or group of contaminants to the Drinking Water industry under local conditions, ease of monitoring, removal of contaminant during water treatment also play a significant role during the prioritization of organic contaminants for monitoring in the drinking water value chain.

The role of stakeholder consultation and expert judgment is a crucial element in the development of a generic protocol for the selection of organic contaminants for monitoring in the drinking water value chain. This ensures transparency and incorporation of industry specific information**.**

Qualitative approaches can be successfully employed in the selection and prioritization of organic contaminants. During the screening exercise, it was recognized that the task was complex requiring numerous classification or selection judgments in a context where data are often uncertain, inadequate or missing, hence the adoption of the qualitative approach and use of tailor made criteria proposed by experts and other relevant parties.

Tailor made prioritization criteria reflective of the Drinking Water industry perspective are important and has proved to be successful in selecting and prioritizing organic contaminants for monitoring in the drinking water value chain. The organic contaminants in the current study were successfully prioritized in three classes, short-term priority for analysis, medium term priority for analysis and long term priority for analysis. This is a very important guide for water

utilities to assist in optimizing their resources while not compromising the role of public health protection.

A final priority list of organic contaminants for monitoring in the drinking water value chain has been produced from the study. The priority list has been presented to Rand Water Management for consideration of upgrading the current organics monitoring programme. A period of 5 years has been recommended to the water utilities for the review and assessment of the priority list of organic contaminants.

5.4 References

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CHAPTER 6 GENERAL RECOMMENDATIONS

6.1 INTRODUCTION

These recommendations draw on the results of this study and focus on the disseminating and implementation of the protocol by the Drinking Water industry and relevant stakeholders. The recommendations address the challenges faced during the validation of the protocol and opportunities for further research.

6.2 Disseminating the protocol

The protocol has been developed and validated in a prototype drinking water value chain. Its components have been validated by experts within the Drinking Water industry. Possible methods of disseminating the protocol include;

- Publishing articles in appropriate accredited journals
- Developing a visual presentation for conferences at which the wider Water industry participants are covered such as the Water Institute of South Africa [WISA] or the World Water Congress.
- Engaging organizations such as the Department of Water Affairs [DWA], the Water Research Commission [WRC] in South Africa and the South African Local Government Association [SALGA] in order to get support into the protocol as a regulatory and information dissemination tool.

6.3 Recommendations on the implementation of the protocol

It is recommended that the protocol be implemented by water utilities in the field of drinking water provision. In addition, the protocol could be duplicated by other users such as Waste Water Treatment Plants. [WWTPs] This will assist in regulating organic contaminants that are discharged into the aquatic environment through the wastewater effluent discharge system.

The protocol's objective is to enable the water utilities to be able to select and prioritize organic contaminants for monitoring in their drinking water value chains. This process should be transparent and facilitate public participation as well as to learning by doing in order to control uncertainties. The adaptive management approach stresses the need for practical action in the face of uncertainty, it also emphasizes the need to tailor made management decisions to the nature and quality of information available at any moment in the process. It is recommended

therefore that in implementing this protocol, water utilities should use criteria reflective of their needs as proposed in this study and follow iterative process until they get products that are sustainable and applicable. Based on this, there is a need to iteratively test and refine the selection and prioritization approach. This will include elements such as evaluative criteria for each phase, adaptive learning process, characterizing data quality, transparency and use of expert judgment.

The following conceptual framework for implementing the selection and prioritization protocol [Figure 6.1] has been developed taking into consideration the fact that sometimes decisions for water quality improvement might be incorrect and result in a waste of resources and non-compliance to public health protection. Adaptive implementation (AI) means that the implementations plan is continually updated and revised based on new information to reduce technical uncertainties and align the organizational strategy and needs to the internal and external environment. Events like climate change, industrialization leading to increased land-use activities may result in more organic contaminants being released to surface and groundwater. Continuous assessments of organic contaminants in the drinking water value chain at least twice a year will therefore be necessary.

6.3.1 Recommendation for automation of protocol components

The protocol implementation can be made easy by use of automation. It is recommended that software for the implementation of the protocol be developed. For example for the automation of Step I selection of the “pool of organic contaminants” , a program which can link the user to key drinking water and health related databases or websites and extract those organic contaminants of interest could be developed. The criteria for the selection and prioritization could be built into the program and optimized on an ongoing basis. Software engineering techniques that allow communication among these links could be developed to facilitate the process.

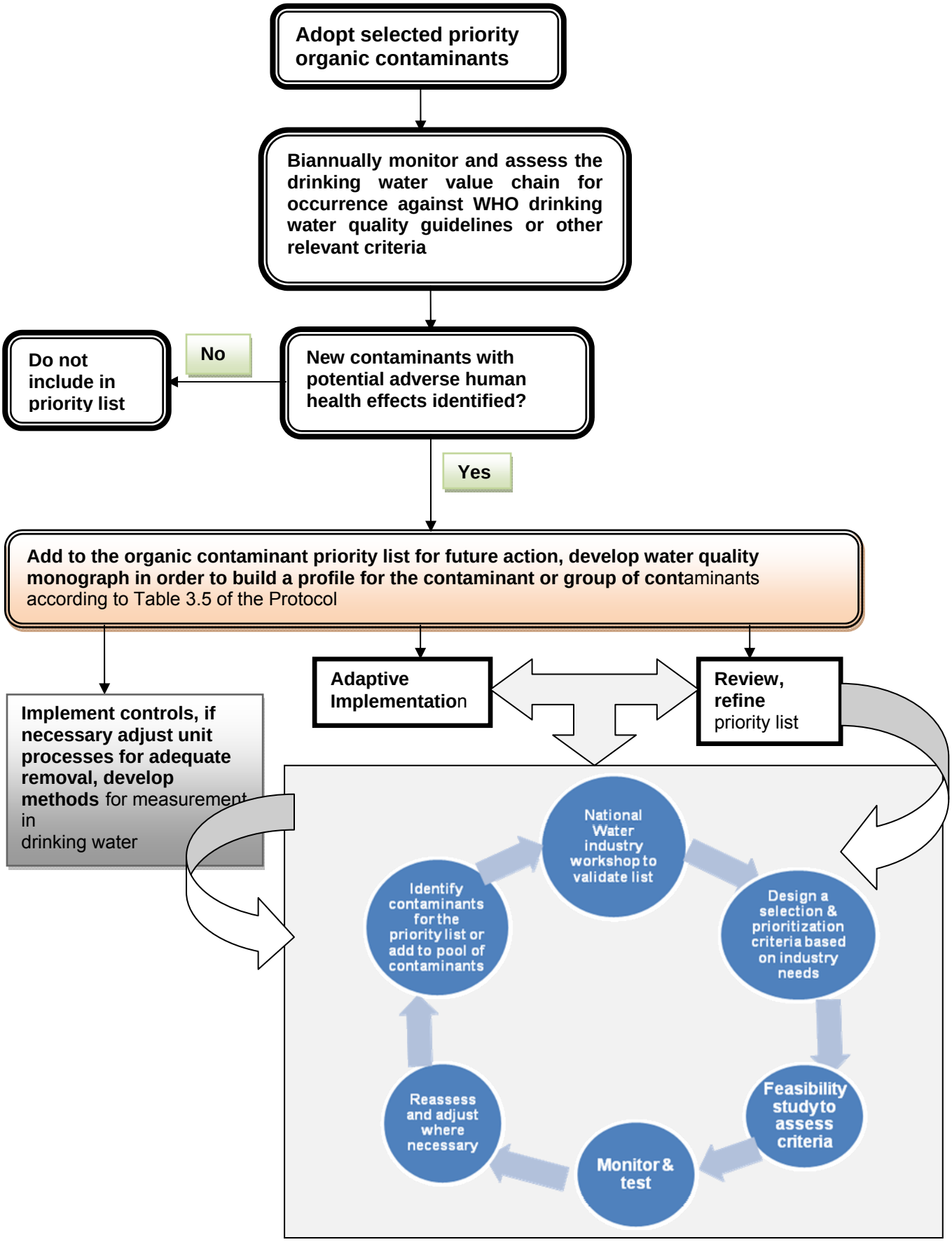

Figure 6.1: A conceptual model for the implementation of the selection and prioritization protocol

6.4 Recommendations on capacity building

The protocol development process resulted in tangible products that can be of use to the whole Drinking Water industry. A non-solicited WRC project can be proposed or suggestion to work in collaboration with existing projects addressing the issue of organic contaminants be made to facilitate the roll-out. Currently a project on the assessment of organic contaminants in South African surface water systems is underway. The following can assist the process;

- The lists of organic contaminants of concern and the priority lists as produced in this study can be shared with the organization and create a platform of information sharing and application of the findings concerning organic contaminants and the use of the Drinking Water industry perspective criteria to identify organic contaminants of concern to the industry.
- The protocol itself is an important educational tool on its own. For example in South Africa, Water utilities which are tasked with the provision of safe drinking water to consumers at the end of the drinking water value chain can be trained in using the protocol and how to implement it under their areas of jurisdiction. Funding can be solicited for producing training manuals and electronic production of copies for the information related to the protocol.

6.4.1 Recommendations on the use of water quality monographs

The industry have known monographs as produced by organizations such as the International Agency on Cancer Research [IARC] to be volumes of documents addressing the evidence of a contaminant or substantiating proof that a contaminant is a human carcinogen, probable or possible human carcinogen or not classifiable as a human carcinogen. The current water quality monographs have been synthesized to produce key information pertaining to all sections of the drinking water production business throughout the drinking water value chain. They are user friendly and easy to apply. The following is recommended for their implantation;

A training manual on the production or development and use of water quality monographs can be produced to facilitate their dissemination. CD-ROMs on the water quality monographs can be produced and distributed with the manual. This manual and the water quality monographs could be used by;

- Plant operators in the optimization of unit processes or to determine which method to use for the optimal removal or a particular group of organic contaminants.

- Analytical scientists and Managers in deciding which method to use for the measurement of a particular contaminant or group of contaminants in a particular matrix of interest. The information will also assist them in deciding whether to use target analysis or multi-residue approach.
- Water quality Assurance Managers in developing risk assessment measures as the water quality monographs contain all health risk and water quality risk related information for a particular organic contaminant or a group of organic contaminants.
- Operation Managers in deciding which water treatment chemicals to use in optimizing unit processes and how to manage challenges that come with it such as impurities in original chemicals and water treatment residues that are produced as a result of their use. This forms part of the requirement of the Water Safety Plans and is the first critical control point to manage in ensuring safe drinking water.

It should be noted that the current water quality monographs are produced for the organic contaminants. However, for complete public health protection they should cover all health-related, physical and organoleptic properties. A project to complete the scope should be initiated immediately for continuity and completeness. Once the whole scope of drinking water quality has been completed, the manuals can be placed as intellectual property to train key audiences in the Water Sector and all relevant industries that need to understand the water business. For example the other target audiences can be Water Quality Managers, Plant operators, University students, Local Authority Water and Sanitation officials. A programme similar to the current Water Wise Environmental Education programme can be put in place for educating the public about organic contaminants using these water quality monographs. It will however be necessary to use graphic language rather than being too technical.

The water quality monographs will need to be revised on an ongoing basis. The custodian of these water quality monographs in any organization should be the Water Quality Assurance department. A rolling revision should be ensured in order to stay abreast with new developments and update the water quality monographs on an ongoing basis.

6.5 Recommendations for testing in environmental samples

In this study, organic contaminants were sampled twice a year. This arrangement could be ideal for some pesticides based on seasonal patterns of growth and harvesting periods. It is therefore recommended that in light of growing activities in catchments, more advanced techniques should be developed for the measurement of organic contaminants in the drinking water value chain. Although relevant databases and lists exist for many categories of potential drinking water contaminants, other categories have no lists or databases, for example the

"emerging organic contaminants" or products of environmental degradation. Such organic contaminants or groups of organic contaminants need to be identified from the literature for accurate testing. It might be prudent to consider toxicity testing followed by analytical chemistry measurement methods such as IC-MS and GC-MS. Based on physico-chemical properties and available data, those compounds that degrade into metabolites should be identified and monitored along the drinking water value chain. Such are metabolites of the S-Triazine herbicides. [Table 6.1]

6.6 Recommendation for further research

Due to health concerns on the fate and behaviour of "emerging organic contaminants" and the perceive risks research in this area is gaining momentum. A lot of answers still remain unanswered. Figure 4.2 of Chapter 4 gives the group of organic contaminants of concern that were identified in surface water systems worldwide. This shows that the extent of the occurrence of organic contaminants in source waters used for drinking water production is currently not well covered. It is therefore recommended that research in this area be conducted with the aim of:

- Obtaining full coverage of organic contaminants that occur in catchments.
- Investigating potential analytical methods which combine current chromatographic methods with high resolution mass spectrometry to ensure that organic contaminants can be detected at ng/l to pg/l using a single enrichment method. The methods should be able to cover a wide spectrum of organic contaminants and allow their detection within hours. The preparation of samples should minimize human interference. These methods should also allow the detection of unknown organic contaminants appearing in environmental samples.
- Investigating key degradation products or metabolites of each organic contaminant or group of organic contaminants of concern for public health protection through the provision of safe drinking water. [Table 6.1] This is based on the fact that oxidation processes such as chlorination or ozonation of drinking water including natural microbial processes breakdown organic contaminants into new ones with high potential to cause adverse health effects

Table 6.1 Triazine herbicides and their degradation products

TRIAZINE HERBICIDE	DEGRADATION PRODUCTS
Atrazine	Deethylatrazine(DEA) Deisopropylatrazine (DIA) Hydroxyatrazine (HA) Didealkyl atrazine (DDA) Deethylhydroxyatrazine (DEHA) Deisopropylhydroxyatrazine (DIHA) Dide alkylhydroxyatrazine (DDHA)
Simazine	DIA Monodeethylsimazine Hydroxysimazine
Propazine	DEA Hydroxypropazine
Atraton	Deisopropylatraton
Terbutylazine (TBA)	Deethylterbutylazine
Metribuzin	Deamino metribuzin (DAM) Diketo metribuzin (DKM) Deaminodiketometribuzin (DADKM)

6.7 Recommendations for successful public health protection

The ultimate goal of the contaminant selection and prioritization process is the protection of public health by providing drinking water that is safe from these contaminants. To meet this goal; the selection process must place high priority on the protection of vulnerable subpopulations as intended by the South African National Drinking Water Standard, SANS 241 and other relevant legislative documents. These include;

- The elderly,
- All women of child bearing age,
- The unborn child,
- The immune-compromised,
- People with an acquired or inherited genetic disposition that makes them more vulnerable to certain organic contaminants or a group of organic contaminants,
- Those that are particularly sensitive to an array of organic contaminants,
- Individuals with specific medical conditions that make them more susceptible such as dialysis patients and
- Groups of the population experiencing malnutrition.

The selection and prioritization exercise should be extended to include all drinking water constituents of concern, as is international practice. The exercise should include biological, physical, organoleptic, inorganic chemical parameters.

ANNEXURES

ANNEXURE I

ORGANIC CONTAMINANTS ASSESSED IN THE RAND WATER VALUE CHAIN DURING STEP IV OF THE PROTOCOL

Date **22-May-07**

Matrix	Contaminant or Pesticide residue	Method of Analysis	Lab
Water	Endrin	GC-MS	BioCrop
	Acephate	GC-MS	BioCrop
	Dimethoate	GC-MS	BioCrop
	Methadithion	GC-MS	BioCrop
	Terbufos	GC-MS	BioCrop
	Cypermethrin I	GC-MS	BioCrop
	Cypermethrin II	GC-MS	BioCrop
	Cypermethrin III	GC-MS	BioCrop
	Cypermethrin IV	GC-MS	BioCrop
	Cyfluthrin I	GC-MS	BioCrop
	Cyfluthrin II	GC-MS	BioCrop
	Cyfluthrin III	GC-MS	BioCrop
	Cyfluthrin IV	GC-MS	BioCrop
	Deltamethrin	GC-MS	BioCrop
	Esfenvalerate	GC-MS	BioCrop
	Fenvalerate	GC-MS	BioCrop
	Permethrin I	GC-MS	BioCrop
	Permethrin II	GC-MS	BioCrop
	Cyhalothrin	GC-MS	BioCrop
	PCB-153	GC-MS	BioCrop
	Metalochlor	GC-MS	BioCrop
	HBC	GC-MS	BioCrop
	Volatile organic compounds		
	Benzene	Purge&Trap GC-MS	CSIR
	Toluene	Purge&Trap GC-MS	CSIR
	Ethylbenzene	Purge&Trap GC-MS	CSIR
	m,p-Xylene	Purge&Trap GC-MS	CSIR
	o-Xylene	Purge&Trap GC-MS	CSIR
	Chlorobenzene	Purge&Trap GC-MS	CSIR
	1,4-Dichlorobenzene	Purge&Trap GC-MS	CSIR
	1,2-Dichlorobenzene	Purge&Trap GC-MS	CSIR
	1,2,4-Trichlorobenzene	Purge&Trap GC-MS	CSIR
	1,2,3-Trichlorobenzene	Purge&Trap GC-MS	CSIR
	Phenol	GC-MS	CSIR
	2-Methylphenol	GC-MS	CSIR

4-Methylphenol	GC-MS	CSIR
2,4-Dimethylphenol	GC-MS	CSIR
2-Chlorophenol	GC-MS	CSIR
4-Chloro-3-methylphenol	GC-MS	CSIR
2,4-Dichlorophenol	GC-MS	CSIR
2,4,6-Trichlorophenol	GC-MS	CSIR
2,4,5-Trichlorophenol	GC-MS	CSIR
Pentachlorophenol	GC-MS	CSIR
Naphthalene	GC-MS	CSIR
Acenaphthylene	GC-MS	CSIR
Acenaphthene	GC-MS	CSIR
Fluorene	GC-MS	CSIR
Phenanthrene	GC-MS	CSIR
Anthracene	GC-MS	CSIR
Fluoranthene	GC-MS	CSIR
Pyrene	GC-MS	CSIR
Benzo[a]anthracene	GC-MS	CSIR
Chrysene	GC-MS	CSIR
Benzo[b]+[k]fluoranthene	GC-MS	CSIR
Benzo[a]pyrene	GC-MS	CSIR
Indeno-[1,2,3-cd]pyrene	GC-MS	CSIR
Diben[a,h]anthracene	GC-MS	CSIR
Benzo[g,h,i]perylene	GC-MS	CSIR
Dimethylphthalate	GC-MS	CSIR
Diethylpthalate	GC-MS	CSIR
Di-n-butylphthalate	GC-MS	CSIR
Butylbenzylphthalate	GC-MS	CSIR
Bis(2-Ethylhexyl)phthalate	GC-MS	CSIR
Di-n-octylphthalate	GC-MS	CSIR
Bisphenol A	GC-MS	CSIR
Organochlorine pesticides	AOAC international	SABS
α-BHC	AOAC international	SABS
γ-BHC	AOAC international	SABS
β-Endosulfan	AOAC international	SABS
Heptachlor	AOAC international	SABS
Aldrin	AOAC international	SABS
Heptachlor epoxide	AOAC international	SABS
α-Endosulfan	AOAC international	SABS
Endosulfan Sulphate	AOAC international	SABS
Dieldrin	AOAC international	SABS
p-p'-DDE	AOAC international	SABS
Endrin	AOAC international	SABS
p,p'-DDD	AOAC international	SABS
o,p'-DDT	AOAC international	SABS
p,p'-DDT	AOAC international	SABS

Methoxychlor	AOAC international	SABS
Organophosphorus pesticides		
Dichlorvos	AOAC international	SABS
Mevinphos	AOAC international	SABS
Sulfotep	AOAC international	SABS
Diazinon	AOAC international	SABS
Pirimifos-Methyl	AOAC international	SABS
Fenithrothion	AOAC international	SABS
Parathion	AOAC international	SABS
Malathion	AOAC international	SABS
Fenthion	AOAC international	SABS
Chlorpyrifos	AOAC international	SABS
Chlorfenvinphos	AOAC international	SABS
Profenophos	AOAC international	SABS
	AOAC international	SABS
Synthetic pyrethroids		
	AOAC	
Cypermethrin	**international**	SABS
Deltamethrin	AOAC international	SABS
Cyhalothrin	AOAC international	SABS
Cyfluthrin	AOAC international	SABS
	AOAC international	SABS
PCB congeners		
	AOAC	
PCB- 291	**international**	
PCB-293	AOAC international	SABS
PCB-294	AOAC international	SABS
PCB-297	AOAC international	SABS
PCB-296	AOAC international	SABS
PCB-298	AOAC international	SABS
Triazines	AOAC international	SABS
Simazine	AOAC international	SABS
Atrazine	AOAC international	SABS
Terbutylazine	AOAC international	SABS
	AOAC international	SABS
Chloroacetamides		
Acetochlor	AOAC international	SABS
Alachlor	AOAC international	SABS
S-Metolachlor	AOAC international	SABS
Trifluralin	AOAC international	SABS
	AOAC international	SABS
Phenoxycarboxylic acids		
2,4-D	EPA Method 625	SABS

MCPA	EPA Method 626	SABS
Dichlorprop	EPA Method 627	SABS
	EPA Method 628	SABS

Carbamate pesticides

Aldicarb	Method AM 127	SABS
Aldicarb sulphoxide	Method AM 128	SABS
Aldicarb sulphone	Method AM 129	SABS
Carbaryl	Method AM 130	SABS
Carbofuran	Method AM 131	SABS
Carbosulfan	Method AM 132	SABS
Propoxur	Method AM 133	SABS
	Method AM 134	SABS

ANNEXURE 2: Questionnaire for Drinking Water Utilities- Organic contaminant Analysis in the drinking water value chain

Information or data requested for organic contaminants analysis in the drinking water value chain (source water, process, distribution network and the consumer's tap (final drinking water, at the consumption point)

Q1: Do you analyze for any of the organic contaminants on the attached Table?

Answer: Yes_____ No_____

Q2: If your answer to Q1 is "yes", please fill in the information requested in the attached table.

Q3: Are there any other organic contaminants that you have analyzed for that are not on the provided list? Please provide the names on the section provided below:

i)_____ ii)_____

iii)_____ iv)_____

v)_____ vi)_____

Q4: If your answer to Q3 was "Yes" please state the reasons that prompted you to analyze for the specific organic contaminants you listed in the above section.

N.B-All answers will be treated in high confidence, no list of organic contaminants will be provided to a third party without permission from the institution or organization that provided it. An example of a response is attached for your convenience.

The information can be provided in Ms Word version 2003 or 2007 or as an Excel spreadsheet version 2003 or 2007. You are also welcome to fax or courier hard copies to the following details: Ms Esper Ncube, Rand Water, 522 Impala Rd, Glenvista, JHB 2000. Tel:+27116820075, Fax:+27116820733,Cell:+27823892358 E-mail: encube@randwater.co.za

ANNEXURE 2.1: Recommended list of priority organic contaminants for analysis in the drinking water supply chain

Organic contaminant	Classification	Concern to the Drinking water industry	Currently being analyzed for?	Method for analysis in place?	Need for New Method development?
INDUSTRIAL CHEMICALS					
Benzene	VOC	chronic lymphatic leukemia	Y	P/T, GC-MS	N
Chlorobenzene	VOC	Liver and kidney toxicity	N		Y, P/T, GC-MS
1,2-Dichlorobenzene	VOC	Liver and kidney toxicity	N		Y, P/T, GC-MS
1,2,4-Trichlorobenzene	VOC	Changes in adrenal glands	N		Y, P/T, GC-MS
1,4-Dichlorobenzene	VOC	cirrhosis of the liver	N		Y, P/T, GC-MS
Benz [a] pyrene	PAH	Human carcinogen, EDC	Y	SPE, GC-MS	N
Bisphenol A	Plasticizer	Endocrine disruption	N		Y, SPE-HPLC
Dibutylphthalate (DBP)	Plasticizer	Endocrine disruption	Y	SPE, GC-MS	Standards available
Di (2-ethylhexyl) phthalate	Plasticizer	Endocrine disruption	Y	SPE, GC-MS	
Ethylbenzene	VOC	Taste and odour, health	Y	P/T, GC-MS	N
Glycol esters	VOC	Taste and odour	N		Y
Octylphenol	Surfactant	Endocrine disruption	Y	SPE, GC-MS	N
p-Nonylphenol	Surfactant	Endocrine disruption	Y	SPE, GC-MS	
Polychlorinated biphenyls [PCBs	PCB	Teratogenic	Y, PCB-153	SPE, GC-MS	
Toluene	VOC	Taste and odour	Y	P/T, GC-MS	
Xylene isomers	VOC	Taste and odour	Y	P/T, GC-MS	
2,3,7,8-Tetrachlorodiphenyldioxin(TCDD	Dioxin	Endocrine disruption, Teratogenic	N	No capacity in SA	Dioxin, not in SA
Nitrilotriacetic acid (NTA)	Detergent metabolite	2B carcinogen, IARC	N		Need to research
Di-2-(ethylhexyl) adipate (DEHA)	Plasticizer	Endocrine disruption	Y		N
Dibutyltin (DBT)	Organotin	Reproductive toxicity	N		Y, SPE, LC-MS
Dimethyltin (DMT)	Organotin	Reproductive toxicity	N		Y, SPE, LC-MS
Tributyltin (TBT)	Organotin	Endocrine disruption	N		Y, SPE, LC-MS
PESTICIDES					
2,4-Dichlorophenoxyacetic acid	Herbicide	Internal haemorrage	N	Standards available	Y, SPE, HPLC
Aldrin	Organochlorine pesticide	Liver & CNS toxicity	Y	SPE, GC-MS	N
Atrazine	S-triazine herbicide	Endocrine disruption	Y	SPE, GC-MS	
Chloropyrifos	Organochlorine pesticide	Decreased plasma ChE	Y	SPE, GC-MS	
Cyhexatin	Organotin pesticide	Reproductive toxicity	N		Y
DDT	Organochlorine pesticide	Endocrine disruption	Y, p,p- and o,p-	SPE, GC-MS	N
DDE	DDT metabolite	Endocrine disruption	Y, p,p- and o,p-	SPE, GC-MS	
Dieldrin	Organochlorine pesticide	Endocrine disruption	Y	SPE, GC-MS	N
Diquat	Bipyridillium salt pesticide	Liver & kidney toxicity	N		Y, SPE, LC-MS
Endosulfan	Organochlorine pesticide	Class II human carcinogen, EDC	Y, I and II	SPE, GC-MS	

Annexure 2.1 cont.

Endrin	Organochlorine pesticide	Liver problems	Y	SPE, GC-MS	N
Heptachlor	Organochlorine pesticide	Liver and CNS damage	Y	SPE, GC-MS	
Heptachlor epoxide	Organochlorine pesticide	Liver toxicity	Y	SPE, GC-MS	
Lindane [γ-BHC]	Organochlorine pesticide	Severe liver , CNS damage	Y	SPE, GC-MS	
MCPA	Phenoxy acetic acid herbicide	Male reproductive toxicity	N	Develop method	Y, SPE, LC-MS
Methoxychlor	Organochlorine pesticide	Reproductive problems, EDC	Y	SPE, GC-MS	
Paraquat	Bipyridillium salt pesticide	Chronic pneumonitis	N	Develop method	Y, SPE, LC-MS
Simazine	S-triazine Herbicide	Endocrine disruption	Y	SPE, GC-MS	N
Terbutylazine (TBA)	S-triazine herbicide	Reduced body weight	Y	SPE, GC-MS	
Vinclozolin	Fungicide	Endocrine disruption	Y	SPE, GC-MS	
Cis-Chlordane	Metabolite of Chlordane	Hepatic necrosis	Y	No cost, standard available SPE, GC-MS	
Trans-Chlordane	Metabolite of Chlordane	Hepatic necrosis	Y		
B-Endosulfan	Metabolite of Endosulfan	Class II human carcinogen, EDC	Y		
Endosulfan sulphate	Metabolite of endosulfan	Endocrine disruption	Y		
Acetochlor	Chloroacetamide,pesticide	Salivation, decrease sugar levels	N	method to be develop	Y
Acetochlor ethane sulfonic acid	Reaction product of Acetochlor	-	N		Y
Acetochlor oxanilic acid	Reaction product of Acetochlor		N		Y
Alachlor	Chloroacetamide,pesticide	Liver , kidneys problems	N	method to be develop	Y, SPE, GC-MS
Alachlor ethane sulfonic acid	Reaction product of Alachlor	-	N		Y
Alachlor ethane oxanilic acid	Reaction product of Alachlor		N		Y
Hexachlorocyclohexane isomers - β-HCH - α-HCH -δ-HCH	Metabolites of HCH organochlorine pesticide	Chronic pneumonitis	Y	No cost, standard available SPE, GC-MS	N
2-(2,4,5-TrichloroPhenoxy acetic, Silvex, Fernoprop	Phenoxy acetic acid herbicide	Hepatic and renal toxicity	N	standards, New method to be developed	Y, SPE, HPLC
2,4,5-T-(Trichlorophenoxyacetic acid)	Phenoxyacetic acid herbicide	Reduced body weight, increased liver, kidney weight	N		Y, SPE, HPLC

Annexure 2.1: cont.

Organic contaminant	Classification	Concern to the Drinking water industry	Currently being analyzed for?	Method for analysis in place?	Need for New Method development?
DISINFECTION BY-PRODUCTS					
2-Chlorophenol	Phenol	Reproductive effects, T&O	Y	SPE, GC-MS	N
2,4-Dichlorophenol	Phenol	Delayed sensitivity response, T&O	Y	SPE, GC-MS	
2,4,6-Trichlorophenol	Phenol	Mutagenic *in vivo,* T&O problems	Y	SPE, GC-MS	
Pentachlorophenol	Phenol	Cancer, liver and kidney effects	Y	standard available SPE, GC-MS	N
Chloroform	Disifection by-product	Kidney and liver toxicity	Y	HS, GC-ECD	N
Bromoform	Disinfection by-product	Kidney, bladder, renal effects	Y	HS, GC-ECD	
Bromodichloromethane	Disifection by-product	Renal cytomegaly, liver effects	Y	HS, GC-ECD	
Dibromochloromethane	Disifection by-product	Liver & kidney damage	Y	HS, GC-ECD	
Dichloroacetonitrile	Disinfection by-product	Developmental toxicity	N		Y, P/T, GC-MS
Dibromoacetonitrile	Disinfection by-product	Reduced body weight	N		Y, P/T, GC-MS
Trichloroacetonitrile	Disinfection by-product	Lachrymator, severe eye irritant	N		Y, P/T, GC-MS
Monochloroacetic acid	Disinfection by-product	Genotoxic, cytotoxic	N		Y, SPE, GC-MS
Dichloroacetic acid	Disinfection by-product	CNS damage, liver &kidney effects	N		Y, SPE, GC-MS
Trichloroacetic acid	Disinfection by-product	Cytotoxic	N		Y, SPE, GC-MS
Bromoacetic acid	Disinfection by-product	Genotoxic, Cytotoxic	N		Y, SPE, GC-MS
Bromochloroacetic acid	Disinfection by-product	Reproductive effects	N		Y, SPE, GC-MS
Dibromoacetic acid	Disinfection by-product	Liver toxicity	N		Y, SPE, GC-MS
Formaldehyde	Disinfection by-product	Irritates nasal cavity	N		Y
Trichloroacetaldehyde			N		
SYNTHETIC ORGANIC POLYMER RESIDUES					
Acrylamide	Water Treatment residue	Nerve damage, benign tumours	N		Y, P/T, GC-MS
Epichlorohydrin	Water treatment residue	Increased cancer risk over time	N		Y, P/T, GC-MS
Diallyldimethylammonium Chloride	Water treatment residue	Genotoxic	N		Y, P/T, GC-MS
Dimethylamine	Water treatment residue	Tissue destruction	N		Y, P/T, GC-MS
1,3-Dichloro-2-propanol	Water treatment residue	-	N		Y, P/T, GC-MS
2,3-Dichloro-1-propanol	Water treatment residue	-	N		Y, P/T, GC-MS
3-Chloro-1,2-propanediol	Water treatment residue	-	N		Y, P/T, GC-MS
NATURAL AND SYNTHETIC HORMONES					
17-Estradiol	Hormone	Endocrine disruption	N		Y, SPE, LC-MS
Estriol	Hormone	Endocrine disruption	N		Y, SPE, LC-MS
Estrone	Hormone	Endocrine disruption	N		Y, SPE, LC-MS
17-Ethinylestradiol	Hormone	Endocrine disruptio	N		Y, SPE, LC-MS
Dietylstilbestrol (DES)	Hormone	Endocrine disruption	N		Y, SPE, LC-MS

Annexure 2.1: cont.

Organic contaminant	Classification	Concern to the Drinking water industry	Currently being analyzed for?	Method for analysis in place?	Need for New Method development?
ALGAL TOXINS					
Microcystin-(LR+YR+RR)	Cyanotoxin	Hepatotoxins (liver toxins)	Y	SPE, GC-MS	N
Anatoxin-a	Cyanotoxin	neurotoxin	N		Y, SPE, LC-MS
Homoanatoxin-a	Cyanotoxin	neurotoxin	N		Y, SPE, LC-MS
Anatoxin-a(S)	Cyanotoxin	neurotoxin	N		Y, SPE, LC-MS
Saxitoxins	Cyanotoxin	Paralytic Shellfish poisoning	N		Y, SPE, LC-MS
Cylindrospermopsin	Cyanotoxin	Liver toxicity	N		Y, SPE, LC-MS
Nodularin	Cyanotoxin	Liver toxicity	N		Y, SPE, LC-MS

Legend

Y-Yes

N-N0

P/T-Purge and Trap Gas Chromatography

SPE -Solid Phase Extraction

GC–MS - Gas Chromatography Mass spectrometry

LC-MS-Liquid Chromatography-Mass spectrometry

HS, GC-ECD-Head Space Gas Chromatography with Electron Capture Detector

T&O- Taste and odour

EDC-Endocrine disrupting Chemical

CNS-Central Nervous System

ChE-Cholinesterase Enzyme

ANNEXURE 2.2: An example of a response

Group of organic contaminants	Organic contaminants analyzed for	Concentrations in groundwater	Concentrations in source water	Concentrations along the distribution network	Concentrations in tap water	Analytical Method used	Limit of Detection (LOD)	Limit of Quantification (LOQ)
Volatile organics	Benzene Chlorobenzene 1,2-Dichlorobenzene Trichlorobenzene 1,4-Dichlorobenzene							
Pesticides	Hexachlorocyclohexane DDT and metabolites Dichlorvos Heptachlor Deltamethrin Aldicarb							
Polynuclear Aromatic hydrocarbons (PAHs)	Benzo[a]pyrene Chrysene Fluorene Anthracene							
Disinfection by-products (DBPs)	Trihalomethanes Haloacetic acids Nirosodimethlamine							
Polychlorinated Biphenyls (PCBs)	Arochlor 1016 Arochlor 1254 Arochlor 1248 Arochlor 1260							
Cyanotoxins	Anatoxin-a Saxitoxin Anatoxin-a (S) Homoanatoxin-a Nodularin Microcystin-LR							
Natural and Synthetic Hormones	17β-Estradiol (E2) Estriol (E3) Estrone (E1) 17α-Ethinylestradiol Diethylstilbestrol (DES)							

ANNEXURE 3: PROOF OF ORIGIN ARTICLES SUBMITTED

ANNEXURE 3.1: ARTICLE SUBMITTED TO THE WATER SCIENCE & TECHNOLOGY JOURNAL

Original Message-----
From: Michelle Herbert [mailto:mherbert@iwap.co.uk]
Sent: Wednesday, April 21, 2010 4:21 PM

To: Esper Ncube
Subject: RE: Your submission to Water Science and Technology

Dear Esper,
Thank you for sending your paper to us again. I have taken a quick look at it now and I will be able to pass it through to an editor for peer review in the next couple of days.
Kind regards,

Michelle

Michelle Herbert

Journals Production Assistant

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From: em.wst.0.1a59e8.07bf9f84@editorialmanager.com

[mailto:em.wst.0.1a59e8.07bf9f84@editorialmanager.com] On Behalf Of Water Science and Technology

Sent: Wednesday, April 14, 2010 10:02 PM

To: Esper Ncube

Subject: Submission Confirmation for A GENERIC PROTOCOL FOR THE SELECTION AND PRIORITIZATION OF ORGANIC CONTAMINANTS FOR MONITORING IN THE DRINKING WATER VALUE CHAIN

Dear Mrs Ncube,

Your submission entitled "A GENERIC PROTOCOL FOR THE SELECTION AND PRIORITIZATION OF ORGANIC CONTAMINANTS FOR MONITORING IN THE DRINKING WATER VALUE CHAIN" has been received and will

now be peer reviewed for possible publication in the journal Water Science and Technology

You will be able to check on the progress of your paper by logging on to Editorial Manager as an author. The URL is http://wst.edmgr.com/.

You will shortly be notified of the reference number assigned to your submission.

Thank you for submitting your work to this journal.

Kind regards,

Michelle Herbert

Journals Production Assistant

Water Science and Technology

A GENERIC PROTOCOL FOR THE SELECTION AND PRIORITIZATION OF ORGANIC CONTAMINANTS FOR MONITORING IN THE DRINKING WATER VALUE CHAIN

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ABSTRACT

The occurrence of organic contaminants in the drinking water value chain is of growing concern for the Drinking Water industry and its consumers given the high risk these contaminants can cause. Because of the large numbers of these organic contaminants and the need to effectively optimize on the use of resources and protect public health, selecting and prioritizing those few organic contaminants of priority is necessary. There are currently many selection and prioritization approaches but the literature review revealed that a few approaches address the needs of the Drinking Water industry and there is no generic approach to the selection, prioritization and monitoring of organic contaminants in the drinking water value chain. This has led to the need for the development of a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain (from source to tap).This paper describes the methodology followed to develop the protocol including its structural components as relevant to the Drinking Water industry. The methodology emphasizes on expert judgment and stakeholder participation. The approach is intended to provide guidance to Water Services Providers on the selection and prioritization of organic contaminants for monitoring in the drinking water.

Key words: prioritization; organic contaminants; drinking water; validation.

ANNEXURE 3.2 Proof of the submitted Rand Water Position paper on organic contaminants monitoring in the drinking water value chain

FOR INFORMATION OF THE
Scientific Services Management Committee (SSMC)

Prepared by: Esper Jacob Ncube (WQSb)
WATER QUALITY SPECIALIST SERVICES DEPT

RAND WATER

CONFIDENTIAL

SSMC MEETING 25 February 2010

PRIORITY ORGANIC CONTAMINANTS FOR MONITORING IN THE DRINKING WATER SUPPLY CHAIN

INTRODUCTION

Safe drinking water is in everybody's interest, yet providing safe drinking water on an ongoing basis is complex requiring a great deal of knowledge, tenacity and attention to detail. This task is also becoming more difficult in that man, in the 21st century, has become reliant on a vast number of manufactured chemicals and substances to enhance the quality of life with little thought given to what happens to these chemical substances once they have been used and discarded. Drinking water is generally most direct source of human exposure to waterborne contaminants and accordingly receives the most attention in water-related health risk assessments. As a result, effective monitoring and treatment of drinking water will always be required for public health protection. The information contained in Figure I illustrates the magnitude of this problem which now resides with Water Services Authorities that are charged with the responsibility of ensuring that the water that consumers receive on tap is safe and wholesome for lifelong consumption.

- 18 million substances are listed and described in the "Chemical Abstracts"
- 400 million tons of chemicals were produced worldwide in 2000. (Compared to 1 million ton manufactured in 1930)
- 100 000 chemicals were listed with the European Community in 1981 (old chemicals)
- 720 chemicals were listed under the Swiss Ordinance on Environmental Pollutants between 1988 and 2000
- 8 700 different food additives are known
- 3 300 substances are being used as drugs in human medicine
- 8,4million substances are commercially available and 240,000 are reported to be inventoried/regulated chemicals according to Chemical Abstract Services website
- 82,000 industrial chemicals are in the US Toxic Substances Chemical Agents inventory
- Nano-materials reported to be toxic to humans exist in more than 116 sunscreens, cosmetics and personal care products currently on the market
- 458 pesticides are registered for use in South Africa alone as per the PAN-UK database

Figure I – Some facts on industrially produced Chemicals

The consequences of these substances in drinking water are largely inconclusive and controversial and therefore the setting of guidelines/standards for these constituents is tenuous. Often very stringent water quality standards are set because a lack of adequate information engenders the concept of rather safe than sorry. Complicating the situation is the large number of organic compounds produced, the rapid rate at which new compounds are developed, the hazardous potential of many of these substances, the demand for organically derived compounds, the stability of many of these substances in the environment, the ability of many of these substances to accumulate through the food chain and the many derivatives that can be formed from particular substances.

ANNEXURE 3.3: Proof of Original article prepared for the Water SA Journal

IMPLEMENTATION OF A GENERIC PROTOCOL FOR THE SELECTION AND PRIORITIZATION OF ORGANIC CONTAMINANTS TO THE RAND WATER SITUATION

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ABSTRACT

Approaches that prioritize chemicals according to their importance as environmental contaminants have been developed by government agencies and private industries. However, it has been noticed that a few approaches such as one published by the United States Environmental Protection Agency (USEPA), address the needs of the Drinking Water industry. There is also no generic approach to the selection, prioritization and monitoring of organic contaminants in the drinking water value chain. To safeguard Drinking Water industry customers, it was necessary to develop a generic protocol to assist with the identification of a list of organic contaminants for monitoring in the drinking water value chain. Once the protocol was developed, it was validated in a prototype drinking water value chain. This paper describes the implementation of such a generic protocol. The exercise comprised of testing each step of the protocol from the selection of the "pool of organic contaminants (Step I) to recommending the final priority list of organic contaminants (Step VII). The implementation was successfully conducted in the Rand Water drinking water value chain (from catchment to tap). Expert judgment was emphasized during the implementation as each step was validated and the opinion of key stakeholders used to shape the process. The tailor made prioritization criteria reflective of the Drinking Water industry perspective proved to be successful in selecting and prioritizing organic contaminants for monitoring in the drinking water value chain. The organic contaminants in the current study were successfully prioritized in three classes: short-term priority for analysis, medium term priority for analysis and long term priority for analysis. This is a very important guide for water utilities to assist in optimizing their resources while not compromising the role of public health protection. A priority list of organic contaminants has been identified for use by Rand Water and other water utilities.

Key words: generic protocol, organic contaminants, validation, selection and prioritization, drinking water value chain, expert judgment

INTRODUCTION

Today's vast chemical industry and particularly its giant offspring, the production of synthetic organic chemicals (Middleton and Rosen,1956) have introduced new challenges to the scientists and public officers engaged in providing and protecting public health through the provision of safe drinking water. This challenge was noticed more than half a century ago (Middleton and Rosen, 1956). Industrial contamination of water while important is not the only factor to consider in the complex organic pollution situation. Domestic sewage, natural run-off and materials derived from the life cycle of aquatic plants and animals contribute substantial quantities of organic materials to streams. (Meintjes et al, 2000, Kolpin et al 2004, Cheevaporn et al 2005, Voutsa et al 2006, Ellis, 2006)

ANNEXURE 4: PROOF OF ETHICS COMMITTEE APPROVAL

FWA 00002567, Approved dd 22 May 2002 and Expires 24 Jan 2009
IRB 0000 2235 IORG0001762 Approved dd Jan 2006 and Expires 21 Nov 2008

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Date: 7/03/2007

PROTOCOL NO.	**22/2007**
PROTOCOL TITLE	Selection and prioritization of organic contaminants for monitoring in the drinking water value chain.
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DEPARTMENT	School of Health Systems and Public Health
STUDY DEGREE	PhD in Public Health
SPONSOR	None.
MEETING DATE	28/02/2007

This Protocol and Informed Consent have been considered by the Faculty of Health Sciences Research Ethics Committee, University of Pretoria on 28/02/2007 and found t be acceptable.

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* = Members attended the meeting on 28/02/2007.
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