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]

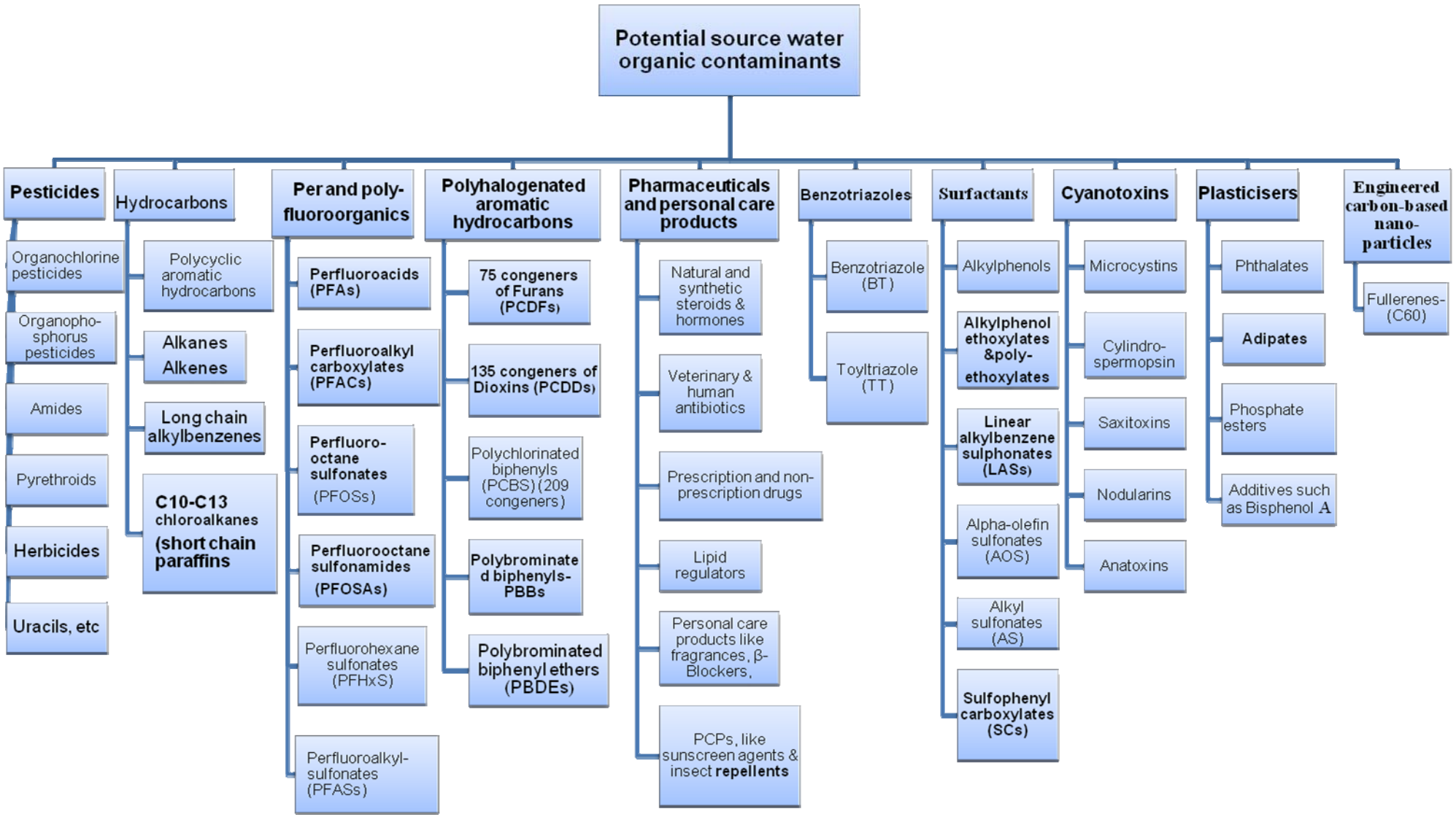


Figure 4.2 Potential source water organic contaminants found in the literature

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).

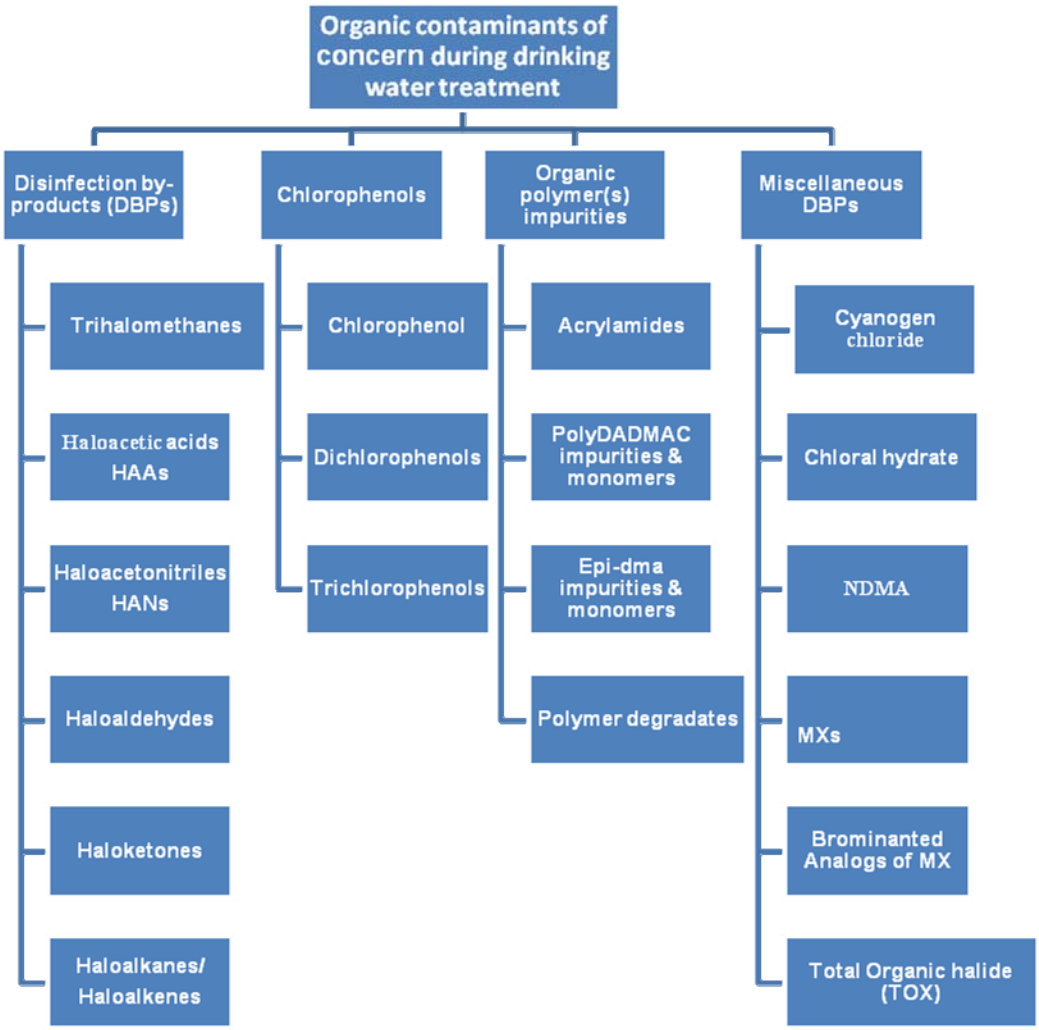


Figure 4.3: Organic contaminants from drinking water treatment chemicals

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

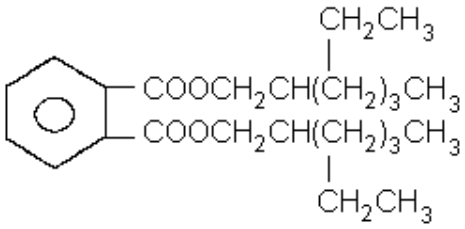
CASRN	117-81-7
Toxic	Yes
Mutagenic	Yes
Carcinogen	Yes
Endocrine Disruptor	Yes
Aesthetic	No
Priority pollutant	Yes
Accumulative	Yes
Persistent	Yes
Essential element	No
Teratogenic	Yes
R_fD	-
A.D.I/TDI	25µg/kg/day bw , UF = 100
L.O.A.E.L	666 mg/kg/day bw based on reduced fetal weight (oral, rats)
N.O.A.E.L	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]**

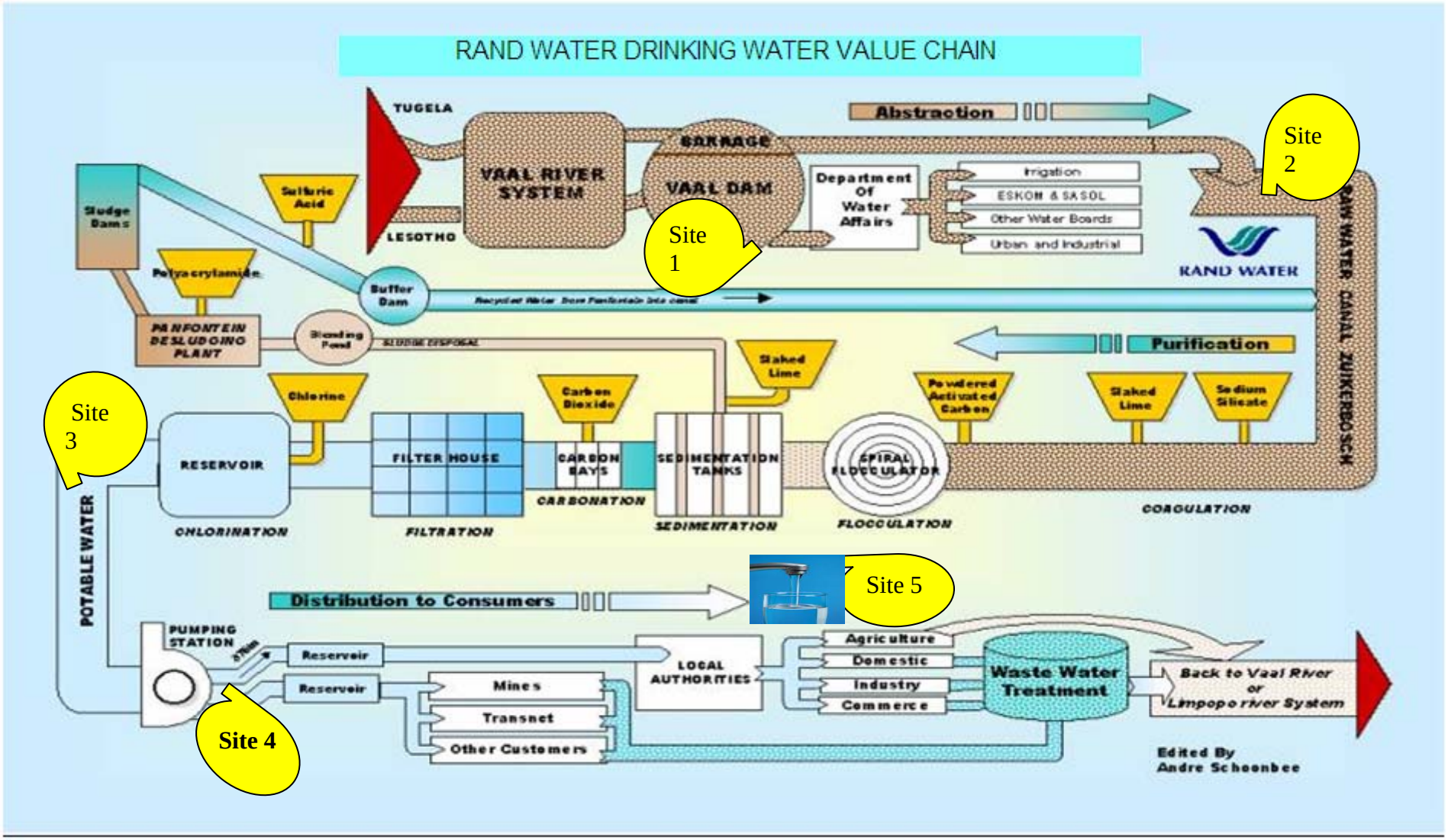

Figure 4.4 Sample site locations for the assessment of organic contaminants along the Rand Water drinking water value chain (*courtesy of A.Schoonbee*)

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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