CHAPTER 1 GENERAL INTRODUCTION

1.1 BACKGROUND TO THE STUDY

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

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

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

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

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

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

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

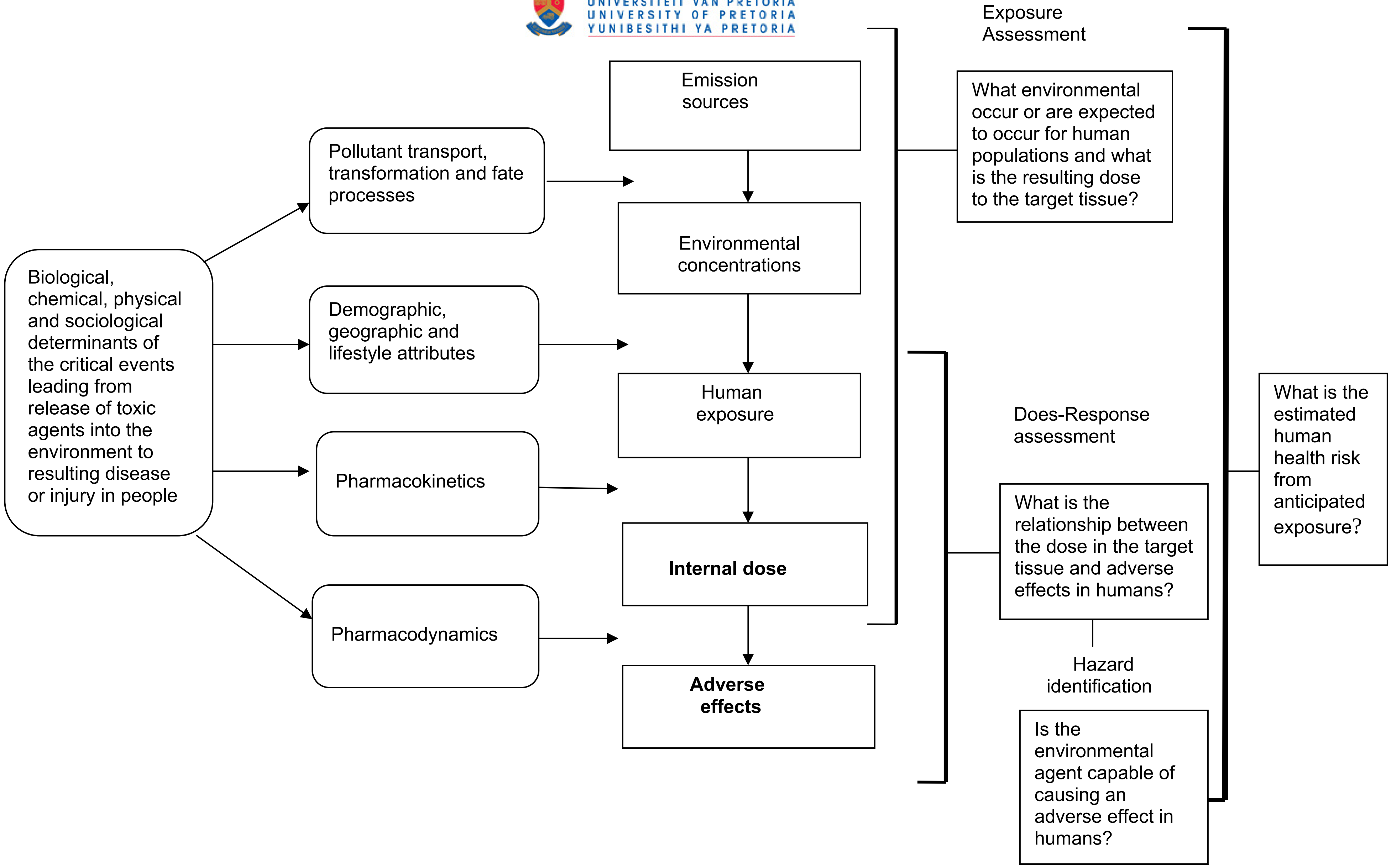


Figure 1.1: An environmental health paradigm and its relationship to the risk assessment framework adopted and modified from Sexton et al. 1995 [33]

1.2.1 The human risk

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

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

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

1.3.1 Sources of organic contaminants

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

Point Sources

Point source means any discernible, confined and discrete conveyance including but not limited to any pipe, ditch, channel, tunnel, conduit, well, container, rolling stock, discrete fissure, concentrated animal feeding operation or vessel or other locating craft from which pollutants are or may be discharged. The term does not include agricultural storm water discharges and return flows from agriculture. For these types of sources, contributions of contaminants originate from discrete sources whose inputs into aquatic systems and can often be defined in a spatially explicit manner through measurement of chemical residues [Table 1.1] Point sources usually result in direct discharges to water courses, [Figure 1.1] whereas the route for non-point sources may involve partial deposition before reaching the water course. [52]

Non-point sources

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

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

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

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

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

Table 1.2*:* Examples of non-point source pollution

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

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

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

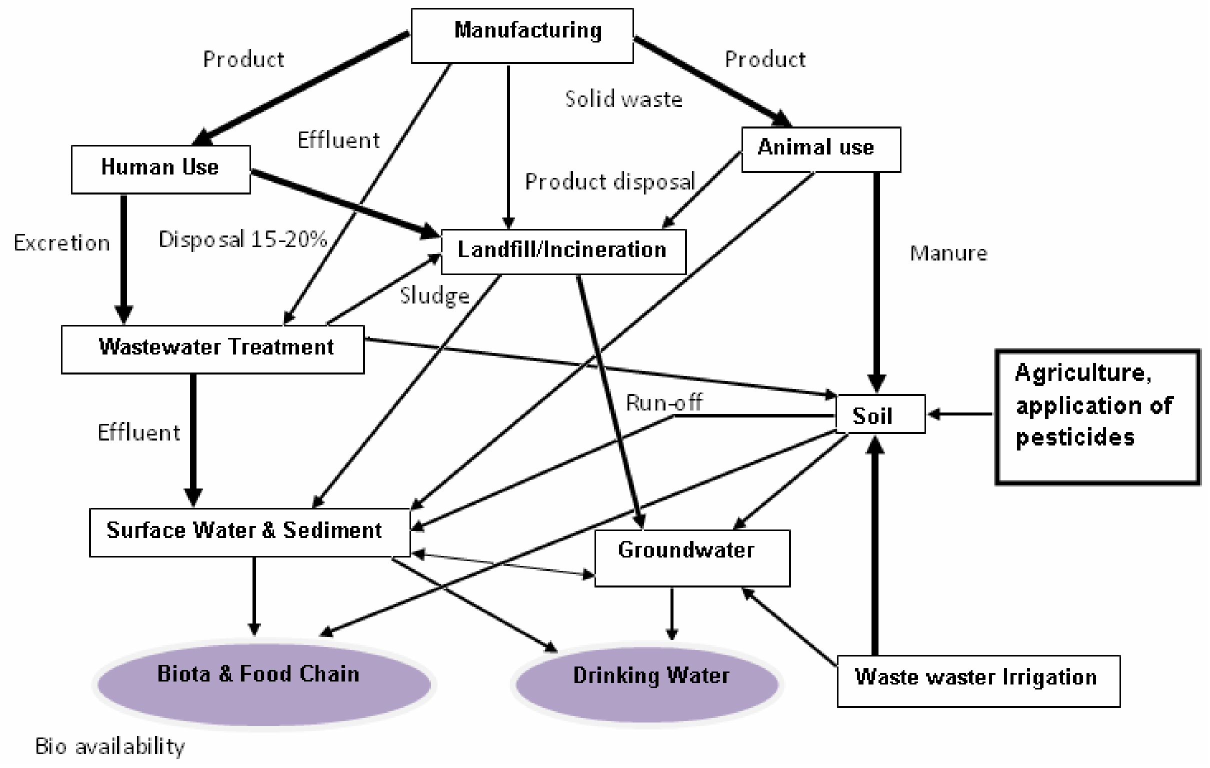


Figure 1.2: Potential sources, pathways and sinks of organic contaminants in the environment, adopted and modified from Schnoebelen et al. 2006 [70]

Organic contaminants occurring through atmospheric deposition

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

Organic contaminants from surface run-off

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

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

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

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

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

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

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

- *Transformation (biodegradation, hydrolysis, photolysis, speciation).*

  Transformation is of major importance in determining the persistence of a chemical. The mechanisms may vary depending on temperature, light intensity and numbers of competent bacteria. Dissolution is the route by which many other substances can enter a watercourse. For example the main source of organotins is from dissolution of tributyltin (TBT) and related compounds used as antifouling agents. [72]

- *Uptake (bioaccumulation, bioconcentration).*

  Two different modes of action of uptake can be distinguished, passive and active uptake. In fish, passive uptake occurs via the skin and or gills of the truly soluble fraction while active uptake occurs via the digestive tract. Uptake and subsequent concentrations in biomass depend on the bioavailability of the substance. [72] The measured total environmental concentration of a substance does not necessarily represent the actual concentration to which the individual species will be exposed. The most important physicochemical properties of a substance that impact on its fate and distribution in the environment are its molecular weight (MW), vapor pressure (V_p), water solubility (S), octanol/water partition coefficient (K_{ow}), organic carbon-water partition coefficient (K_{och}), Henry's Law Constant (H_c), bioconcentration factor in fish (BCF_{fish}) and half-life ($T_{1/2 \text{ water, air, soil}}$) in the compartment of interest. [52, 72] Based on these properties organic contaminants will fall into different categories or classes.

1.5 MAIN CATEGORIES OF ORGANIC CONTAMINANTS OF CONCERN

1.5.1 Classical organic contaminants

Until the beginning of the 1990s, non polar hazardous compounds such as persistent organic pollutants (POPs) and heavy metals were a focus of interest and awareness as priority pollutants, hence they were part of intensive monitoring programs. [73] Today, these compounds are as important as emerging contaminants for the industrialized countries since a dramatic reduction of emissions has been achieved through the adoption of appropriate measures and the elimination of the dominant sources of pollution. However, due to their persistence in the environment, ability to travel across the atmosphere and be deposited at distances far from their origin, bioaccumulation in fat tissues and toxicity to wildlife and human beings this has led to their continuous regulation and monitoring in the environment which is evident in the contents of the Stockholm Convention of 2001 and other relevant conventions. [3-8] In this convention a group of organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins and furans are singled out as the “dirty dozen”. These contaminants are listed in water quality standards and guidelines worldwide for safeguarding public health. [3-8]This group of compounds will be referred in this document as “classical organic contaminants”. [Table 1.3]

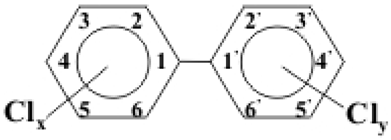
1.5.2 Emerging organic contaminants

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

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

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

Table 1.3: Examples of classical organic contaminants of concern

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

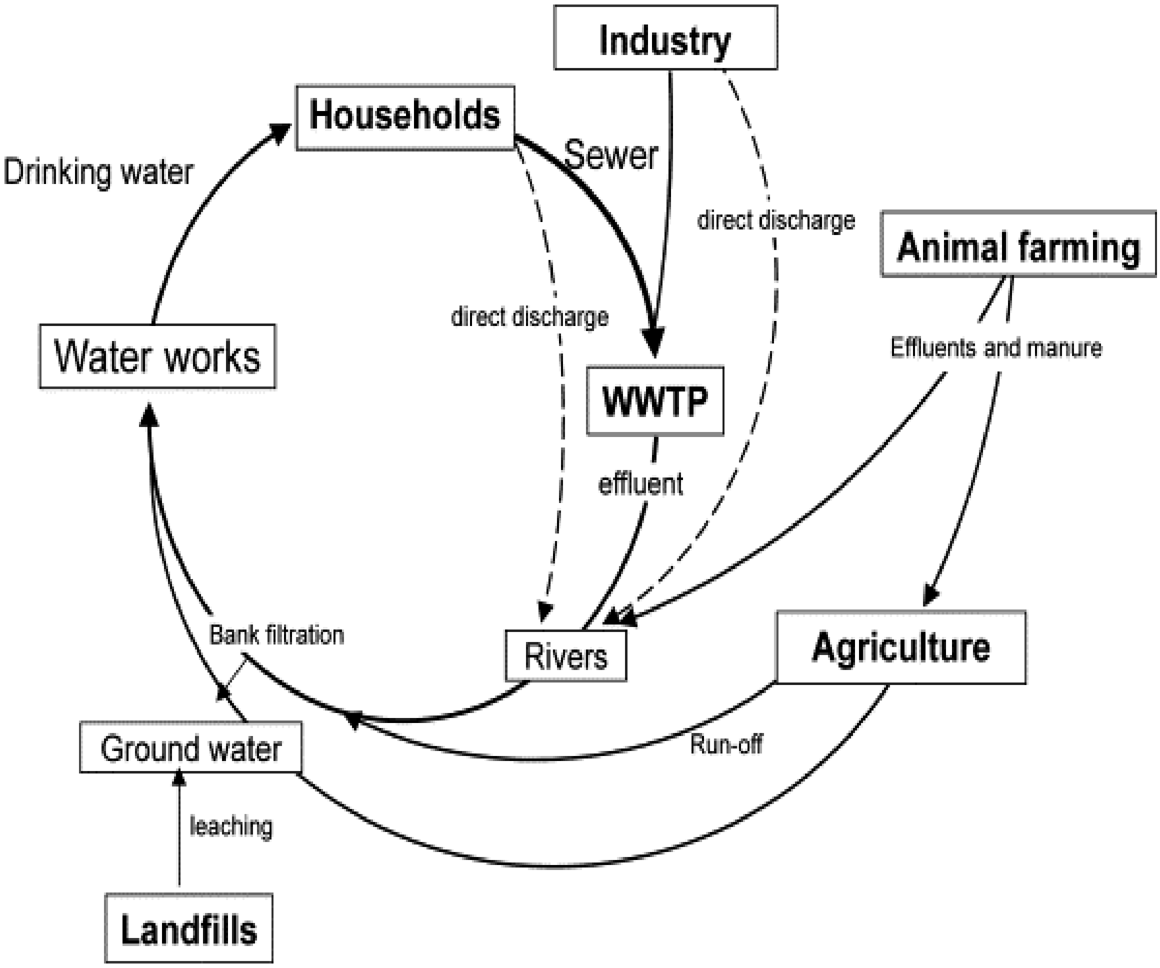


Figure 1.3 Routes of entry of emerging organic pollutants into the aquatic environment [49]

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

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

1.6 ASSESSMENT OF HUMAN HEALTH IMPACTS

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

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

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

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

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

Organic contaminants are capable of causing other problems other than adverse human health effects. These problems include impairing the organoleptic properties of drinking water such as taste, feel, physical appearance and occurrence of offensive odours. These properties constitute the aesthetic aspects of water which consumers are capable of identifying. Examples include, the visual nuisance causing discolouration, offensive taste and odours and high turbidity in water bodies. The presence of high organic content in water bodies can result in de-oxygenation, resulting in oxygen depletion and death of some organisms. Disturbance of temperature and pH regimes and promotion of eutrophication could result in nutrient loading in water supplies resulting in the release of algal toxins into the water. This has resulted in a shift in environmental research to try and ameliorate these effects and protect not only source water resources but the entire drinking water value chain.

1.7 OVERALL ASSESSMENT

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

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

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

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

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

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

  There is lack of reference methods for certain groups of concern. For example, the European Union in its implication of the European Water Framework Directive [82] has been able to identify the need for the development of reference methods for four priority substances namely nonylphenol, octylphenol, polybrominated diphenyl esters (PBDEs) and C10-C13 chloroalkanes which consists of groups of chemicals consisting of a large number of congeners and isomers. [82] Available monitoring data for these groups of chemicals often refer to different congeners so that it is difficult to compare data. [82] Enough effort should be made to identify indicator substances and reference materials whenever possible and secondly to define a consensus reference method for each of these priority substances. [82] Where there are available, the cost to purchase them has been high.

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

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

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

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

1.7.1 Key challenges for the Drinking Water Industry

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

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

1.8 PROBLEM STATEMENT

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

1.9 AIMS AND OBJECTIVES

1.9.1 Aim

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

1.9.2 Objectives

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

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

2.1 INTRODUCTION

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

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

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

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

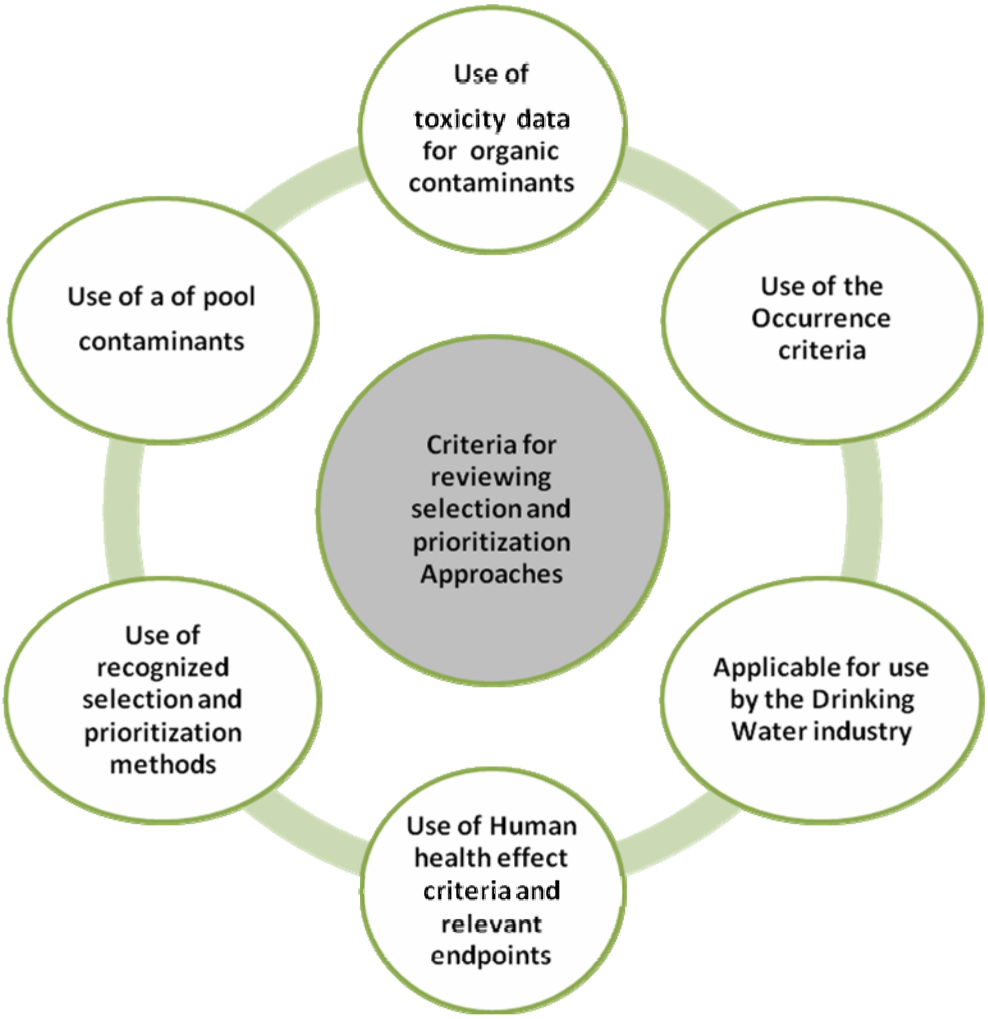


Figure 2.1: Review criteria for the selection and prioritization Approaches

2.2 SELECTION AND PRIORITIZATION APPROACHES BY GOVERNMENT AGENCIES AND PRIVATE INDUSTRIES

2.2.1 The United States Environmental Protection Agency (USEPA) approach

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

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

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

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

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

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

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

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

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

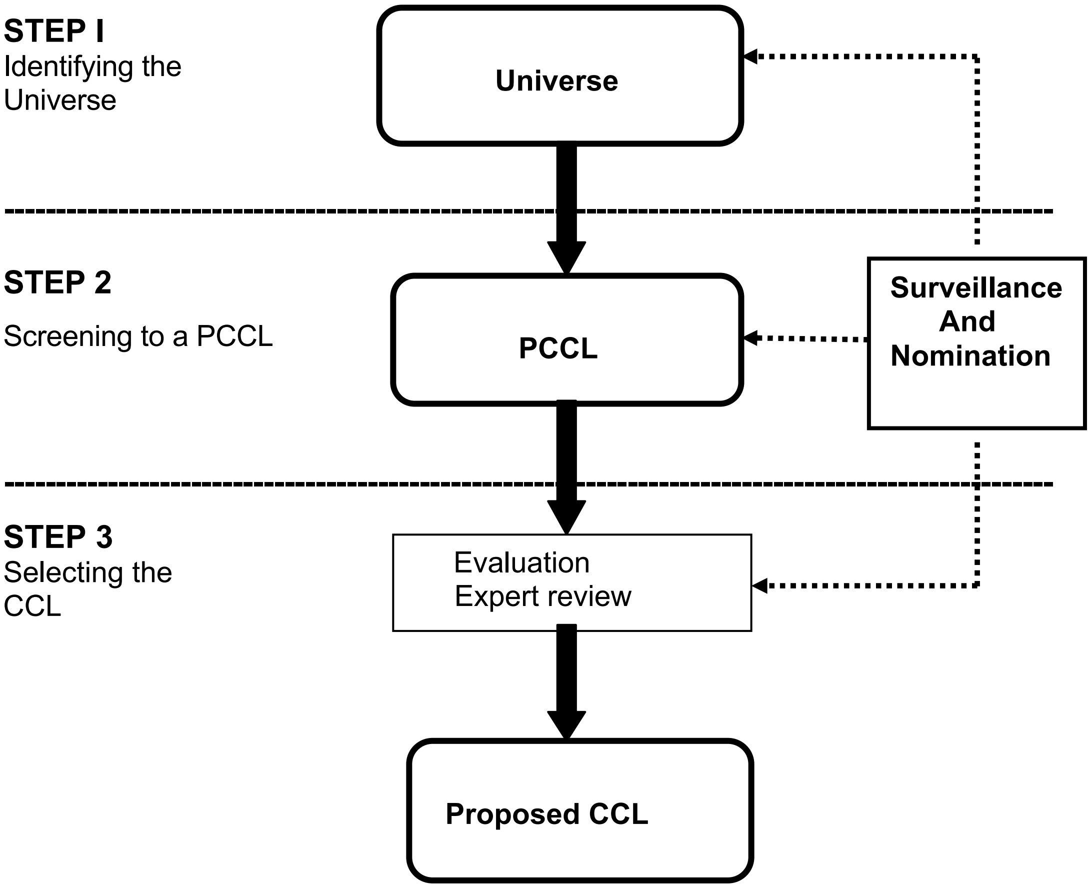


Figure 2.2: USEPA selection and prioritization approach for drinking water contaminants, schematic of CCL classification process. [10]

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

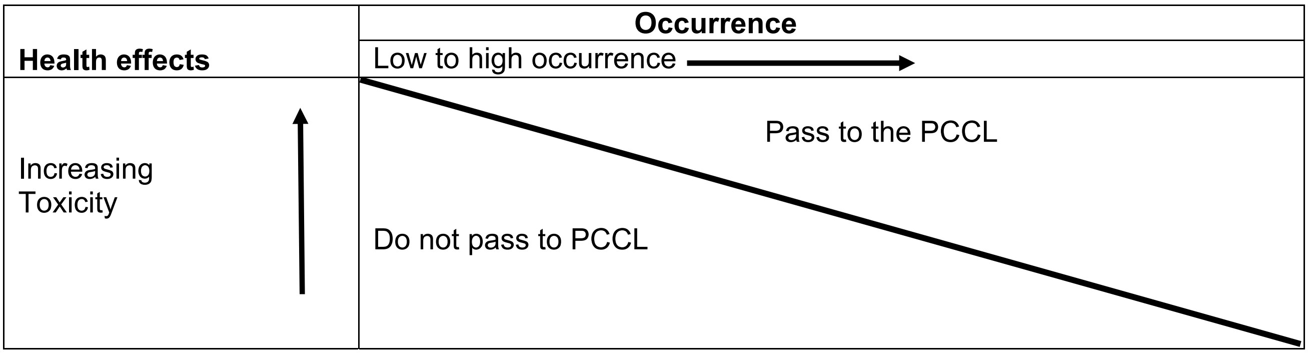
Occurrence data elements

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

The data evaluated included;

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

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



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

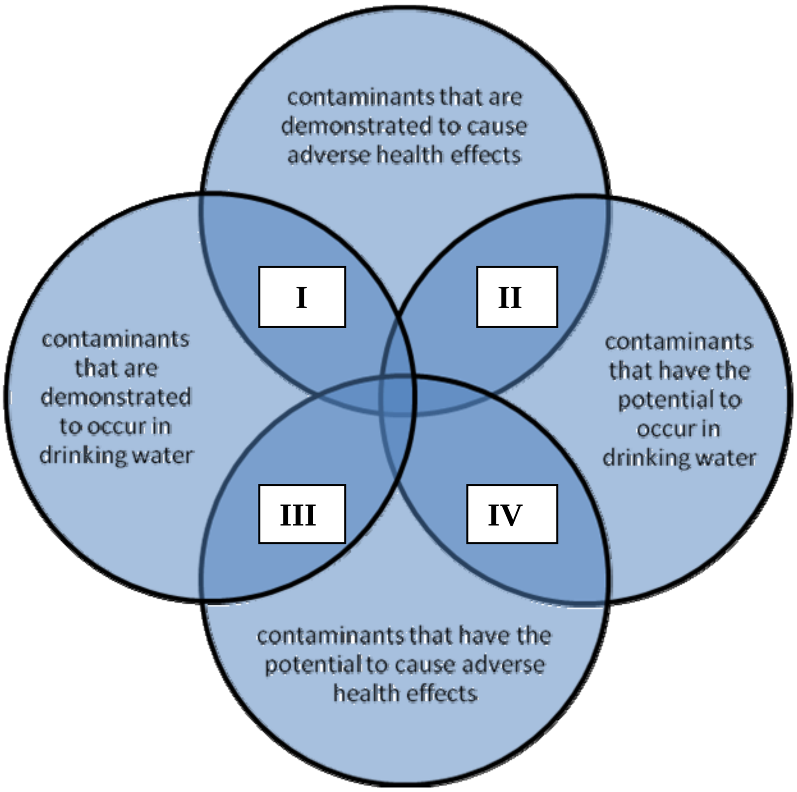


Figure 2.3-USEPA Screening criteria for drinking water contaminants-modified from EAWAG, 2002. [11]

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The five hundred and thirty two (532) chemical contaminants obtained from the universe were considered. The USEPA used structured classification model as tools to evaluate and identify drinking water priority contaminants. The model results were used to prioritize the chemicals and the best available data to identify contaminants that may occur in public water systems and cause adverse health effects. The USEPA used the health effects and occurrence attributes to develop the scales and scoring protocols. [10]

Health effect attributes

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

Table 2.5: Scoring equations for potency proposed by the USEPA

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

Scoring severity

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

Occurrence Attributes

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

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

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

Both a straightforward, additive approach and a collective rank-order approach were initialized to provide a prioritized listing of contaminants to be considered further and evaluated for possible inclusion on the draft CCL. **Out of the 532 chemicals on the PCCL, thirty two chemicals did not have data; hence 500 were considered [10].** The PCCL consisted of chemicals with variable health data, ranging from reference doses (R_fD) to lethal doses (LD_{50}) and occurrence data ranging from measured water concentration data from public water systems to production volume data, the characterization tagged data elements with high certainty and low certainty. The combined certainty to measure for a single contaminant (i.e. health effects and occurrence tags) was used to place contaminants in bins of high, medium and low certainty. [10]

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

2.2.1.4 Assessment of the USEPA Approach [Figure 2.2]

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

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

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

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

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

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

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

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

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

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

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

2.2.2.1 Selecting the "Pool of contaminants"

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

The different legislation, regulations or guidance documents from which the individual chemicals or groups of compounds were obtained were tabulated, indicating the country or organization of origin. [4] In total a pool of nearly 600 chemicals or group of chemicals were added to the spreadsheet. In addition further information was obtained through a postal questionnaire survey of Environmental Health Officers (EHOs), Directors of Public Health (DsPH) in Great Britain and the general public on compounds that were perceived to be of greatest concern. [4] The objective of the survey was to identify specific compounds (and risk issues) that are the cause of concern to the general public as perceived by those who filled in questionnaires and those who are active in the field of environmental health during the course of their professional activities. [4]

2.2.2.2 Screening the “Pool of contaminants”

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

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

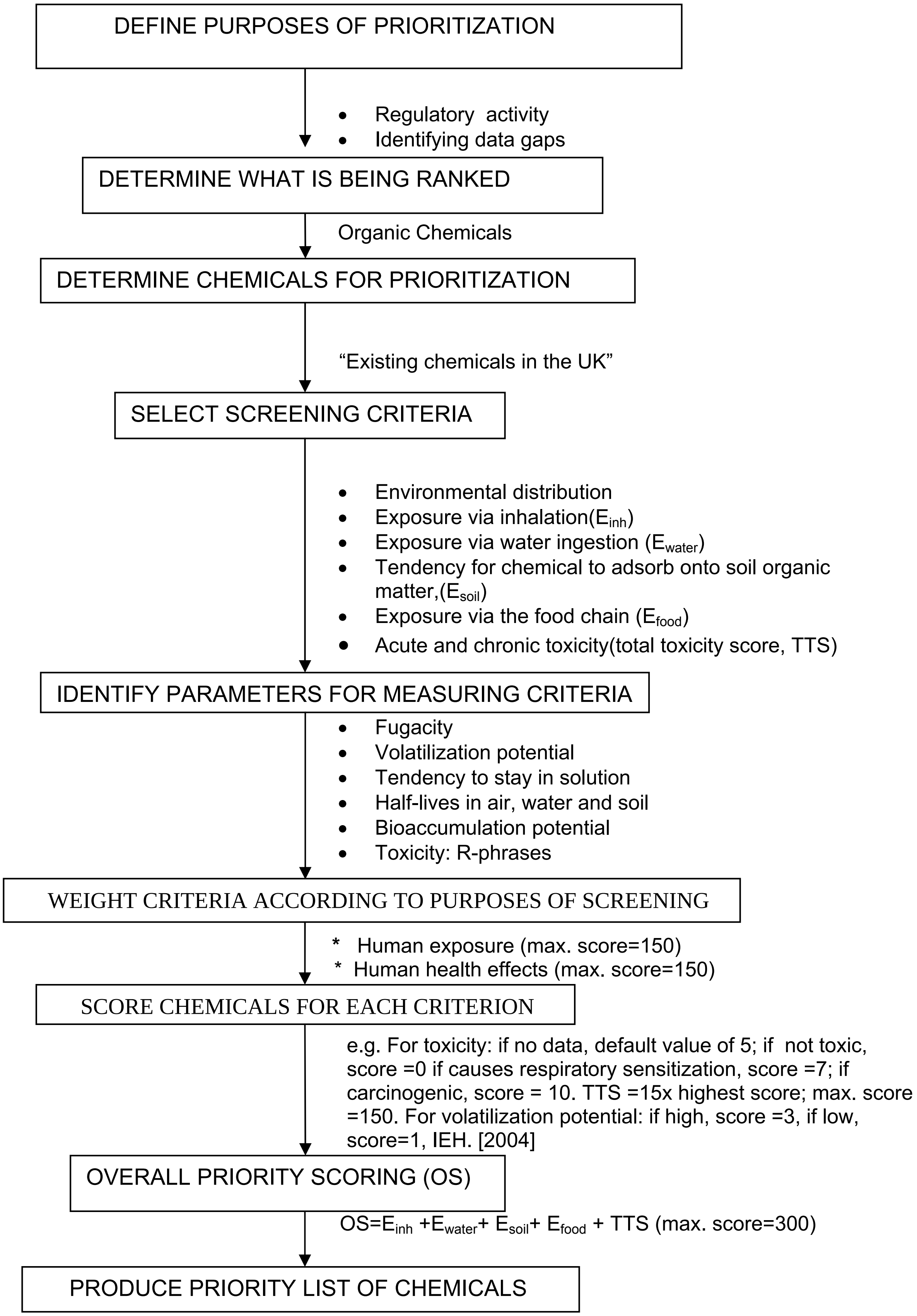

Figure 2.4: Model used in the prioritization scheme [4]

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

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

2.2.2.3 Prioritization of chemicals

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

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

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

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

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

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

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

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

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

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

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

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

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

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

2.2.3.1 Initial Selection, Selection of a “pool of contaminants”

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

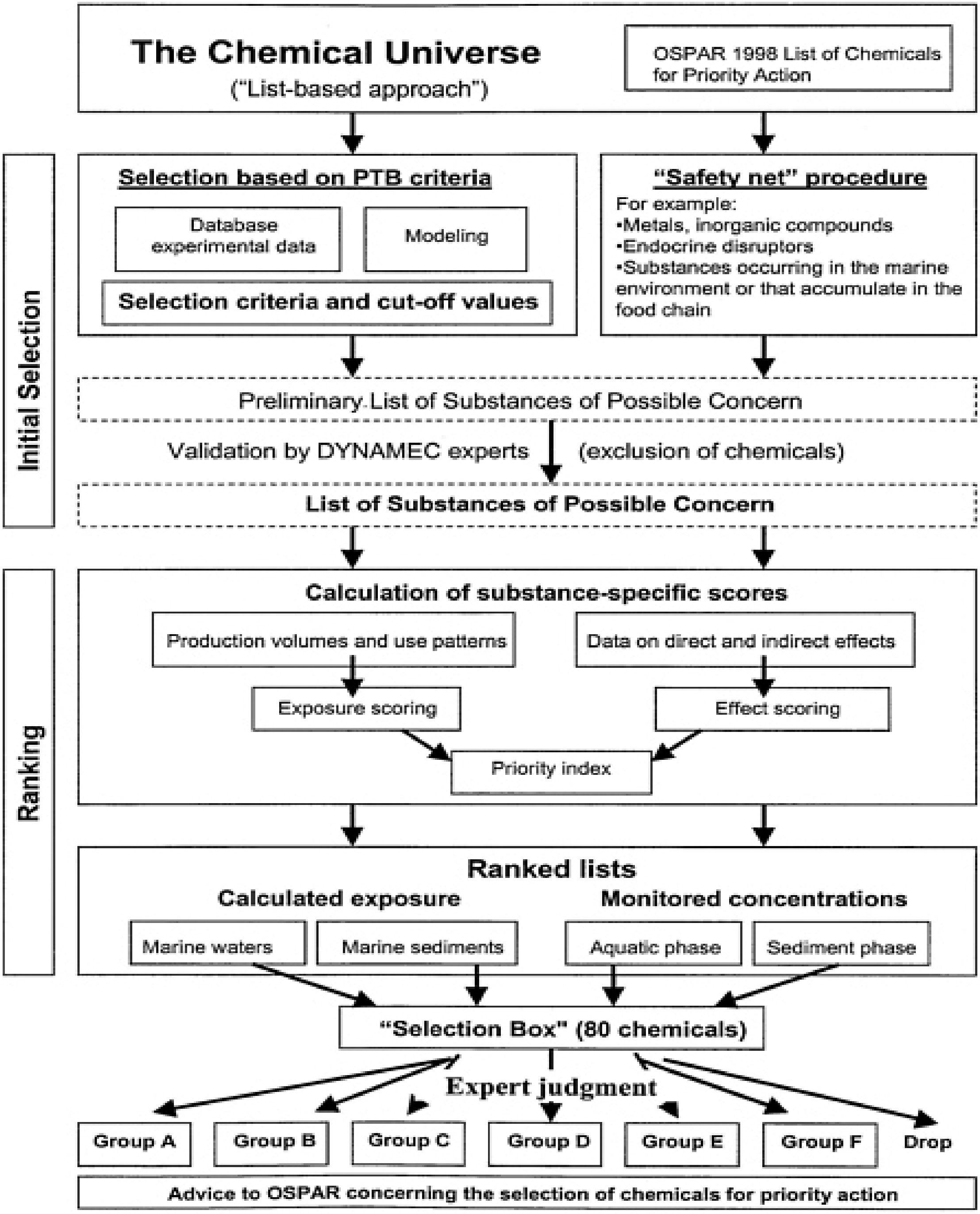

Figure 2.5: A dynamic Mechanism for the selection and prioritization of hazardous substances (DYNAMEC)-OSPAR COMMISSION [12]

2.2.3.2 Establishing a ranking list for substances of concern

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

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

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

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

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

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

Table 2.9: Selection Box Groups. [12]

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

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

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

Use of Fact Sheets

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

Flagging Substances

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

2.2.3.3 Ranking of Substances on the list of substances of concern

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

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

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

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

The ranking however, also took into account effects of the so called CMR (carcinogenic, mutagenic, toxic to the reproductive system) substances that may enter the human body through the ingestion of contaminated sea food. Consideration was also given to persistence in the calculation of the overall ranking score and differentiation of biodegradation was spread in the scaling. **Of the 400 substances in the preliminary selection list, only about 200 could be placed on the four ranking lists. [Figure 2.5, 12]**

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

2.2.3.4 Assessment of the OSPAR COMMISSION METHODOLOGY [Figure 2.1]

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

One unique feature of the DYNAMEC although similar to the IEH methodology is the fact that all matrices of concern are accounted for. The occurrence criterion is used both in a qualitative and quantitative manner through monitoring concentration levels in respective matrices of interest. The lists ranked for each compartment is again verified by stakeholders before it passes on to the phase for priority action. Based on Figure 2.5, it is evident that the DYNAMEC procedure can be modified to suit the drinking water environment, where one will assess contaminants in the biota, sediment phase and aquatic phase. Also some of the steps in conceptual model can be adopted especially Step I of the model.

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

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

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

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

2.2.4.1 Mechanism-Based Structure-Activity Analysis

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

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

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

2.2.4.2 Selection of a "Pool of contaminants"

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

2.2.4.3 Screening the "Pool of contaminants"

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

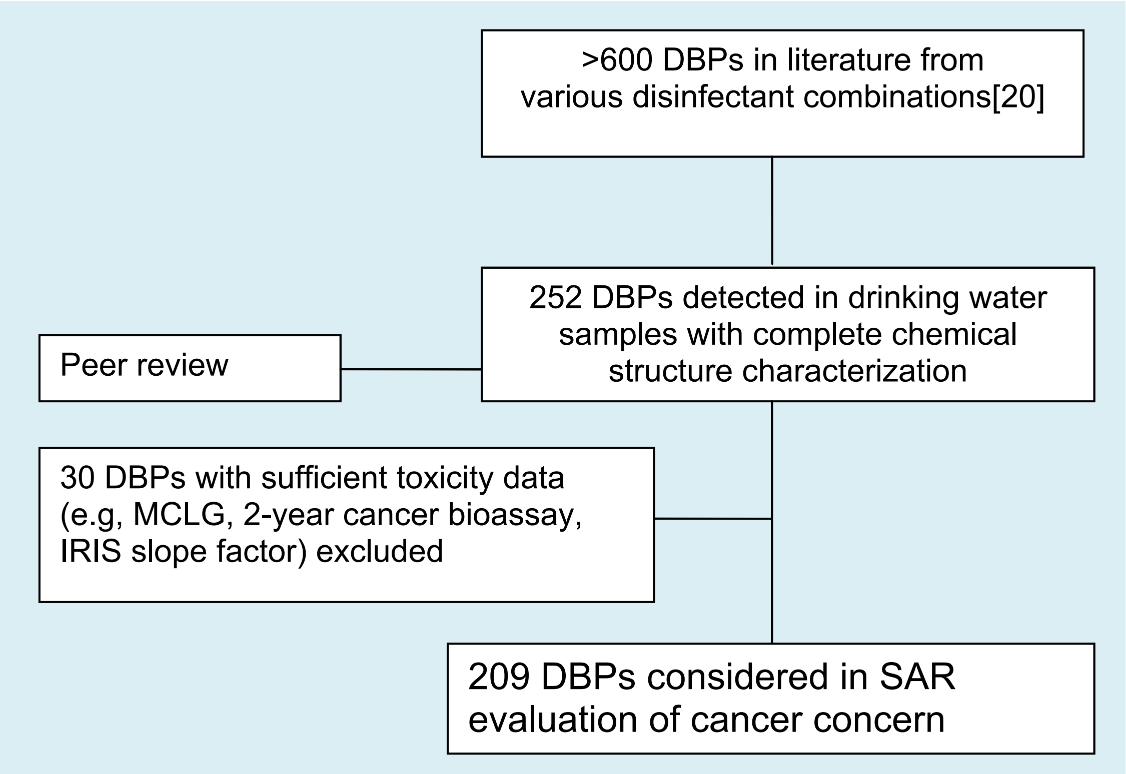

Figure 2.6: Selection of DBPs for SAR analysis, Woo et al. 2002 [17]

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

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

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

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

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

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

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

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

2.2.4.5 Assessment of the USEPA QSAR Approach [Figure 2.1]

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

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

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

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

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

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

2.2.5.1 Selection of a “Pool of contaminants”

The data set of 54 non-ionic organic pesticides comprising of acetanilides, carbamates, dinitroanilines, organochlorines, organophosphates, phenylureas and triazines was selected from a bigger data set studied in previous years. [16]These pesticides have already been the subject of QSPR studies using theoretical molecular descriptors in modelling the Koc, the leaching and volatility indices (LIN and VIN).[16] The main goal of the authors was to develop a simple procedure based on a QSAR/QSPR (Quantitative Structure Activity or Property relationships) approach for a preliminary screening, ranking and classification of organic pesticides (including those not yet synthesized) according to their environmental partitioning using only the knowledge of their chemical structure.[16]

2.2.5.2 Ranking of pesticides

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

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

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

Use of molecular descriptors

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

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

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

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

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

Use of Chemo metric methods

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

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

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

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

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

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

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

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

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

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

The Amu Darya River, one of the most important water resources for Uzbekistan and Turkmenistan was declared a world disaster zone in 1991. [21] The great increase in irrigation and the use of pesticides had led to both a lack of water and drinking water contamination. The aim of the study by Papa et al. 2004, part of an EU project on water management guidelines, was to evaluate the Leachability of 71 organic pesticides commonly employed in the area and to assess the compounds that could potentially contaminate the river and impair drinking water [21]. The most important problem was the drying up of the Aral Sea and "returning water". This is water withdrawn from the river for irrigation purposes that returns to the river from irrigated land, in lower volumes but enriched with a large content of salts and other pollutants, especially pesticides. [21] Pesticide pollution and salination had led to lack of groundwater resources for drinking water purposes, cancer was reported to be under spread and the areas had the highest level of child mortality in Central Asia. [21] A multi active approach is proposed for pesticide screening, condensing information from different environmental partition indexes (groundwater ubiquity score (GUS), modified LEACH (modified leaching index and leach ability index (LIN) into a single ranking, the Global Leachability Index (GLI). [21]

2.2.6.1 Selection of a "Pool of contaminants"

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

2.2.6.2 Screening of pesticides

Three indexes were used to calculate leachability. Two traditional, the Groundwater Ubiquity Score (GUS) and the Leaching Index (LEACH) and a third, recently introduced by Gramatica and Di Guardo (LIN-Leachability Index), based on principal component analysis (PCA) of pesticides physico-chemical properties. [21] The basis of this method is the fact that environmental behaviour is strongly influenced by properties inherent in the compounds themselves, particularly physico-chemical properties [Table 2.10] such as solubility in water, vapour pressure and partitioning coefficients between organic matter in soil or biota and water. [4,16, 20] All the indexes were calculated using models and trigger values used to classifying pesticides. [Table 2.10] The GUS index was used to assess the leachability of molecules and the possibility finding these compounds in groundwater. This index is based on two parameters: mobility in soil, given by the organic carbon partition coefficient (Koc, adimensional) and soil persistence, quantified by the disappearance half-life in the soil, defined in field conditions and expressed in days ($t_{1/2}$). [21]

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

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

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

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

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

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

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

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

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

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

3 OVERALL ASSESSMENT OF REVIEWED APPROACHES

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

Table 2.12: Prioritization schemes reviewed in this study

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

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

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

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

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

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

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

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

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

4 CONCLUSIONS

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

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

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

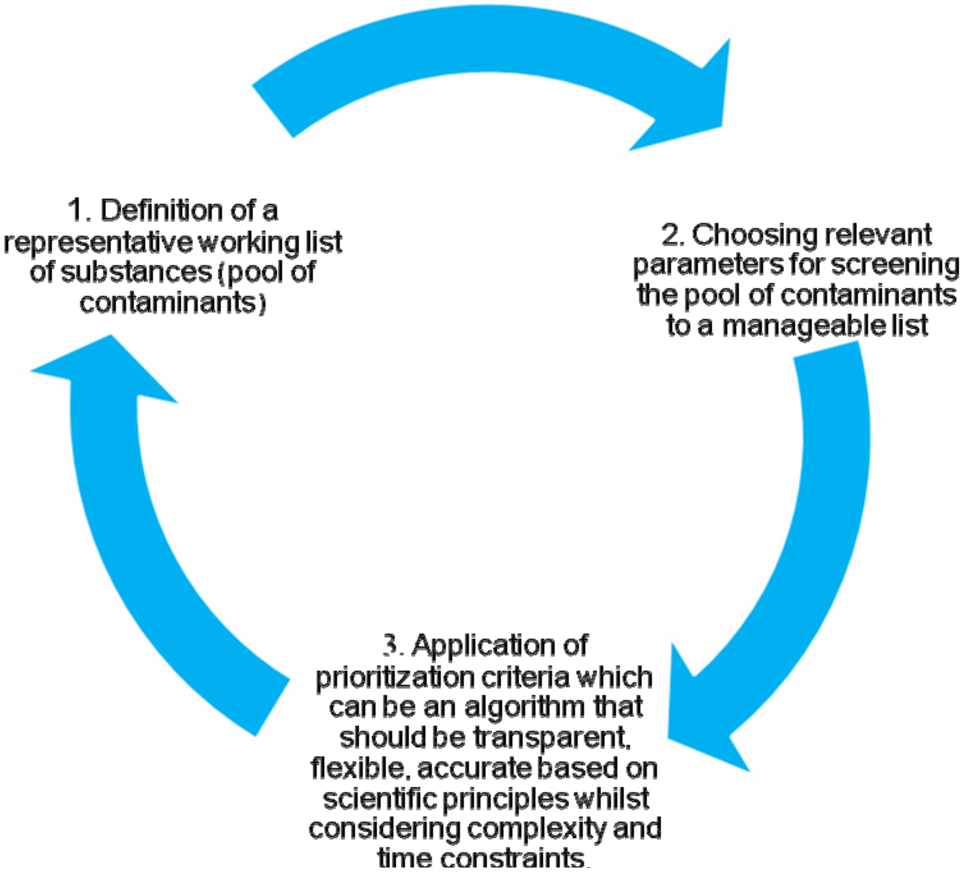

Figure 2.7: A generic conceptual framework for the selection and prioritization of contaminants as illustrated by reviewed methodologies.

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