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

## 3.1 GENERAL INTRODUCTION

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

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

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

Table 3.1: Industrially produced Chemicals

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

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

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

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

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

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

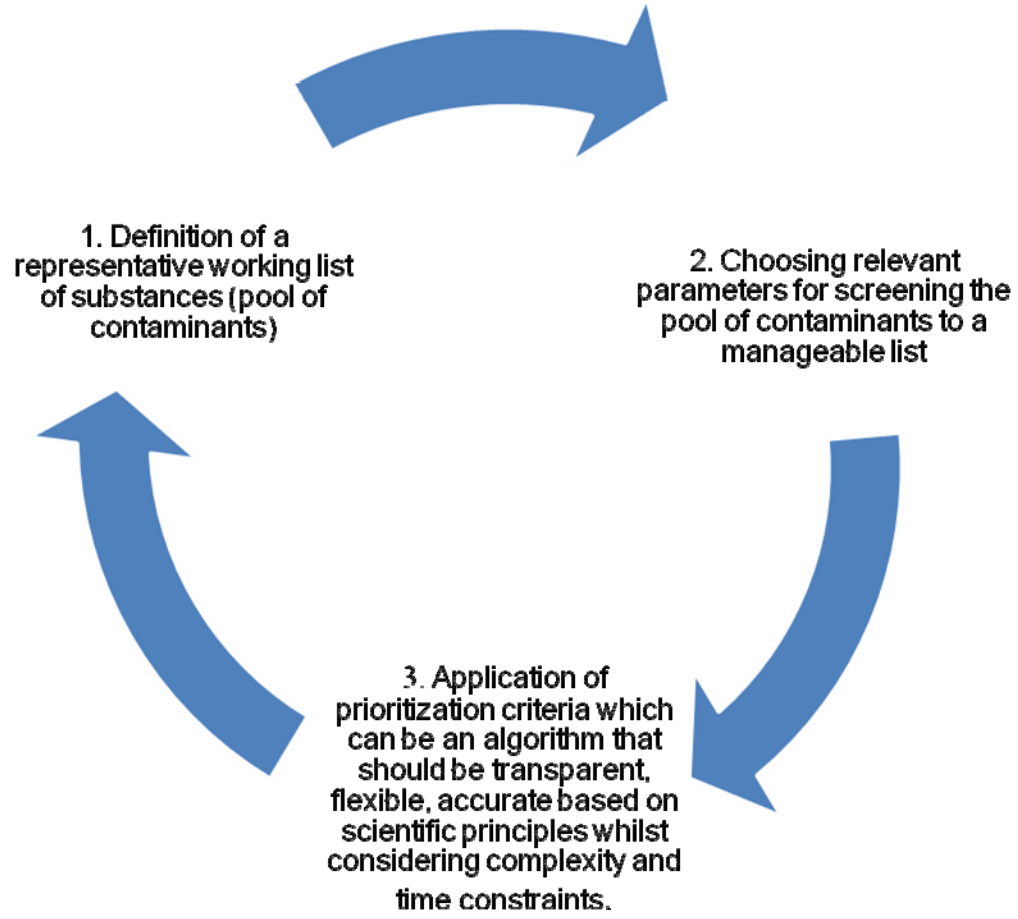


Figure 3.1: A generic conceptual framework for the selection and prioritization of contaminants as illustrated by reviewed methodologies.

### 3.1.1 Purpose of the protocol

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

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

## 3.2 Specific components of the protocol

### 3.2.1 General principles on which the protocol was developed

This protocol is based on the following principle assumptions;

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

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

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

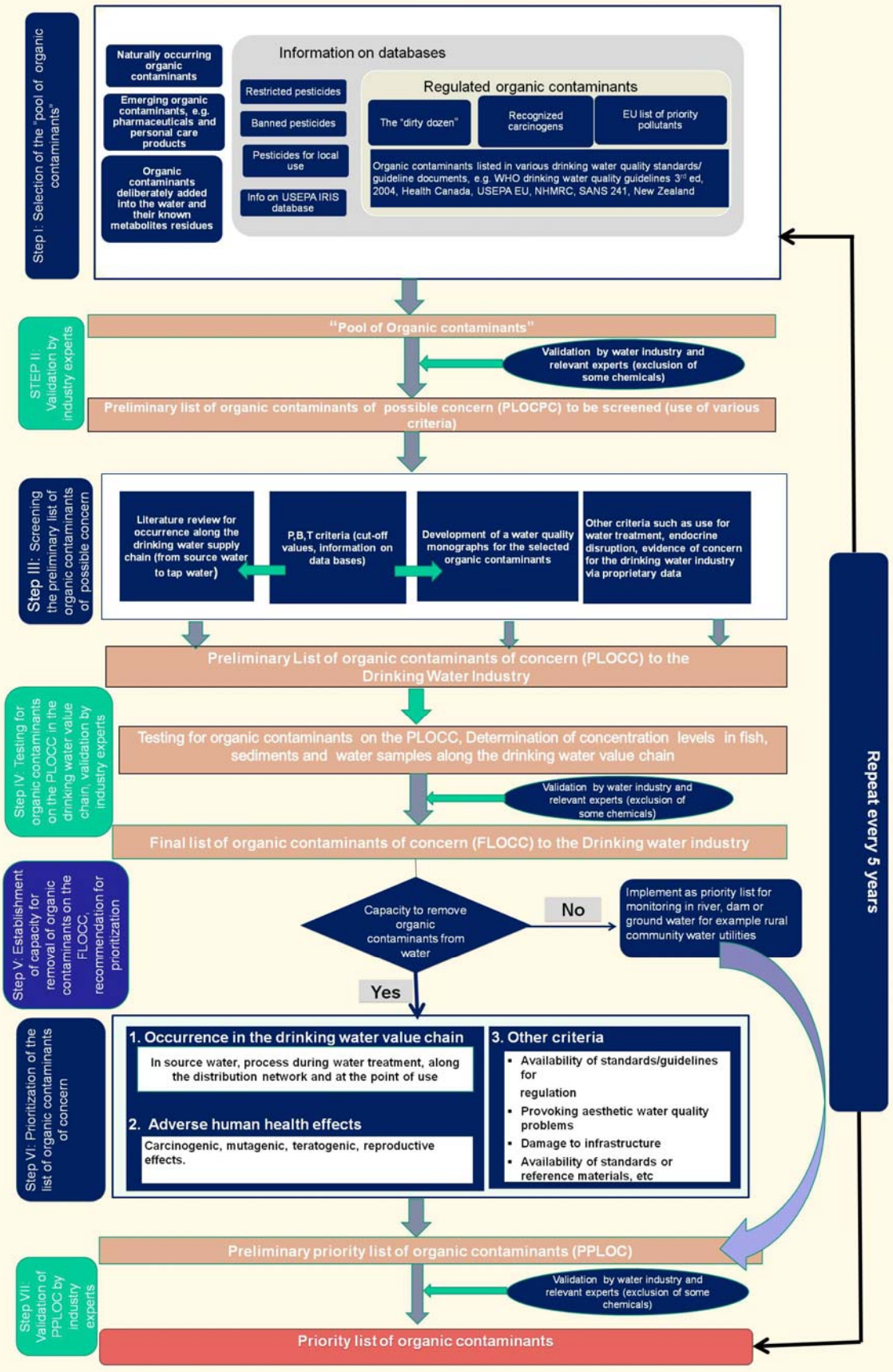


Figure 3.2 A generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain.

## 3.3 The selection and prioritization approach

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Table 3.4: Cut-off values for selected parameters

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

#### 3.3.3.3 Step III: The development of Water quality monographs

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

Table 3.5: Water Quality Monograph template

## A. GENERAL INFORMATION

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

## B. OCCURENCE

## C. PROPERTIES/STRUCTURE

## D. FATE AND BEHAVIOUR

## E. MEASUREMENT

## F. HUMAN EXPOSURE

## G. TOXICOLOGY

## REMOVAL DURING WATER TREATMENT

## I. NATIONAL AND INTERNATIONAL DRINKING WATER CRITERIA

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

## J. GENERAL DISCUSSIONS

## K. REFERENCES

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

**A. General information**

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

**B - Occurrence**

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

**C - Properties/structure**

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

**D – Fate and Behaviour**

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

**E - Measurement**

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

**F - Human exposure**

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

**G –Toxicology**

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

**H - Removal during water treatment**

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

**I - National and international drinking water quality criteria**

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

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

**J - General discussion**

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

**K-References**

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

#### 3.3.3.4 Step III Use of other criteria

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

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

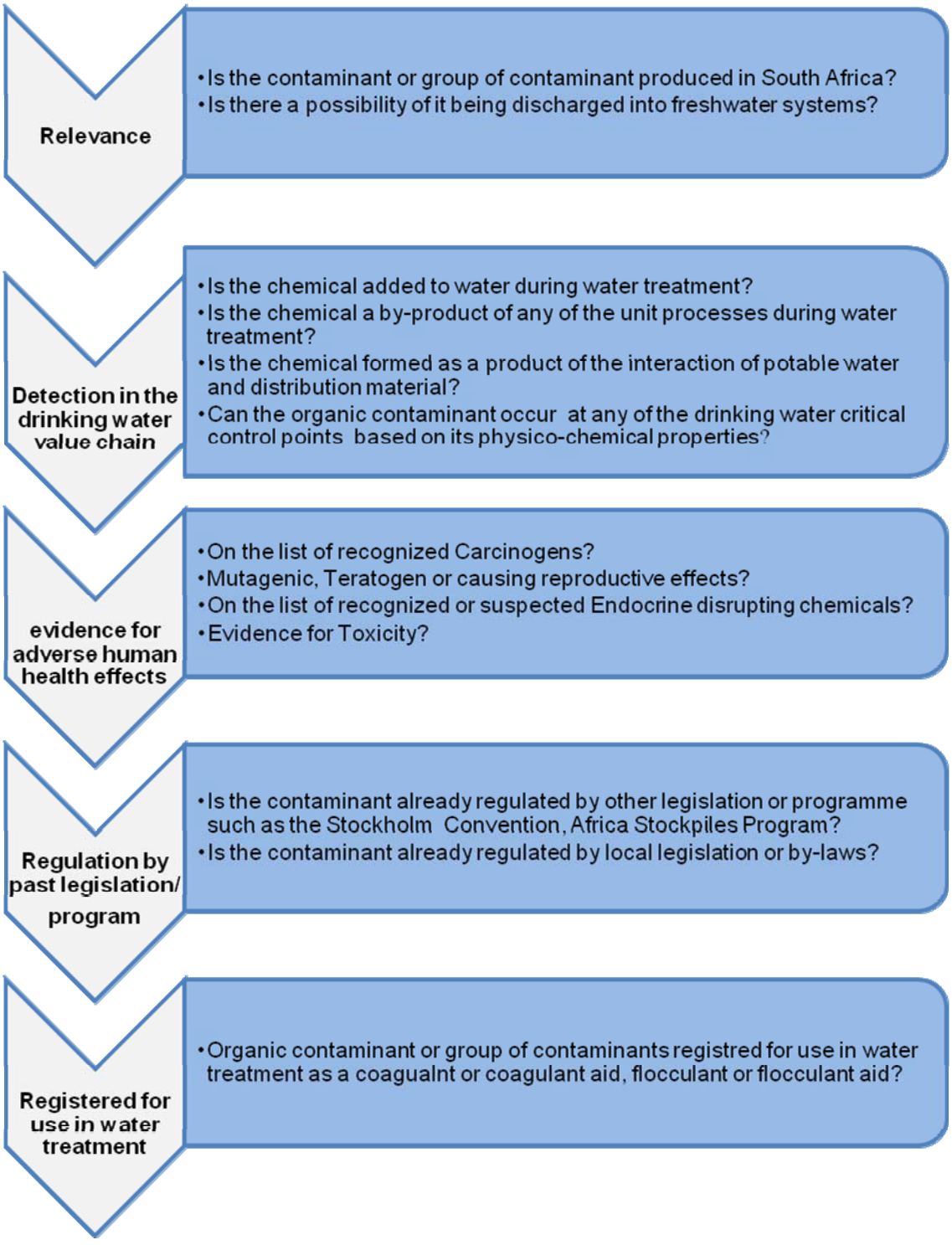


Figure 3.3 Other criteria for screening the preliminary list of organic contaminants of possible concern.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

### 3.3.6.2 Step VI: Adverse human health criterion

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

At this stage, the prioritization approach identifies;

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

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

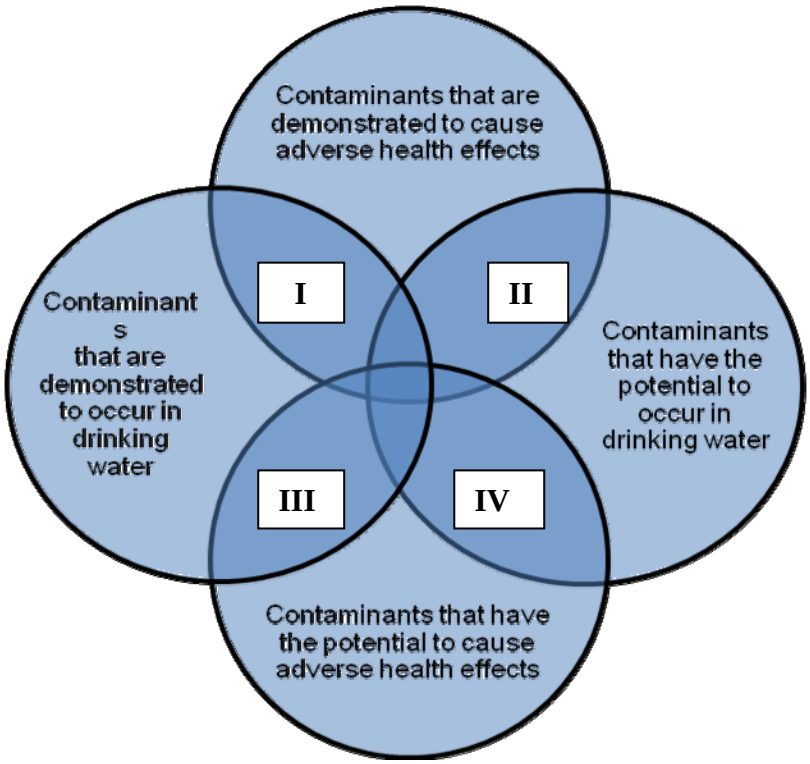


Figure 3.4: Prioritization criteria for drinking water contaminants-modified from the USEPA. [15]

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

#### 3.3.6.3 Step VI: Other criteria

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

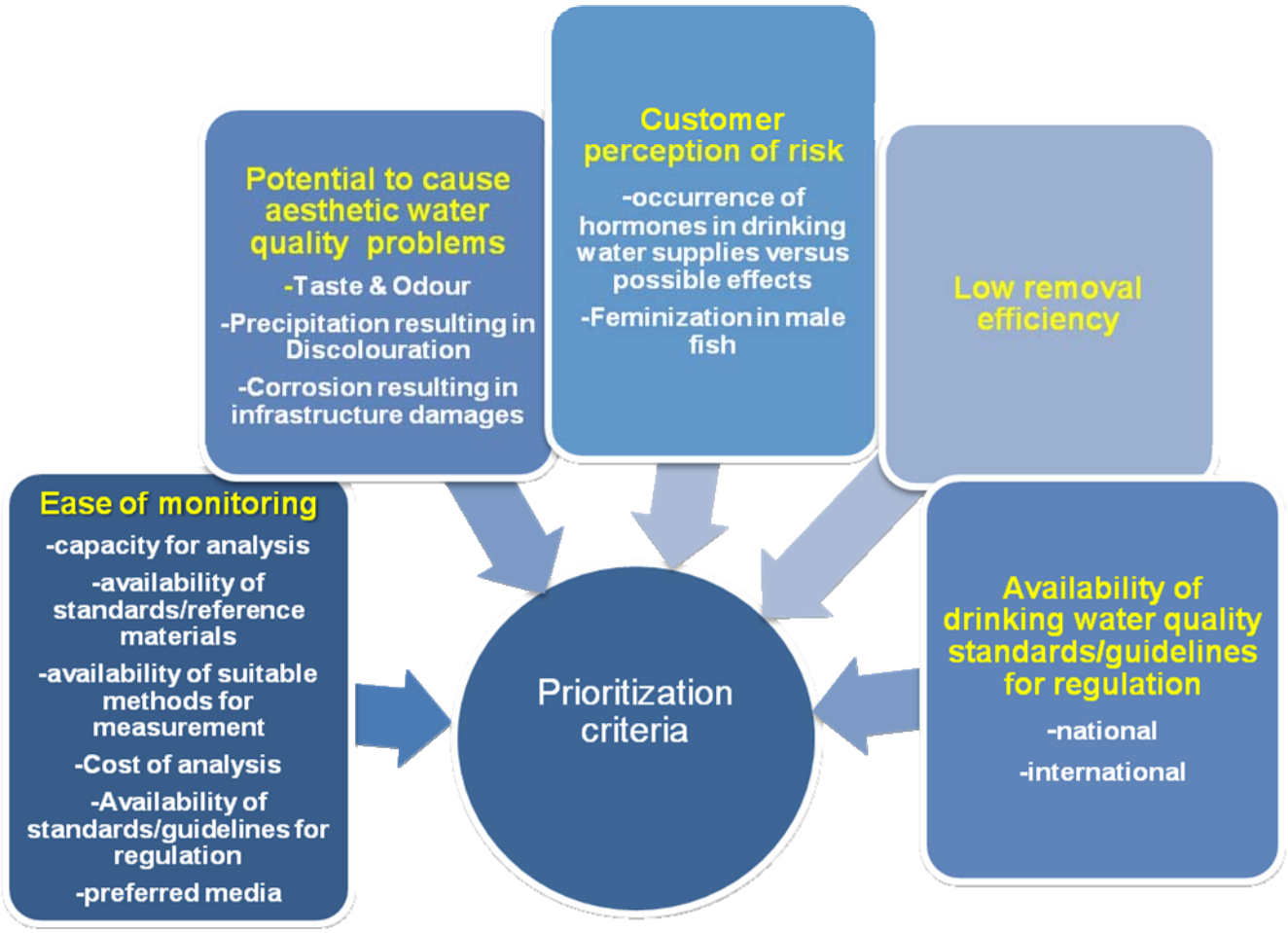


Figure 3.5: Prioritization criteria for the substances on the FLOCC

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

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

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

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

-No resources in place to support ease of monitoring;

-Removed from drinking water using conventional water treatment methods;

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

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

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

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

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

### 3.3.8 Review of priority list

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

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

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