CHAPTER 5 GENERAL DISCUSSIONS AND CONCLUSIONS

5.1 INTRODUCTION

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

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

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

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

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

<table>
<thead>
<tr>
<th>Other Names</th>
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<tbody>
<tr>
<td>1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester; Phthalic acid, bis(2-ethylhexyl) ester; Bis(2-ethylhexyl) 1,2-benzenedicarboxylate; Bisoflex 81; Compound 889; Di(ethylhexyl) phthalate; Dioctyl phthalate; DEHP; DOP; Ethylhexyl Phthalate; Eviplast 80; Eviplast 81; Fleximeter; Flexol DOP; Kodaflex DOP; Octoil; Octyl phthalate; Palatinol AH; Phthalic acid diocyl ester; Pittsburgh PX-138; Sicil 150; Staflex DOP; Trufflex DOP; Vestinol AH; Vinicizer 80; Witcizer 312; 1,2-Benzene dicarboxylic acid, bis(ethylhexyl) ester; 2-Ethylhexyl phthalate; o-Benzenedicarboxylic acid, diocyl ester; Dioctyl-o-benzenedicarboxylate; Bis-(2-ethylhexyl)ester kyseliny ftalove; DAF 68; Di(2-ethylhexyl)orthophthalate; Ergoplast fd; Good-rite gp 264; Hatcol dop; Mollan O; Nuoplaz dop; Platinol ah; Platinol dop; Rcre waste number U028; Reomol dop; Reomol D 79P; Ergoplast FDO-S; Bis(2-ethylhexyl) o-phthalate; DOF</td>
</tr>
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</table>

It is crucial for the person compiling this list to accurately identify the organic contaminants otherwise an inaccurate list can be used. An attempt was made to clean the list of all the unnecessary and irrelevant compounds or groupings which appeared after the amalgamation of the respective lists such as inorganic pesticides, plant extracts, inorganic essential oils, human medicinal estrogens, chlorinated benzenes, diesel engine exhaust, dialkyltins, foaming agents, solvents, hydrolyzed proteins just to mention a few examples. For the protocol to work individual organic contaminants or groups of contaminants that can be accurately quantified or an indicator chosen for them should be used. Examples that fall in this category are Polynuclear aromatic hydrocarbons, Polychlorinated biphenyls, Halogenated aromatic compounds, typified by the polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and diphenylethers (PCDEs), are industrial compounds or byproducts which have been widely identified in the environment and in chemical-waste dumpsites. Halogenated aromatics are invariably present in diverse analytes as highly complex mixtures of isomers and congeners and this complicates the hazard and risk assessment of these compounds. Several studies have confirmed the common receptor-mediated mechanism...
of action of toxic halogenated aromatics and this has resulted in the development of structure-activity relationships for this class of chemicals. [8] The most toxic halogenated aromatic is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and based on in vivo and in vitro studies the relative toxicities of individual halogenated aromatics have been determined relative to TCDD [i.e., toxic equivalents]. [8] As a result such a compound can be used to represent the group of contaminants on the “pool of organic contaminants” and not “dioxin-like organic compounds” or “polychlorinated or polybrominated aromatic organic compounds”.

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

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

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

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

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

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

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

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

A \rightarrow C \text{ will indicate potential occurrence while;}
D \rightarrow G \text{ will indicate demonstrated occurrence in the drinking water value chain hence the placement of the organic contaminant on the priority list of organic contaminants for monitoring in the drinking water value chain.}

This arrangement extended the screening process especially the occurrence criterion resulting in a four tier process. The first tier being the verification through the literature survey, followed by the development of water quality monographs, expert input and finally the assessment of concentration levels of organic contaminants in the matrix of interest along the drinking water value chain. For industrial organic contaminants, the potential for occurrence in the drinking water value chain may be estimated using a combination of production volume information and water solubility. Those of concern will show high production volumes and high water solubility.
indicating high possibility of recharge. However, getting this data has proved to be difficulty, hence the use of qualitative approaches. Based on the above analyses, a contaminant which was positively identified in any part of the drinking water value chain during the testing exercise will therefore be placed on the priority list.

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

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

- **Nondetect = value for the method reporting limit (MRL), a most conservative assumption for a risk assessment, because it will tend to bias data on the high side.** When this approach is used, there is a high degree of confidence that the analyte is probably present, but at a level that is at or just below the MRL.
- **Nondetect = value of 0, indicating that the analyte is absent.** This assumption is a nonconservative approach because it potentially will bias data on the low side. Assigning a value of 0 may be acceptable if it is highly unlikely that the analyte is present in the sample. An example would be the case for background samples where there is no history of the target analyte being detected.
- **Nondetect = “no value” given.** This is different than providing a value of “0” in as much as “0” value does having meaning if a statistical analysis of the data is performed. The “no value” approach is also a nonconservative approach.
• Nonndetect = value that is 1/2MRL. This is "middle-of-the-road- approach" where it is possible that the analyte would be detected in the sampling location and it "could be" as high as 1/2MRL.

• Nondetect = value that is the percentage of not detects (NDs) in a data set multiplied by the MRL. This is a statistical approach that takes into consideration the number of ND reports in relation to the overall number of data points in the data set. As an example if there are 25% of the data were NDs. Therefore 25% of the MRL would be the value given to the ND data.

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

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

The behaviour of S-Triazine herbicides in the drinking water value chain also indicated the importance of considering degradation products when managing organic contaminants in the drinking water value chain. S-Triazine herbicides have been found to form stable degradation products under both aerobic and anaerobic conditions in the environment. [Table 5.2] Transformation products of organic contaminants have the potential to be similarly or even more mobile, persistent or toxic than their parent compounds. These should therefore be
included in the assessment of water quality, sediment and biota in order to safeguard human health. [5]

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

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

<table>
<thead>
<tr>
<th>TRIAZINE HERBICIDE</th>
<th>DEGRADATION PRODUCTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>Deethylatrazine(DEA)</td>
</tr>
<tr>
<td></td>
<td>Deisopropylatrazine (DIA)</td>
</tr>
<tr>
<td></td>
<td>Hydroxyatrazine (HA)</td>
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<td>Didealkyl atrazine (DDA)</td>
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<tr>
<td></td>
<td>Deethylhydroxyatrazine (DEHA)</td>
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<tr>
<td></td>
<td>Deisopropylhydroxyatrazine (DIHA)</td>
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<tr>
<td></td>
<td>Dide alkylhydroxyatrazine (DDHA)</td>
</tr>
<tr>
<td>Simazine</td>
<td>DIA</td>
</tr>
<tr>
<td></td>
<td>Monodeethylsimazine</td>
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<tr>
<td></td>
<td>Hydroxysimazine</td>
</tr>
<tr>
<td>Propazine</td>
<td>DEA</td>
</tr>
<tr>
<td></td>
<td>Hydroxypropazine</td>
</tr>
<tr>
<td>Atraton</td>
<td>Deisopropylatraton</td>
</tr>
<tr>
<td>Terbutylazine (TBA)</td>
<td>Deethylterbutylazine</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>Deamino metribuzin (DAM)</td>
</tr>
<tr>
<td></td>
<td>Diketo metribuzín (DKM)</td>
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<tr>
<td></td>
<td>Deaminodiketometribuzín (DADKM)</td>
</tr>
</tbody>
</table>
5.2.4.1 Compiling the final list of organic contaminants of concern (FLOCC)

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

5.2.5 Establishing the capacity for the removal of organic contaminants on the FLOCC.

Recommendations for water utilities without capacity

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

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

This step is the most difficult of all steps presented for the protocol. During this step, it has to be decided, which of the organic contaminants is of priority for the protection of public health. Some researchers have proposed the use of prototype classification approaches such as using neural networks as proposed by the USEPA methodology discussed in section 2.2 of Chapter 2. In this study, the “occurrence criteria” as described in Figure 3.4 and the evidence of occurrence in environmental samples collected along the drinking water value chain and expert judgment was considered adequate for an organic contaminant to be placed on a “priority list of organic contaminants for monitoring in the drinking water value chain. For health effects, the
USEPA used severity and potency as attributes while prevalence, magnitude and persistence—mobility is used for the occurrence attributes. Given the complexity and time needed to assess these attributes for example, in the case of severity assessment, one needs to evaluate the disability adjusted life years lost from exposure to a contaminant which might further be complicated by confounding factors and complexity of experimental design when using human subjects. It was decided that for the prioritization process, criteria reflective of the Drinking Water industry needs and for use by the industry should be adopted. [Figure 5.2] The approach was successful.

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

Organic contaminants that fall into this category include surfactants, pesticides, pharmaceuticals and personal care products [PPCPs], plasticizers, petroleum products and polychlorinated dioxin-like compounds. Table 3.1 of Chapter 3 gives an estimation of the magnitude of this problem. Table 4.12 of Chapter 4 listed those organic contaminants that were positively identified in the drinking water value chain. S-Triazine herbicides especially Atrazine, DDT and its metabolites, Heptachlor and its epoxide, Dieldrin, Endosulfan and its isomers, Hexachlorocyclohexane isomers and Lindane were detected in most surface water systems worldwide. In South Africa, the mostly detected pesticides according to the literature and validation exercise include DDT and its metabolites and S-triazine herbicides like Atrazine, Simazine and Terbutylazine. Some old pesticides are still found in surface water systems. These include Endosulfan and its metabolites, HCH isomers, Aldicarb, Heptachlor and
Chlordane. Bisphenol A is an industrial compound manufactured in large quantities, most production being used as a monomer for the production of polycarbonate and epoxy resins. [9] Because of its ubiquitous nature and of its endocrine effects, it is an important organic contaminant. It has been shown to have an estrogenic effect on human health breast cancer cells. [9] Hence, it was prioritized in this study for monitoring in the drinking water value chain.

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

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

Availability of standards for regulating a contaminant
Although standards for safe drinking water are mostly guidelines developed by health organizations like the World Health Organization [WHO], Health Canada and the United States Environmental Protection Agency [USEPA] they play a significant role in regulation of contaminants with a perceived risk or proven risk for public health protection. The availability of
a standard or guideline for drinking water quality was enough proof that the contaminant needs to be prioritized. However, to do this, other aspects of relevance needed to be considered. Actual statutory standards or guidelines are not available for most organic contaminants. This is the case in most developing countries. Hence benchmarking with these organizations especially the WHO is considered the best practice.
Unlike professional toxicologists and scientists or medical doctors, consumers depend on reliable sources such as media for their public health protection. Reality has shown that with technological advancement customers have become more informed than ever. A good example, are developments in the field of “emerging organic contaminants” which is gaining research momentum at a fast rate. From the literature review it was evident that like the pesticides, PPCPs were the highly researched group of contaminants. Several pharmaceutically active compounds have been detected in surface water systems. Their presence in the drinking water value chain has caused serious public concern due to their perceived risks. Mostly effects from natural and synthetic hormones such as endocrine disrupting effects even at low concentrations and suspected synergistic effects of different hormones have been noted hence their addition to the priority list in this study. The hormones have been found to cause feminization in male fish at concentrations as low as 1ng/l. [9]

Potential to cause aesthetic water quality problems [Figure 5.2]

Water quality is the physical, chemical and biological characteristics of water. It is most frequently used by reference to a set of standards against which compliance can be assessed. The most common standards used to assess water quality relate to drinking water quality. The norm for setting these standards is public health protection through guaranteeing the safety of consumers. Once the quality is impaired and the water cannot be used for its intended purpose or purposes it constitutes a water quality problem. Water quality problems that are crucial to the water services provision business are organoleptic properties. The majority of customers that drink the water provided by water utilities have no insight into the chemical and biological characteristic of the water but can judge its safety using its appearance, taste and odour. This is regarded highest on the drinking water quality provision agenda as inadequate satisfaction of these qualities can force customers to use unsafe water sources or use home treatment devices which can render water unsafe for its intended use especially the children, immuno-compromised and the elderly. As a result, organic contaminants that contribute to taste and odour problems such as the BTEX group, chlorophenols, Geosmin, 2-Methylisrrnoneol and other cyanobacteria related toxins were considered as priority organic contaminants for having the potential to cause taste and odour problems in water as well as their potential adverse health effects.
Low removal efficiency [Figure 5.2]
Activated carbon filtration is an excellent treatment step for polar organic molecules. However, most water utilities cannot afford full operation on these filters or have them at all in their drinking water value chain. Evidence from the literature and validation exercise showed that some organic contaminants depending on their physico-chemical properties are not removed or are partially removed by conventional water treatment methods. The contaminants of concern in this case include cyanobacteria related compounds such as Geosmin and 2-MIB, PPCPs, some pesticides, disinfection by-products such as N-nitrosodimethylamine [NDMA] and detergents metabolites such as Nitrilotriacetic acid (NTA). The latter organic contaminants are very small and polar. They are also very mobile in the environment and difficult to remove using conventional water treatment methods even by those with activated carbon filtration resulting in them escaping the system and being detected in drinking water. Nanofiltration has been proposed for their removal. [9] The other concern about NDMA is that it is a member of a family of extremely potent carcinogens, the N-Nitrosoamines. The study by Stackelberg et al. [2007] [10] indicated that combined water treatments [clarification, disinfection and GAC filtration] were effective at degrading or removing many organic compounds from source water supplies to concentrations below analytical detection. However, the concern is inadequate knowledge of the effects of these compounds at those low levels.

Ease of monitoring [Figure 5.2]
Although an organic contaminant or group of organic contaminants can be identified as a priority organic contaminant for monitoring in the drinking water value chain, it is crucial that the ease of monitoring in terms of the following elements be satisfied. It was noted however, that this can be a national or regional challenge which has to be addressed by each utility depending on available resources. The aspects to consider include assessing the capacity for analysis, the availability of standards/reference materials, the availability of suitable methods for measurement, the cost of analysis, possibility of increasing or decreasing the frequency of analysis depending on the availability of resources and preferred media for optimal coverage of contaminants of concern.

5.3 General conclusions
The aim of this study was to develop a generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain. This aim has been fully achieved both on a theoretical and practical level. The initial step was a critical evaluation of the literature for approaches used for selecting and prioritization of organic variables of priority to the drinking water industry. This objective was successfully conducted resulting in a simple
model. A generic protocol for the selection and prioritization of organic contaminants for monitoring in the drinking water value chain has been successfully developed and validated in a prototype drinking water value chain. This covers objectives 2 and 3 of this study. The area in which the protocol was tested is one of the biggest water utilities in Africa and the assessment covered the whole drinking water value chain from catchment to tap.

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

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

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

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

Tailor made prioritization criteria reflective of the Drinking Water industry perspective are important and has proved to be successful in selecting and prioritizing organic contaminants for monitoring in the drinking water value chain. The organic contaminants in the current study were successfully prioritized in three classes, short-term priority for analysis, medium term priority for analysis and long term priority for analysis. This is a very important guide for water
utilities to assist in optimizing their resources while not compromising the role of public health protection.

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

5.4 References

CHAPTER 6 GENERAL RECOMMENDATIONS

6.1 INTRODUCTION

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

6.2 Disseminating the protocol

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

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

6.3 Recommendations on the implementation of the protocol

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

The protocol’s objective is to enable the water utilities to be able to select and prioritize organic contaminants for monitoring in their drinking water value chains. This process should be transparent and facilitate public participation as well as to learning by doing in order to control uncertainties. The adaptive management approach stresses the need for practical action in the face of uncertainty, it also emphasizes the need to tailor made management decisions to the nature and quality of information available at any moment in the process. It is recommended
therefore that in implementing this protocol, water utilities should use criteria reflective of their needs as proposed in this study and follow iterative process until they get products that are sustainable and applicable. Based on this, there is a need to iteratively test and refine the selection and prioritization approach. This will include elements such as evaluative criteria for each phase, adaptive learning process, characterizing data quality, transparency and use of expert judgment.

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

6.3.1 Recommendation for automation of protocol components

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

Biannually monitor and assess the drinking water value chain for occurrence against WHO drinking water quality guidelines or other relevant criteria

New contaminants with potential adverse human health effects identified?

Do not include in priority list

Yes

Add to the organic contaminant priority list for future action, develop water quality monograph in order to build a profile for the contaminant or group of contaminants according to Table 3.5 of the Protocol

Implement controls, if necessary adjust unit processes for adequate removal, develop methods for measurement in drinking water

Adaptive Implementation

Review, refine priority list

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

E.J. Ncube

University of Pretoria - 2009
6.4 **Recommendations on capacity building**

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

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

6.4.1 **Recommendations on the use of water quality monographs**

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

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

- Plant operators in the optimization of unit processes or to determine which method to use for the optimal removal or a particular group of organic contaminants.
• Analytical scientists and Managers in deciding which method to use for the measurement of a particular contaminant or group of contaminants in a particular matrix of interest. The information will also assist them in deciding whether to use target analysis or multi-residue approach.

• Water quality Assurance Managers in developing risk assessment measures as the water quality monographs contain all health risk and water quality risk related information for a particular organic contaminant or a group of organic contaminants.

• Operation Managers in deciding which water treatment chemicals to use in optimizing unit processes and how to manage challenges that come with it such as impurities in original chemicals and water treatment residues that are produced as a result of their use. This forms part of the requirement of the Water Safety Plans and is the first critical control point to manage in ensuring safe drinking water.

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

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

6.5 Recommendations for testing in environmental samples

In this study, organic contaminants were sampled twice a year. This arrangement could be ideal for some pesticides based on seasonal patterns of growth and harvesting periods. It is therefore recommended that in light of growing activities in catchments, more advanced techniques should be developed for the measurement of organic contaminants in the drinking water value chain. Although relevant databases and lists exist for many categories of potential drinking water contaminants, other categories have no lists or databases, for example the
emerging organic contaminants” or products of environmental degradation. Such organic contaminants or groups of organic contaminants need to be identified from the literature for accurate testing. It might be prudent to consider toxicity testing followed by analytical chemistry measurement methods such as IC-MS and GC-MS. Based on physico-chemical properties and available data, those compounds that degrade into metabolites should be identified and monitored along the drinking water value chain. Such are metabolites of the S-Triazine herbicides. [Table 6.1]

6.6 Recommendation for further research

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

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

<table>
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<tr>
<th>TRIAZINE HERBICIDE</th>
<th>DEGRADATION PRODUCTS</th>
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<tbody>
<tr>
<td>Atrazine</td>
<td>Deethylatrazine (DEA)</td>
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<td></td>
<td>Deisopropylatrazine (DIA)</td>
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<tr>
<td></td>
<td>Hydroxyatrazine (HA)</td>
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<td></td>
<td>Didealkyl atrazine (DDA)</td>
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<td>Deethylhydroxyatrazine (DEHA)</td>
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<td>Simazine</td>
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<td>Monodeethylsimazine</td>
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<tr>
<td>Metribuzin</td>
<td>Deamino metribuzin (DAM)</td>
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<td>Diketo metribuzin (DKM)</td>
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<td></td>
<td>Deaminodiketometribuzin (DADKM)</td>
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6.7 Recommendations for successful public health protection

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

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

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