EMERGING CONTAMINANTS IN WASTEWATER TREATED FOR DIRECT POTABLE REUSE: THE HUMAN HEALTH RISK PRIORITIES IN SOUTH AFRICA

CD Swartz, B Genthe, J Chamier, LF Petrik, JO Tijani, A Adeleye, CJ Coomans, A Ohlin, D Falk and JG Menge

VOLUME II: A PRIORITISATION FRAMEWORK FOR MONITORING CONTAMINANTS OF EMERGING CONCERN IN RECLAIMED WATER FOR POTABLE USE

WATER RESEARCH COMMISSION

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VOLUME II:

A PRIORITIZATION FRAMEWORK FOR MONITORING CONTAMINANTS OF EMERGING CONCERN IN RECLAIMED WATER FOR POTABLE USE

Report to the

Water Research Commission

by

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The outputs of this research project are presented in three separate publications:

Volume I: A concise research report (**WRC Report No TT 742/1/17)**
Volume II: A prioritization framework for monitoring contaminants of emerging concern in reclaimed water for potable use (**This report**)
Volume III: Occurrence, fate, removal and health risk assessment of chemicals of emerging concern in wastewater treated for potable reuse 9**WRC Report No TT 742/3/17**)

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EXECUTIVE SUMMARY

BACKGROUND

Wastewater reuse acts as a possible exposure pathway to a high number of emerging contaminants and their metabolites. Many of these compounds may pass through conventional wastewater treatment systems without removal and accumulate in potable water supplies. Thus, there is uncertainty over the magnitude of risk of human exposure to emerging contaminants of concern in wastewater treated for direct potable reuse. The possible presence of emerging contaminants in reclaimed municipal wastewater is of critical concern because of potential adverse impacts to human health. Specific health effects criteria in the evaluation of water recycling for human consumption include (1) primary health concerns of wastewater reuse that are the long-term health outcomes of ingesting chemical contaminants found in recycled water, (2) health risks of using recycled water as a potable water supply compared against similar risk by conventional water supplies, and (3) the need for extensive toxicity programs. This project was undertaken to identify the emerging contaminants of concern in reclaimed potable water, their sources, pathways and receptors, potential risk from exposure to these chemicals, indicative removal potential of these chemicals by water reclamation and wastewater treatment plants, and risks for potable water reuse.

AIMS

The aims of the project were as follows:

- Compile an up-to-date list of all types of emerging contaminants of concern in reclaimed potable water.
- Produce a report which identifies the sources, pathways and receptors by which these compounds enter drinking water systems, including resistance to wastewater treatment, their toxicity and the consequent potential risks from exposure to these chemicals.
- Draw up an assessment report on performance of water reclamation treatment systems and potential for failures in reliability and consequent risks for direct potable water reuse.
- Develop guidelines for implementation of appropriate treatment barriers, monitoring programmes and assessment programmes to eliminate or minimise risks.

This report (Volume II) comprises a detailed study focussing on the development of a list of priority compounds which should be monitored and methods for their detection for drinking water.

SUMMARY OF RESULTS

The table that follows shows a list of chemicals that are recommended as the first priority list of contaminants of emerging concern (CECs) for assessing water quality for direct potable reuse. The risk assessment that was undertaken has shown that the vast majority of the contaminants are reduced to insignificant levels during the treatment process (with the exception of 17α-ethinylestradiol). More research about hormones, their degradation products and possible treatment technologies are needed to better understand the risks in reclaimed water. It is suggested that further risk assessments are conducted including more contaminants as well as microbial risks.

GROUP	TYPE	CHEMICALS
Industrial chemicals	Flame retardants	TDCPP and TCEP
	X-ray contrast fluid	Iopromide
	PAH	Benzo(a)pyrene
Pesticides, biocides and herbicides	Herbicide	Atrazine
	Herbicide	Terbuthylazine
	Insecticide	Imidacloprid
	Pesticide	Simazine
Natural chemicals	Stimulant	Caffeine
	Hormone	17-beta estradiol
Pharmaceuticals and metabolites	Antiretroviral drugs	Lamivudine Stavudine
	Anti-epileptic drugs	Carbamazepine
	Anti-malarial drugs	Cinchonidine Cinchonine
	Analgesic	Paracetamol
	Antibiotic	Sulfamethoxazole
Personal care products	Anti-microbial	Triclosan
Household chemicals and food additives	Plasticiser	Bisphenol-A
Transformation products	By-product	N-Nitrosodimethylamine (NMDA)

RECOMMENDATIONS

With the rise in utilisation of chemical compounds on a daily basis, thousands of regulated and unregulated emerging contaminants have been discharged and detected in the aquatic environment. If not adequately treated, reclaimed water can serve as an exposure route for emerging contaminants. In order to conduct a thorough risk assessment of emerging micro-pollutants for humans, there is a need to put in place appropriate facilities for analysis; assess the exposure rate and the actual dose in order to predict the associated adverse health effects. During wide discussions within the water sector in the course of carrying out this project, including and in particular also the DWS, the conclusion was reached that it is imperative that a national (virtual) centre for analysis of contaminants of concern (including all specialised chemical and microbiological analyses) be established, consisting of a network of laboratories. More specifically, the following is recommended:

- That a national laboratory network for advanced water quality analysis be established, and that it will have the framework of a virtual centralised facility, but consisting of regional laboratory networks in four of the provinces, namely Western Cape, Gauteng, KwaZulu-Natal and Free State.
- It is the intention that the national laboratory network for advanced water quality analysis will:
  - Facilitate regional cooperation between the laboratories.
  - Propose validated, standard operating procedures.
  - Provide competitive analysis costs (different packages) for WSPs.

- Develop regional capacity and expertise
- Promote the exchange of scientific data and technical knowledge.

- Support (financial and institutional) by the Department of Water and Sanitation (DWS) will be crucial in ensuring the success and sustainability of the water reuse RLNs. DWS is the sector leader and as such needs to set the tone regarding the importance of credibility in water quality testing results. Private-public partnerships (PPP) could also be a viable option for this purpose, either as part of the Strategic Water Partners Network (SWPN) or similar thereto.
- A further important factor, and one that needs to be addressed from the outset, is the need for well-trained and experienced personnel and managers for the regional laboratory networks (RLNs). Follow-up projects by the WRC, WISA, Universities, Water Boards and EWSETA will be required to create and enabling climate for planning the staffing and career development in the RLNs. Capacity building initiatives in current WRC projects are already driving this strongly.

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ACRONYMS AND ABBREVIATIONS

ADI	acceptable daily intake
AOP	advanced oxidation process
AOX	adsorbable organic halogens
ASP	activated sludge process
AWT	advanced water treatment
AWTP	advanced water treatment plant
BAC	biological activated carbon
BNR	biological nutrient removal
BW	body weight
CCP	critical control point
CEC	chemical of emerging concern
COD	chemical oxygen demand
CSIR	Council for Scientific and Industrial Research
DAF	dissolved air flotation
DOC	dissolved organic carbon
DEAT	Department of Environmental Affairs and Tourism
DoH	Department of Health
DPR	direct potable reuse
DWA	Department of Water Affairs
DWS	Department of Water and Sanitation
EC	electrical conductivity
ED	exposure duration
EDCs	endocrine disrupting compounds
EDSP	Endocrine Disruptor Screening Programme
EDSTAC	Endocrine Disruptor Screening and Testing Advisory Committee
EE2	17α-ethinylestradiol
EEQ	estradiol equivalents
EIA	environmental impact assessment

ELISA	Enzyme Linked Immuno-sorbent Assay
ETEM	events triggered enhanced monitoring
GAC	granular activated carbon
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GWRC	Global Water Research Coalition
GWRS	groundwater replenishing system
HPC	heterotrophic plate count
HPLC	High Pressure Liquid Chromatography
IPR	indirect potable reuse
IR	intake rate
IWA	International Water Association
IX	ion exchange
LC	Liquid Chromatography
Lft	Lifetime
LRV	log removal value
MCDA	multi-criteria decision analysis
MF	Microfiltration
MLE	Modified Ludzack-Ettinger
MS	Mass Spectrometry
NF	Nanofiltration
NLNAWQA	National Laboratory Network for Advanced Water Quality Analysis
NOEL	no-observed-effect-level
NPR	non-potable reuse
NTMP	National Toxicity Monitoring Programme (South Africa)
O_3	Ozone
PAC	powder activated carbon
PAH	Polycyclic Aromatic Hydrocarbons
PBT	persistence, bioaccumulation and toxicity

PCB	Polychlorinated Biphenyls
PFC	Perfluorinated compound
PFOS	Perfluorooctanesulfonic acid
PI	performance indicator
POP	persistent organic pollutants
PPCPs	pharmaceuticals and personal care products
QSAR	Quantitative Structural Analysis Relationship
REACH	regulation, evaluation, authorisation and restriction of chemicals
RO	reverse osmosis
SANS	South African National Standards
SCADA	supervisory control and data acquisition
TDI	tolerable daily intake
TDS	total dissolved solids
TECHNEAU	EU FP6 project
TEQ	Toxic Equivalency Factor
TOC	total organic carbon
TRI	toxic release inventory
TSS	total suspended solids
TTC	thresholds of toxicological concern
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV	ultraviolet irradiation
UV254	UV absorbance at 254 nm
WQG	water quality guidelines
WHO	World Health Organisation
WRC	Water Research Commission
WRP	water reclamation plant
WSP	water safety plan
WWTW	waste water treatment works

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

South Africa is a water stressed country, where the demand for water is fast approaching available supply. To cope with the scarcity of water and growing water supply demand, increasing attention has been given to the reclamation of water from wastewater sources for direct potable reuse. The use of treated wastewater for direct potable applications can play an integral role in meeting future water demands. However, wastewater reuse that has not been adequately treated can be a possible exposure pathway to a high number of emerging contaminants and their metabolites. Various definitions of these chemicals of emerging concern were examined and are covered in the all-encompassing definition provided by the US Geological Society (2014), namely:

> "Any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants." (definition from the US Geological Survey, 2014).

The possible presence of emerging contaminants in reclaimed municipal wastewater is of critical concern because of potential adverse impacts to human health. Given the thousands of chemicals that are potentially present in the aquatic environment and that information about chemicals of emerging concern (CECs) is rapidly evolving, a transparent approach needs to be used to select which chemicals of emerging concern need to be monitored, based on their potential for health effects and their occurrence in waters receiving discharge of wastewater treatment plant effluent and storm water. Numerous international studies have shown that a wide variety of chemicals of emerging concern are present in wastewater effluents, surface waters, and groundwater.

1.2 AIMS

The aims of the project were as follows:

- Compile an up-to-date list of all types of emerging contaminants of concern in reclaimed potable water.
- Produce a report which identifies the sources, pathways and receptors by which these compounds enter drinking water systems, including resistance to wastewater treatment, their toxicity and the consequent potential risks from exposure to these chemicals.
- Draw up an assessment report on performance of water reclamation treatment systems and potential for failures in reliability and consequent risks for direct potable water reuse.
- Develop guidelines for implementation of appropriate treatment barriers, monitoring programmes and assessment programmes to eliminate or minimise risks.

This report (Volume II) comprises a detailed study focussing on the development of a list of priority compounds which should be monitored and methods for their detection for drinking water.

CHAPTER 2: EMERGING CONTAMINANTS OF CONCERN – A REVIEW

2.1 INTRODUCTION

In the recent past, the increase in the human population as well as the production and consumption of pharmaceuticals and other chemicals related products have doubled and has contributed to the generation of different waste constituents originating basically from industries, agricultural activities, domestic operations, municipal treatment works, among others. The sources and occurrence of emerging micropollutants in the aquatic environment has been widely discussed and published in literature (Baker and Kasprzyk-Hordern, 2013). This is due to their environmental persistence, high pharmacological activities as well as psychoactive properties and other yet to be identified impacts on human, animals and aquatic species (Claessens et al., 2013). However, there is limited information regarding the environmental fate, and eco-toxicological behaviour of these compounds in the environment. Environmentalists consider water and wastewater originating from industrial, agricultural or municipal activities as potential sources of micropollutants in the environment. In addition, wastewater treatment plants, landfilling areas, and agricultural run-off are other routes through which these micropollutants enter the surface water. In spite of extensive published articles and reviews on the sources, occurrence, transport and fate of emerging micropollutants in the literature, very little information exists on the pathways, particularly from sources to receptors. This is not only due to lack of adequate data, but also related to interconnectedness of the complex physicochemical characteristics of the compounds.

The health effects associated with exposure of aquatic organisms to contaminants of concern, such as low sperm count, high incidence of certain cancers, the incidence of intersex fish within the water system, and others, have been documented in the literature. However, the human health effects associated with exposure to emerging contaminants have yet to be clearly established. Proper identification of contaminants of emerging concern that may have future implications on human health is considered necessary and requires attention.

2.2 CLASSES OF EMERGING CONTAMINANTS

Chemicals of emerging concern identified in reclaimed water can be broadly classified as follows:

- Pharmaceuticals and veterinary medicines (prescribed and over-counter drugs)
- Endocrine disrupting compounds (an exogenous compound that mimics or block hormonal functions in the body
- Personal care products (active ingredients in cosmetics, fragrances, soap, insect repellents, toothpastes, e.g. antiseptics (triclosan/triclocarban)
- Flame retardants (active ingredient incorporated into consumer products such as electronics, plastic and children's toys)
- Perflorinated and brominated substances (used as dirt-repellent coatings, spray for leather and textiles (Houtman, 2010; Fawell and Ong, 2012)
- Pesticides and herbicides
- Nanomaterials, among others

2.2.1 Pharmaceuticals

Pharmaceuticals are specially designed medicines or drugs meant for specific prevention of diseases in humans and animals (Fawell and Ong, 2012). Life would have been practically difficult without the availability of medical service and human healthcare deliveries (Agunbiade and Moodley, 2014). Today, there are thousands of pharmaceutically active substances distributed and available at various health centres and pharmacy stores globally. The most common pharmaceuticals detected in water, wastewater and even drinking water at low concentration are shown in Table 2-1: below.

Table 2-1: List of common pharmaceuticals present in water/wastewater

TYPES OF PHARMACEUTICALS	SPECIFIC COMPOUND
Analgesic / anti-inflammatories	diclofenac, naproxen, ibuprofen, ketoprofen, acetaminophen, indomethacine, ketorolac, clofibric acid, paracetamol, phenazone propyphenazone, fenoprofen
Cytostatics	cyclophosphamide, ifosfamide
Antibiotics	amoxicillin, ciprofloxacin, clarithromycin, crythromycin, sulfamethoxazole, doxycyclin, methronidazole, norfloxacin, ofloxacin, roxithromycin, sulfamethoxazole, sulfapyridin, tetracyclin, trimethoprim
X-ray contrast	diatrizoate, iopamidol, iopromide, iohexol, iomeprol
Anticonvulsants / tranquilisers	carbamazepine, 4-aminoantipyrine, antipyrin, codein
Liquid regulators	bezafibrate, clofibrate, gemfibrozil, fenofibric acid, acebutolol
Betablockers/anti-hypertensives	atenolol, sotalol, propanolol, celiprolol, metoprolol

(Sources: Deblonde et al., 2011; Jiang et al., 2013; Rivera-Utrilla et al., 2013)

Exposure to these anthropogenic as well as naturally occurring contaminants is somehow inevitable. Many come from everyday products such as shampoos, plastics, pharmaceuticals and flame retardants. Pharmaceuticals include antibiotics, anti-diabetics, anti-epileptic, antimicrobials, anti-anxiety medications, analgesics and anti-inflammatory drugs, antibiotics and bacteriostatics, anti-epileptics, beta blockers, blood lipid regulators, contrast media, cytostatics, hormones (including oral contraceptives), antidepressants and anxiolitics, musk fragrances, disinfectants and antiseptics (Richardson, 2008; Baker and Kasprzyk-Hordern, 2013). As a consequence of increasing diseases outbreak, more and more pharmaceuticals are being manufactured to prevent the widespread of such epidemic. Although many of the therapeutic drugs are fashioned to respond to quite a large range of health challenges at low physiological doses (mg/kg), some are more dynamic and can perform best at ng/kg concentrations than others. After accomplishing the specific functions in the body, they still interact even at low dose with multiple non-therapeutic receptors, which over the long term produces negative harmful effects on non-targeted receptors both in human and aquatic species (Daughton and Ternes, 1999).

In recent years, the occurrence or perhaps the study of chemistry of pharmaceuticals in aquatic environments have been the subject of extensive investigations among scientists, especially in the developed countries such as China, USA, Germany and European Union since the early nineties (Ternes et al., 2004; Ternes and Joss, 2006). The data on the concentration of these compounds in drinking water, groundwater, wastewater samples in Netherlands, Germany, Spain, Switzerland, Belgium, Canada, France, Austria and USA is available (Kolpin et al., 2002). The survey conducted by Osunmakinde et al.

(2013) highlighted the most possible prescribed pharmaceuticals used in private and public health sector in South Africa (Table 2-2). From the survey conducted, it was realised that the most prescribed drugs in the private health sector in South Africa was analgesics followed by non-steroid anti-inflammatory drugs, antihistamine and asthmatic while hypertensive drugs top the list of the most widely prescribed medicines in the public health institution. This was followed by analgesics, ARV and antibiotics. The prescription pattern determines the level of occurrence in the environment.

Table 2-2: List of most prescribed drugs in both private and public sectors in South Africa (Osunmakinde, 2013)

PRODUCT	DRUG	CLASS	PRESCRIPTION
Ridaq	Hydrochlorothiazide	Hypertension	12119557
Austell paracetamol	Paracetamol 500 mg	Analgesic	10712781
Pharmapress	Enalapril maleate & Hydrochlorothiazide	Hypertension	9751575
Vitamins B complex	Vitamins	Vitamins	7335796
Co-trimoxazole	Trimethoprim and sulfamethoxazole	ARV	6555480
Methyl salicyl	Methyl salicylate	NSAIDs	5759858
Metformin	Metformin Hydrochloride	Antidiabetic	5543892
Amoxycilin	Amoxycillin	Antibiotics	5320452
Adco-Dol	Paracetamol 450 mg, codeine, caffeine	Analgesic	6670821
Alcophyllex	diphenhydramine, theophyline & etofyline	Cough mixture	6257534
Allergex	Chlorpheniramine Maleate	Antihistaminic	6014431
DPH	Diphenhydramine	Antihistaminic	3944118
Panamor	Diclofenac sodium	Analgesic	3724619
Panado	Paracetamol 500 mg, codeine (8 mg)	Analgesic	2880919
Broncleer with cold	Diphenhydramine 125 mg, codeine	Cough syrup	2859364
Corenza C	Aspirin, Chlorprophenpyridamine	Colds & flu	2334721
Sinucon	Phenylpropanolamine	Anti-itchiness	2157663
Sinuend	Chlorpheniramine and phenyltoloxamin	Antihistamines	2086681

Pharmaceuticals differ in behaviour, chemical structure, and metabolism and as such their level of occurrence in aquatic environment varies from region to region depending on the consumption patterns (WHO, 2011a). Pharmaceuticals that are not completely metabolised by the body, are either excreted in their original or metabolised form. Most pharmaceuticals products are hydrophilic in nature, can easily breakdown and have a short life span (Fent, 2006). Depending on the local industrial output, the age of WWTP, and rainfall patterns, among others, significant amounts of the contaminants were conjugated, and escape the WWTPs and enter the natural aquatic environment (Baker and Kasprzyk-Horden, 2013). Pharmaceuticals enter WWTPs via multiple routes such as domestic sewage, urban wastewater, agricultural activities, showering and bathing and eventually enter the water cycle (Rodil et al., 2012).

While some escape the wastewater treatment plants based on their hydrophilic characteristics, others escape based on their solubility parameter and half-life breakdown in reclaimed water and are occasionally detected in drinking water treatment plants. Thus, continuous exposure to reclaimed water containing emerging pollutants whose fate, behaviour and transport remain poorly understood portend short and long-term environmental health risks to humans and other living organisms (Marcoux et al., 2013). The need to have a sustainable regulatory framework for the purpose of establishing a long-term environmental monitoring programme should not be ignored. This has stimulated research and development towards compiling a list of persistent emerging micropollutants that were not initially considered in most monitoring control systems but are regularly detected in direct reclaimed water (Farré et al., 2008).

2.2.2 Personal care products

Personal care products sometimes include pharmaceuticals; on the other hand, personal care products comprise vast numbers of chemical containing products such as cosmetics, preservatives, fragrances, toiletries among others (Daughton and Ternes, 1999). Most of these products either contain polycyclic musk or parabens applied to guard against bacterial infection. For instance, a disinfectant such as triclosan is widely used in large scale in the production of consumer products such as toothpaste and hand soap (Petrovic et al., 2003). In the same vein, benzophenone is often utilized as an active ingredient in the making of sun screen lotion. Personal care products enter the aquatic environment through showering, bathing, washing dishes, or recreational activities like swimming. Depending on the use and exposure level, personal care products may accumulate in aquatic organisms and cause different adverse health effects (Rahman et al., 2009).

2.2.3 Endocrine disrupting compounds

As far back as 70 years ago, it was discovered that certain compounds block or disrupt endocrine glands or hormonal system from functioning properly and affect the body metabolism. These groups of compounds were called endocrine-disrupting compounds or endocrine disrupting chemicals (EDCs) or hormonally active agents. In 2001, the European Commission included the EDCs in the comprehensive list of emerging contaminants (European Commission Report, 2001). The actual definition of the compounds has generated a series of controversies and as such the subject of EDCs is difficult to comprehend. In spite of diverse views regarding the definition, EPA (1997) defined EDCs as a group of compounds that could block or mimic the development of endocrine glands in the body responsible for the maintenance of reproduction. The most common potential EDCs widely identified in plastic waste are shown in Table 2-3 below. Diamanti-Kandarakis et al. (2009) defined EDCs as a special group of chemicals that interfere with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for development, behaviour, fertility, and maintenance of homeostasis (normal cell metabolism).

Table 2-3: List of substances potentially present in plastic waste (Marcoux et al. (2013)

SUBSTANCE CATEGORY	COMPOUNDS THAT MAY BE PRESENT IN PLASTIC WASTE
Phthalates	Diethyl phthalate (DEP), Di-n-butyl phthalate (DBP), Benzylbutylphthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), Dimethyl phthalate (DMP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP)
Flame retardants	Polybrominated diphenylethers (PBDE), Tetrabromobisphenol-A (TBBP-A), Hexabromocyclodecane (HBCD), Organophosphates
Nanoparticles	Carbon nanotubes (CNTs), AgNPs
Bisphenols	BPA, BPS
Alkyphenols	Nonylphenol, Nonylphenol ethoxylate, Octylphenol, Octylphenol ethoxylate
Linear Alkylbenzene Sulfonates (LAS)	N-butylbenzenesulfonamide (NBBS)
Organostannic compounds	Tributyltin (TBT), Triphenyltin (TPT), Tributylstannane
UV filters	Benzophenones

The subject of EDCs is wide and may include different substances, mostly biologically active chemicals, used in the production of many consumer and industrial products (drugs, pesticides and other plastics related consumer products). Thus, EDCs encompasses both natural and synthetic compounds. Among many potential disruptors, phthalates, phenolic compounds (bisphenol A, nitrophenols and chlorophenols) have recently received great interest in research and development due to their production and use in substantial tonnages.

These compounds possess estrogenic or androgenic activity on the target organisms and are mostly harmful even at trace level such as μgL−1 and ng L−1 range (Liu et al., 2009). Several studies have confirmed the presence of natural and synthetic estrogenic hormones in the aquatic environment at low concentration, although only very few studies did detect estrogenic compounds in drinking water (Fawell and Ong, 2012). However, they enter the water environment via agricultural runoff, human and livestock excretion, etc. Other EDCs include alkyl-phenols, dioxins, various drugs, synthetic birth control pills, pesticides, plasticizers, and phenolic products (Jackson and Sutton, 2008). While some may bio-accumulate others persist and can travel long distances across different nations as far as the North Pole depending on the weather situation. Some are pseudo-persistent and thus rapidly decompose in the environment within a short period of time. No comprehensive list of EDCs exists, because most of the new chemicals are being manufactured continuously.

2.3 SOURCES AND PATHWAYS OF EMERGING MICROPOLLUTANTS

Error! Reference source not found. Table 2-4 summarizes the potential sources of chemicals of emerging concern in the environment while the presence of pharmaceuticals, endocrine disruptors and degradation by products in the environment has continued to increase as a consequence of rapid population growth rate (Kolpin et al., 2002). In addition, the occurrence of different micropollutants in the water cycle seriously affects the water quality and obviously has attracted attention with regard to drinking water supplies to communities.

Table 2-4: Sources of emerging micropollutants in the aquatic environment

CATEGORY	IMPORTANT CLASSES	MAJOR SOURCES (DISTINCT)	MAJOR SOURCES (NON-EXCLUSIVE)
Pharmaceuticals	NSAIDs, lipid regulator, anticonvulsants, antibiotics, β-blockers and stimulants	Domestic wastewater (from excretion), hospital effluents	Sources that are not exclusive to individual categories includes: Industrial wastewater (from product manufacturing discharges) Landfill leachate(from improper disposal of used, defective or expired items)
Personal care products	Fragrances, disinfectants, UV filters, and insect repellents	Domestic wastewater (from bathing, shaving, spraying, swimming, etc.)	
Steroid hormones	Estrogens	Domestic wastewater (from excretion), run-off from CAFOs and aquaculture	
Surfactants	Non-ionic surfactants	Domestic wastewater (from bathing, laundry, dishwashing, etc.), industrial wastewater (from industrial cleaning discharges)	
Industrial chemicals	Plasticizers, fire retardants	Domestic wastewater (from leaching out of the material)	
Pesticides	Insecticides, pesticides and fungicides	Domestic wastewater (from improper cleaning, run-off from gardens, lawns and roadways, etc., agricultural runoff	

CAFOS: Concentrated animal feeding operations Sources: (Luo et al., 2014)

Figure 2-1 depicts generic pathways to receptors. Several investigations have confirmed the presence of pharmaceuticals and their byproducts in municipal wastewater and of course in drinking-water. Emerging micropollutants enter the freshwater system via point and diffuse sources. Conventional wastewater treatment plants (WWTPs) are not specifically designed to removal these compounds. Within the WWTPs, some of these compounds are completely broken down by biological processes while highly persistent ones escape the treatment plants and enter the surface water. The efficiency of WWTPs differ and compounds with low solubility but having high octanol/water partition coefficient are retained in the bottom sediment (Kidd et al., 2007). The concentration of these compounds is quite high in effluents and even in the particulate matter. Thus, WWTPs and untreated urban wastewater have been identified as a channel through which these compounds enter the surface water, groundwater and even drinking water (Radjenovic et al., 2008).

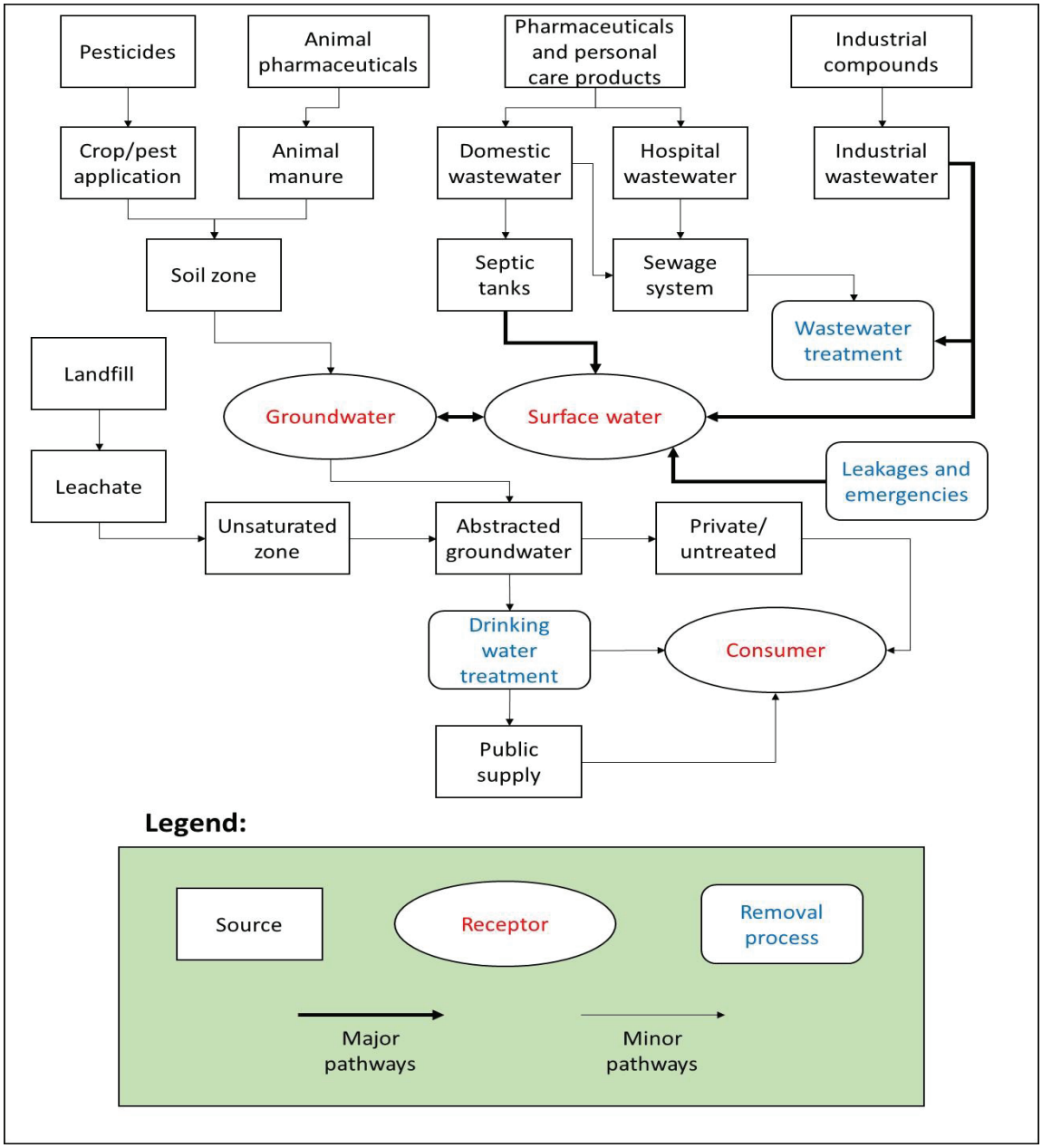

Figure 2-1: Potential sources and pathways of some emerging to receptors and aquatic environment (Stuart et al., 2012)

In most cases, high concentrations of biologically active compounds have been found in drinking water. The higher the population consumption rate the greater the concentration of the contaminants found present in the water cycles (Fawell and Ong, 2012). Furthermore, pharmaceuticals may enter the environment via human excretion, disposal of expired drugs, agricultural activities as shown in Figure 2-1. Barnes et al. (2002) detected an appreciable number of pharmaceuticals such as ciprofloxacin, erythromycin, codeine, carbamazepine, ibuprofen, salicyclic acid in surface and drinking water at low concentrations. Hospital waste water is another source through which contaminants such as disinfectants and musks, radioactive elements, heavy metals, and iodised contrast media get introduced into the aquatic system (Verlicchi et al., 2010; Watkinson et al., 2009). Gómez et al. (2006) detected 16 pharmaceuticals including anti-epileptics and anti-inflammatories in the hospital wastewater.

The use of veterinary medicines, landfill leachates, leaking of septic tank and sewer systems have been identified as other sources of EMs in USA and some parts of Europe. Manufacturing industries equally contribute a substantial amount of unregulated pollutants into our water ways. Other sources include pesticide application, animal manure and livestock activities. Other compounds also enter aquatic environments through recreational and domestic activities such as swimming, showering, bathing or clothes washing. According to Brook et al. (2006) the accidental discharge of PPCPs effluent to ecosystems were responsible for the spread of waterborne diseases that impacted negatively on human health. Buska et al. (2009) identified contaminants such as hormones, pharmaceuticals and flame retardant in the wells closer to landfill sites. More than 80 pharmaceuticals and personal care products detected according to Heberer (2002) originated from reclaimed water used for artificial groundwater recharge. Accidental spills could also be another source of EMs in the aquatic ecosystems. EMs also enter the environment via physical and chemical breakdown during disposal and recycling operations within wastewater treatment plants (WWTPs).

Thus, proper understanding of the variables within the WWTPs is a fundamental key point that determines whether a particular contaminant will be retained, bioaccumulate or perhaps persist in the environment (Gros et al., 2010; Pomiés et al., 2013). Jin et al. (2004) reported high concentrations of BPA in the rivers and marine environments in China, although the exploration of BPA has not been extensive especially in terms of monitoring data for drinking water. Jackson and Sutton (2008) observed that local sources such as poor sanitary sewer systems at different resident, commercial, and industrial locations in California contained high concentration of phthalates, triclosan, and BPA. It is imperative to understand and identify individual pathways into freshwater system as this will help to predict the associated future health risk. Although the concentrations of EM in the environmental matrices are very low, ranging between ngL^{-1} and µg/L a continuous exposure especially of aquatic species may have harmful effects while effects on human remain to be proven.

2.4 EMERGING MICRO-POLLUTANTS IN WATER SOURCES

The presence of emerging micropollutants in reclaimed water has become a global issue of considerable environmental concern (Deblonde et al., 2011; Lapworth et al., 2012). Several new environmental contaminants, both regulated and unregulated, have been identified in wastewater and reclaimed water due to lack of effective treatment technology strategies and thus become ubiquitous substances in the environment (Fent, 2008). However, the concentration of these compounds in the water cycle differ appreciably depending on their consumption and applications purposes. Investigations have shown that some pollutants were removed by WWTPs despite not initially designed for such purpose. Similarly, municipal wastewater treatment plants having secondary treatment have been reported to remove CECs.

Martin Ruel et al. (2012) demonstrated that about 70% of half organic and inorganic pollutants were removed by mere biological treatment. Vertilicchi and colleague (2012) in their review submitted that

elimination of pharmaceutical compounds by conventional activated sludge and membrane reactors was found to depend on the physic-chemical properties of the substances and the operational conditions with the treatment plant. However, the influence of the operating conditions such as temperature, half-life, hydraulic retention time, sludge retention time, hydrophilic character within the WWTPs remain poorly understood. Huerta-Fontela et al. (2010) submitted that the effective removal of emerging contaminants in WWTPs is considered a critical environmental component required for the protection and sustenance of water quality status. Thus, proper understanding of the various variables within the WWTPs is a fundamental key point that determines whether a particular contaminant will be retained, bioaccumulate or perhaps persistent in the environment (Gros et al., 2010; Pomiés et al., 2013). The presence of emerging organic contaminants in reclaimed water meant for direct re-use has over time become a considerable source of environmental concern due to their environmental persistence and high biological activity (Baker and Kasprzyk-Horden et al., 2013; Claessens et al., 2013).

At the moment, research is focused on the persistent emerging contaminants that interfere with the endocrine system (Gavrilescu et al., 2014). Hanh et al. (2012) have demonstrated that despite the prohibition of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) twenty years ago, most of these substances are still being detected at high concentration in wastewater and reclaimed water. Moreover, Kümmerer (2009) and Claessens et al. (2013) reported that persistent pharmaceuticals such as trimethoprim, ibuprofen, salicyclic acid, lipid regulator bezafibrate, β-blockers propranolol and carbamezepine are widely found at low or higher concentration in reclaimed water depending on the population and consumption pattern. Other persistent pharmaceuticals identified in the environment include: paracetamol and atenolol (Yamamoto et al., 2007; De André et al., 2009).

Deblonde et al. (2011) identified and quantified emerging pollutants such as phthalates, Bisphenol-A, PCBs, polyaromatic hydrocarbons, pharmaceuticals in the wastewater influents and effluents. The authors described pharmaceuticals such as analgesics, anti-inflammatories and beta-blockers as being most persistent and resistance to conventional treatment. The classification or inclusion of a particular substance on the list of priority emerging contaminants is based on a series of factors such as persistency in the environment, extensive industrial applications, possession of EDCs properties, occurrence either naturally or synthetically, water solubility and among others (WRC, 2003). In the same vein, Bolong et al. (2009) reported the occurrence level of EDCs such as Nonylphenol, Estrone (E1), Estradiol (E2) Ethinylestradiol (EE2) in municipal wastewaters, surface and drinking in Germany, United Kingdom and Japan respectively. However, the concentration level varied due to difference in the WWTPs performance, population and consumption pattern.

Swartz and colleagues (2008) utilized bioassay techniques to identify emerging contaminants in the reclaimed water obtained from the wastewater reclamation plant in Windhoek. The study demonstrated the presence of nonyphenol, estrone, ethinylestradiol, bisphenol-A, microcystin in Gammams raw and Goreangab raw water. The concentrations were however different with respect to season and the treatment technique adopted. Bookers et al. (2014) enumerated persistent anticancer drugs such as tamoxifen, methotrexate, cylcophosphamid, ifosfamid, mitotane, sorafenib, sunitinib 5-fluorouracil and lapatinib during the survey conducted on some hospitals' wastewater, sewage influents and effluents as well as surface water in North West England. While epirubicin, doxorubicin, capecitabine, cytarabine anticancer drugs were identified pseudo-persistent in the environment based on their half-life. Others may bioaccumulate onto suspended solids and enter the environment. Nonetheless, Bookers and colleagues recommended that the identified compounds should be included in environmental screening programmes. Shaw (2011) categorised polybrominated diphenylethers (PBDEs), triclosan, triclocarban, phthalates and bisphenol-A as priority emerging contaminants of the greatest concern based on their impact on the endocrine system.

Thus, the occurrence of these priority pollutants varies from region to region and could depend on the number of drugs consumed by the population, toxicity and persistency of the compounds once released into the aquatic environment. The contamination of the freshwater environment by biologically active

compounds has become a serious environmental issue due to associated health effects on humans and other living species. Emerging micropollutants that pass through WWTPs were later detected in finished drinking water. The movement of these compounds from wastewater treatment plants into the freshwater environment can be best illustrated using a sources-pathways-receptors concept. The aquatic environment acts as a sink for different kinds of pollutants (Bolong et al., 2009). The pathways taken from the sources vary and are not very clear but mostly depend on the solubility properties of the compounds in questions (Baker and Kasprzyk-Horden, 2013). Humans are exposed to emerging contaminants via different routes such as oral administration (pharmaceuticals), consumption of contaminated vegetables and fruits, air inhalation and drinking water. Considering the numbers of channels through which humans are exposed to these contaminants, there are concerns about human health regarding exposure to emerging micropollutants in drinking water. Receptors also include human beings that consume the tap water, aquatic species as well as other living creatures in the ecosystems. At the moment, there is limited information linking human health effects to exposure to EMs via drinking water, however long-term associated risks of consuming drinking water containing EMs should not be ignored.

In South Africa, two detailed studies funded by the Water Research Commission were recently conducted to initiate selecting CECs relevant for the country (Patterton, 2013; Osunmakinde et al., 2013). In additional to these two projects, an additional project funded by the commission identified chemicals of environmental concern related to agricultural activities (Dabrowski et al., 2014). Patterton (2013) conducted a scoping study on emerging contaminants in drinking water with initial drinking water samples in 2 cities in South Africa screened for more than 600 polar, water soluble compounds. A more detailed screening survey extended to7 cities in South Africa showed 32 compounds, comprising predominantly pharmaceuticals and pesticides, to be present in drinking water (Table 2-5).

Table 2-5: Screening in 7 cities over 4 seasons (Patterton, 2013)

ANALYTE	DESCRIPTION	ANALYTE	DESCRIPTION
Benzocaine	Anaesthetic	Ephedrin	Bronchodilator
Paracetamol	Analgesic	Diphenylamine	Fungicide
Temazepam	Antianxiety	Imazalil	Fungicide
Flecainide	Antiarrhythmic	Thiabendazole	Fungicide
Nalidixic acid	Antibiotic	Atrazine	Herbicide
Sulfisomidine	Antibiotic	Hexazinone	Herbicide
Carbamazepine	Anticonvulsant / antiepileptic	Metazachlor	Herbicide
Oxcarbazepine	Anticonvulsant / antiepileptic	Metolachlor	Herbicide
Phenytoin	Antiepileptic	Propazine	Herbicide
Fluconazole	Antifungal	Tebuthiuron	Herbicide
Telmisartan	Antihypertensive	Terbumeton	Herbicide
Atenolol	Antihypertensive	Terbuthylazine	Herbicide
Minoxidil	Antihypertensive vasodilator	Imidacloprid	Insecticide
Cinchonidine	Antimalarial	Alachlor	Pesticide
Cinchonine	Antimalarial	Sebuthylazine-desethyl	Pesticide
		Simazine	Pesticide

The top 4 compounds detected in the water samples included atrazine, carbamazepine, cinchonidine and terbutylazine. The study carried out by Osunmakinde et al. in 2013 involved compiling a priority list of target analytes relevant to South Africa based on data collected from the health sector (Table 2-6). The

prescription volume of drugs was considered, and in some cases the stability of the drugs was also taken into account. The compounds were often the same as those commonly detected in water systems worldwide. The target compounds from a South African perspective can be grouped into different classes, namely hypertension, analgesics, antiretroviral, antibiotics, hormones and anti-diabetic drugs. Using the prescription data, a suggestion can be made of the amounts in which these contaminants may be found in wastewater. As most pharmaceutical compounds have different persistence and bioaccumulation factors, high prescription values do not necessarily result in high concentrations in the wastewater.

Table 2-6: Most prescribed drugs in public health sector in South Africa grouped according to the class of drug (Osunmakinde et al., 2013)

Drug	Drug Type
Paracetamol	Analgesic
Lamivudine	Analgesic
Albendazole	Antihelmintic
Chlorphenoxamine hydrochloride	Anti-Allergic
Chloramphenicol; Amoxycillin; Ampicillin; Ceftriaxone; Furosemide	Antibiotics
Hydrocortisone acetate	Corticosteroid
Co-trimoxazole; Lamivudine; Efavirenz; Stavudine; Tenofovir disoproxil fumarate	ARV
Salbutamol Sulphate	Asthma
Simvastatin	Cholesterol
Levonorgestrel & Ethinyloestradiol; Norgestrel; Norethisterone	Contraceptive enantate
Cocillana	Cough syrup
Metformin Hydrochloride; Gliclazide; insulin	Diabetic
Hydrochlorothiazide; Enalapril maleate & Hydrochlorothiazide; Amlodipine; Nifedipine; Perindopril; Medroxyprogesterone	Hypertension
Methyl salicylate	NSAID
Atenolol	β-blocker

Osunmakinde (2013) categorized most pharmaceuticals identified in Daspoort WWTP, Pretoria, South Africa water environment into six categories such as hypertension, analgesics, antiretroviral, antibiotics, vitamins and antidiabetic drugs. The results of the investigations revealed the presence of ribavirin, pindolol, famciclovir, carbamazapine, ketoprofen, fenoprofen and ibuprofen in different concentrations. Besides, the pharmaceuticals, bisphenol-A, Estrone (E1), 17β-Estradiol (E2), Estriol (E3), 17α-ethinyestradiol (17α-EE2) and Ethinyestradiol were equally detected in the wastewater. At the moment, the list of persistent emerging organic micropollutants in South Africa keeps growing owing to population growth, industrial activities and perhaps absence of standard regulatory and discharge limits. The list of persistent emerging micropollutants are enumerated in Table 2-7. However, among the listed EDCs in Table 2-7, the following substances were investigation based on their industrial use, production output, persistency level and prevalent rate in wastewater. The chemicals include: steroid oestrogens, alkylphenol polyethoxylates and their metabolites, carbamazepine, ibuprofen, triclosan, acetaminophen, phthalate esters, bisphenol A, as well as certain pesticides and polychlorinated biphenyl compounds.

Table 2-7: Priority list of emerging micropollutants to be monitored according to respective matrices (Osunmakinde et al., 2013)

Categories	Compounds
Hormones	17ß-Estradiol, Estriol, Estrone, 17a-Ethinylestradiol
Pesticides and herbicides	DDT, DDE, DDD, Dieldrin, Aldrin, Endrin, Isodrin, a-Endosulphan, ß-Endosulphan, Endosulphan-sulphate, Heptachlor, Heptachlor epoxide Lindane, Vinclozoli, Parathion Atrazine, Simazine, Terbutylazine
Industrial Chemicals	PCB (total), Glycol ethers p-Nonylphenol, p-Octylphenol, Phthalates: DEPH, DBP, nitrophenols, Bisphenol A
Heavy Metals	Cadmium, Arsenic, Lead, Mercury
Pharmaceuticals	Acetaminophen, caffeine, carbamazepine, ciprofloxacin, diclofenac, erythromycin, fluoxetine, gemfibrozil, ibuprofen, naproxen, naproxen, primidone, sulfamethoxazole, triclosan, trimethoprim

Furthermore, Rahman et al. (2009) submitted that chemicals of emerging concern such as the persistent organic pollutants (DDT, DDE, dieldrin, toxaphene), antibiotics, anti-neoplastics and steroid hormones require special monitoring in the environment. The South African investigation of contamination of water resources by agricultural chemicals and the impact on environmental health (Dabrowski et al., 2014) identified a list of priority pesticides based on volume of usage, toxicity, mobility into the water environment and persistence. The top 15 priority pesticides are presented in Table 2-8 below. The pesticides detected in Patterton's study in addition to being priority pesticides in the agricultural chemical project include atrazine, terbutylazine, imidacloprid and simazine.

Table 2-8: Top 15 priority pesticides in South Africa based on usage, toxicity, persistence and mobility to water environments (Dabrowski et al., 2014)

Rank	Active ingredient	Rank	Active ingredient
1	Atrazine	**9**	Imidacloprid
2	Mancozeb	**10**	Metolachlor
3	Acetochlor	**11**	2,4-D-amine
4	Ethylene-dibromide	**12**	Alachlor
5	Terbuthylazine	**13**	MCPA
6	Glyphosate	**14**	Simazine
7	Sulphur	**15**	Paraquat
8	Copper oxychloride		

In recent times, the occurrence of different classes of emerging micropollutants in South Africa environment has attracted the attention of the general public and the scientific community (Aneck-Hahn et al., 2009; Manickum and John, 2014). The level of these substances in the South African environment are comparable to the concentration determined elsewhere in the world, thus raising serious public concern about the safety of humans. Very recently, Agunbiade and Moodley (2014) reported the presence of caffeine, nalidixic acid, atenolol and acetaminophen predominantly at very high concentration in the estuary mouth and blue lagoon of Umgeni River water in KwaZulu-Natal, South Africa. Similarly, the scoping studies conducted by Patterton and colleagues (2013) on the status of South African drinking water sampled mostly from Johannesburg, Pretoria, Bloemfontein, Durban and Pietermaritzburg, Cape Town and Port Elizabeth over a period of four season revealed the presence of high concentration of pesticides such as atrazine, terbutylazine as well as pharmaceuticals (carbamazepine).

Other compounds such as hexazinone, phenytoin, and tebuthiuron (Durban), telmisartan, simazine, oxadixyl, metolachlor, amphetamine imidacloprid tebuthiuron (Johannesburg), and fluconazole, phenytoin and tebuthiuron (Bloemfontein), cinchonidine, were also quantified during the last three season. The differences in the concentration were ascribed to seasonal variation and dilution factors. The authors identified agricultural run-off, medical waste and pesticides, leaching of pharmaceuticals and pesticides into groundwater reservoirs as possible pathways through the contaminants enter the drinking water.

2.5 SUMMARY

There are concerns regarding the potential risk from exposure to different doses of pharmaceutically active agents in the environment (Fawell and Ong, 2012). With the rise in utilisation of chemical compounds on a daily basis, thousands of regulated and unregulated emerging contaminants have been discharged and detected in the aquatic environment. Depending on their fate and behaviour in the WWTPs and even in the drinking water treatment plants, the probability of human exposure to these compounds is high. In order to conduct a thorough risk assessment of emerging micro-pollutants for humans, there is a need to assess the exposure rate and the actual dose in order to predict the associated adverse health effects. Since the concentration of these compounds in water is low, the acute toxicity may be difficult to evaluate. Subsequently, the risk assessment might be technically hard to calculate based on the fact that long-term exposure data is lacking. Aquatic species are at greater risk for adverse health effects because their exposure to individual or combinations of these compounds is very high.

It has been established that feminization of fish in freshwater system is a direct result of exposure to certain endocrine disruptors. Further research is needed to know whether this exposure had a major impact on entire populations. Strauch (2011) affirmed that the effects of exposure to pharmaceuticals, endocrine disruptors on human toxicity irrespective of their concentration in the water supply is yet to be ascertained but research carried out by Ternes et al. (2004) revealed that estrogenic compounds have a very high bioaccumulation potential with considerable negative effects on aquatic organisms. This environmental bioaccumulation aggravates the abnormal hormonal control, causes reproductive impairments and persistent antibiotic resistant. This acute and chronic toxicity experienced by aquatic species such as fish upon exposure to these compounds in the freshwater system is similar to that of health effects caused by exposure to low concentration of metallic elements.

Studies conducted by Micheal (2001) also revealed that exposure of aquatic species to endocrine disruptors causes low sperm count and reproductive malfunctions. Safe (2000) also observed that exposure of aquatic organisms to organochlorines caused feminizations of fish and gulls, and sexual abnormalities in alligators. However, among the aquatic species, fish remain most susceptible to the high dose of these chemical substances. Studies have shown that exposure to diclofenac and 17α-ethinylestradiol in the aquatic environment induced structural deformities of kidneys and intestines as well as gene alteration thus affected the body's metabolic activities (Kümmerer, 2009). WFN and WWF, Zoological Society of London and Global Footprint Network "Living Planet Report 2014" states that "…for more than 40 years, humanity's demand on nature has exceeded what our planet can replenish. They note that "wildlife populations have more than halved since the 1970s and that freshwater species are declining fastest, with three quarters lost since the 1970s". They urge for collective action to set a new course for a sustainable future.

In addition to increasing occurrences of reproductive and developmental abnormalities in infants and children, recent reports of temporal downward trends in semen quality and testosterone levels as well as increased rates of testicular and thyroid cancers (Stuart, 2012) among adult male populations has generated concern regarding the potential risk of environmental endocrine disrupting chemicals (EDCs) to

men's health. Mackenzie et al. (2005) and Safe (2000) attributed the declining sex ratios in Canada and the United States to over exposure to EDCs.

The potential risk associated with drinking water consumption varies between compounds and often depends on the concentration, exposure time, volume, and metabolism rate. Currently, it is difficult to link human health effects to exposure to EMs due to the existence of background diseases in humans. Very recently, Standford et al. (2010) conducted a comparative survey on the rate of exposure to oestrogenic activity and other compounds presence in US drinking water, food, beverage, and air. The authors concluded that humans are only exposed to a small fragment of pharmaceutically active compounds via consumption of municipal drinking water and there is no evidence of adverse human health effects due to exposure to US drinking water. Fromme et al. (2009) assessed the rate of exposure to perfluorinated octanoic acid and oestrogenic hormone via consumption of Germany and US drinking water and found that the daily exposure rate with respect to population ranged between 0.7 and 2%. Thus, the level of individual or mixtures of pharmaceutically active substances in drinking water is currently considered to be too low to cause a considerable chronic or acute health effects on human. However, the extent of exposure still requires further studies.

CHAPTER 3: DETECTION AND MONITORING OF EMERGING CONTAMINANTS OF CONCERN

3.1 INTRODUCTION

A number of developments in both direct and indirect water reuse have taken place during the last two decades, of which the most important one is the gradual increase in the concern regarding emerging contaminants of concern in reuse water, which have accelerated during the past three years. These contaminants and chemicals include endocrine disrupting compounds (EDCs), and pharmaceuticals and personal care products (PPCPs). If water reclamation is to become a commonplace on a municipal level in South Africa, or any country, there will have to be competent laboratories that can perform the analyses required to ensure that WRPs are performing as intended and that the water supplied to the public is, in fact, safe and complies with the relevant water quality standards. The main categories of micro-pollutants that are found in raw wastewater, secondary treated wastewater and reclaimed water are:

- Microbiology: bacteria, viruses, protozoa (parasites)
- Chemistry:
    - Industrial and household agents (micro-pollutants, micro-metals, synthetic detergents and toxic organic substances)
    - Pesticides
    - Pharmaceuticals
    - EDCs
    - Disinfection by-products (DBPs)
    - Algal toxins
    - Nutrients (NH_4, NO_2 and PO_4)

The above classes form the most important groups from a health perspective that should be included in the water quality management programmes of both direct and indirect potable reuse schemes. The costs of advanced water quality analysis, such as EDCs and emerging contaminants relevant to both water purification and, in particular, water reclamation is limiting for proper monitoring and risk management at such plants. Furthermore, only a few laboratories are able to perform the specialized analyses required for monitoring of treatment process efficiency to minimize risks and health impacts. There is, therefore, a need for the establishment of such a national laboratory network laboratory, to be funded by central government (Department of Water and Sanitation).

3.2 METHODS OF ANALYSIS OF EMERGING CONTAMINANTS – A REVIEW

The analysis of emerging contaminants (ECs) especially in wastewater is a global topic. Concerns on emerging contaminants have been identified by various scientific conferences and a series of publications has been released on the presence of these compounds in the environment. The analysis of EC in municipal wastewater involves the application of highly sensitive techniques, which enables detection limits at a lower concentration range and adequate identification criteria. There have been analytical challenges in the analysis of emerging contaminants, this is not only due to the complexity of the compounds chemical properties, but also due to the low concentrations, matrices complexity of the contaminants (Petrovic et al., 2003). The availability of precise analytical methods that can be effective for measurement at low concentration level (ng/l or lower) is the requirement for accurate risk assessment of contaminants and for

the monitoring of the water (surface, drinking, and wastewater) quality. A characteristic sampling, appropriate sample transportation, proper sample extraction, and the use of suitable analytical instruments are the key steps to obtaining accurate analysis data (quantitative and qualitative) (Figure 3-1). One of the challenges in monitoring of potable water reuse quality is that analytical techniques must be very sensitive, as biological effects can occur from hormone exposure at low ng/L concentrations. Problems may arise due to the complicated matrices of wastewater influent and effluents. Thus, characterizing the limitations of the analytical techniques is very important in these analyses (Drewes et al., 2006).

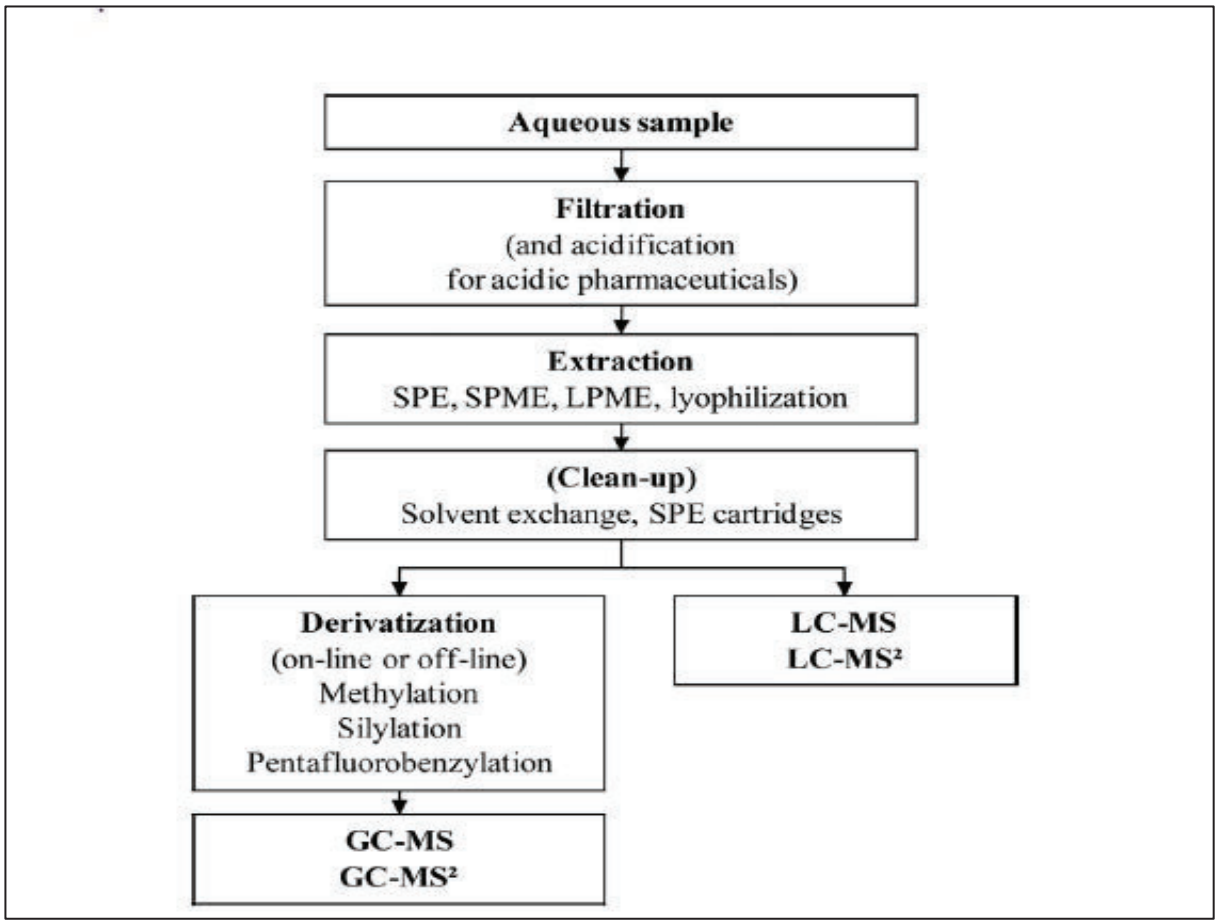

Figure 3-1: Analytical procedure for PPCPs in aqueous matrices (Lynn et al., 2012; Jiang et al., 2013)

The most widely used analytical instruments for detection of CECs are gas chromatography (GC), or High-Performance liquid chromatography (HPLC). Different detectors such as single quadruple mass spectrometry (MS), tandem MS (MS2), triple quadrupole (QqQ) MS, ion-trap MS (IT-MS), time-of-flight MS (QTOF-MS), can be applied in different ionization mode (e.g. atmospheric chemical pressure ionization and electrospray ionization). HPLC has been the most frequently used instrument and mainly coupled with mass spectrometry. Other compounds identified or quantified with GC-MS or LC-MS are highlighted in Table 3-1.

Table 3-1: Summary of methods of analysis of PPCPs in wastewaters

Compounds	Extraction	Derivatization	Chromatographic method	Detection	LOD (ng/l)	Reference
Bezafibrate, diclofenac, ibuprofen, gemfibrozil,carbamezapine	Sequential SPE(C18+polymeric sorbent)	Nil	LC	MS	2	(Loss et al., 2003)
Salicylic acid, ibuprofen, ketoprofen, naproxen, bezafibrate, diclofenac	SPE (polymeric sorbent)	Nil	LC	MS	5-56	
Bezafibrate, clofibric acid, diclofenac, fenoprofen, gemfibrozil, ibuprofen, inomethacin, ketoprofen, naproxen	SPE (C18)	Nil	LC	MS-MS	5-20	(Xiu-Sheng et al., 2002)
Bezafibrate, clofibric acid, ibuprofen	SPE (MCX or polymeric sorbent)	Nil	LC	MS-MS	0.016-2.18	(Calamari et al., 2003)
Ibuprofen, clofibric acid, ketoprofen, naproxen, diclofenac	SPE (HLB)	Diazomethane	GC	MS	0.3-4.5	
Clofibric acid, diclofenac, ibuprofen, phenazone, propyphenazone	SPE (C18)	Pentaflorobenzyl bromide	GC	MS	0.6-20	(Koutsouba et al., 2003)
Clofibric acid, naproxen, ibuprofen	SPE (polar Empore disk)	BSTFA(bis (trimethylsilyl)-trifluoroacetamide)	GC	MS	0.4-2.6	(Glen et al., 2003)
buprofen, naproxen, ketoprofen, tolfenamic acid, diclofenac, meclofenamic acid	SPE (HLB)	MTBSTFA(N-methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide)	GC	MS	20	(Rodriguez et al., 2003)
Clofibrates, clofibric acid, diclofenac, ibuprofen, phenazone, propyphenazone	SPE(ENVI-18 reversed phase RP-C18)	pentafluorobenzyl bromide	GC	MS	Nil	(Heberer & Kummerer, 1998)
Antivira (acyclovir, abacavir, lamivudine, nevirapine, oseltamivir, penciclovir, ribavirin, stavudine, zidovudin) and metabolite (oseltamivir carboxylate)	SPE(Isolute ENVI cartridge)	Nil	LC	MS-MS	0.2-10	(Ternes et al., 2010)
Atenol, Atorvastatin, carbamazepine, diazepam, diclofenan, dilantin, Enalapril, triclosan, etc.	SPE (HLB)	Nil	LC	MS-MS	0.25-10	(Petrovic et al., 2003)

Sources: (Petrovic et al., 2003)

The properties and occurrence level of organic micro-pollutants occurring at the nanograms-per-litre (ng/L) level vary widely, and different analytical methods are required for their quantification. During the last 10 years, multiple methods have been developed and employed for the detection of these compounds and in most cases, include GC/MS usually coupled with derivatization and LC/MS. The use of LC/MS allows the identification of highly polar contaminants without derivatization. To gain enhanced selectivity and sensitivity, tandem MS is increasingly being used for the measurement of organic trace compounds in various environmental matrices. The limitation of GC/MS applications is that analytes need to be transferred to the gas phase either directly or after an appropriate derivatization step. The drawback of LC/MS analysis is the sensitivity to matrix effects resulting in ion suppression. While some of the techniques require expensive and technically challenging instrumentation, others could be used directly or adapted for use in the laboratories of many utilities and contractors. For instance, several utilities have GC/MS systems for the measurement of semivolatile compliance compounds and DBPs. GC/MS can be used directly for the measurement of certain indicators (e.g. octylphenol and phthalates), while other compounds can be derivatized to expand the range of GC-amenable compounds. In addition, utilities often have GC with other detectors that may be applicable for indicator analysis (e.g. electron capture detectors for halogenated by-products, nitrogen-phosphorus detectors for nitrosamines, and flame ionization detectors for several organic compounds).

3.2.1 Sample preparation

Firstly, filtration is suggested before the extraction, to remove particulate matter and to also avoid the solid phase extraction sorbent. However, washing the filters with methanol after filtration is recommended due to the fact that some fraction of the target compound may be removed with the suspended solids. Concentrations of PPCPs in the environment are typically in the ng/L-µg/L or pg/g-ng/g levels, depending on sample matrices. Extraction and clean-up is important to transfer analytes of interest from a complex matrices form to a simple solution and also to purify the extract in order to minimise or eliminate interference co-eluted with analytes prior to analysis. Solid-phase extraction (SPE) has become the most used sample-preparation technique and has replaced traditional liquid-liquid extraction (LLE) for aqueous sample matrices. Solid phase extraction (SPE) is now the most frequently used extraction method for sample enrichment because it overcomes the shortcomings of liquid-liquid extraction. Solid phase micro extraction and lyophilization method extraction has also been reported (Petrovic et al., 2003). Sample extraction and clean-up can be conducted simultaneously with the solid phase extraction (SPE) technique. SPE cartridges packed with different sorbents such as C-18, ion-exchange phases, polymeric phases and nonpolar phases have been used. A typical analytical technique comprises the use of polymeric, octadecylsilica, or hydrophilic-lipophilic balanced (HBL) supports for off-line SPE of water samples, with either disks or, most commonly, cartridges at low pH (mostly pH=2) (Petrovic et al., 2003). Hydrophilic-Lipophilic Balanced (Oasis HLB) cartridge has been the most preferred cartridge for the pre-concentration of polar and non-polar compounds. Online automated SPE is often utilized for direct extraction and analysis. This can be done by coupling an automated SPE directly to LC-MS or LC-MS2 to analyse low-ng/L levels of antibiotics in water samples. This method has been extensively used in pharmaceutical analysis laboratories to improve data quality and efficiency in operation.

3.2.2 Gas chromatography

Gas chromatography (GC) was first used for the analysis of environmental contaminants (Schollée, 2006). One of the disadvantages of GC-MS and GC-MS2 is that it requires derivatization steps, due to low volatility of polar PPCPs. Additional derivatization steps make the sample preparation time consuming, laborious, and increases the possibility of contamination, which often results in sample loss. Furthermore, some

compounds are thermo labile and decompose during GC analysis (e.g. carbamazepine forms iminostilben as degradation product). Derivatization is typically done after sample extraction and clean-up by using organic reactions (e.g. methylation, silylation, and acetylation) and the derivatization agents are carefully selected according to their reactivity with the analytes of interest or the stability of their products to avoid a high degree of hydrolysis. Derivatization with pentafluorobenzyl bromide was shown to be advantageous for more sensitive determinations. In a study conducted by Tauxe-Wuersch (2005) sample analysis was performed with GC-MS to investigate the occurrence of acidic drugs (Clofibric acid, Diclofenac, Ibuprofen, Ketoprofen and Mefenamic acid) in three different sewage plants. Extraction was done with SPE (C18) method followed by derivatization with pentafluorobenzylbromide. The general recoveries after sample pre-treatments filtration, extraction, derivatization and clean-up exceeded 70%. The relative standard deviation on reproducibility (RSD) and standard deviation (SD) on all recoveries varied from 2% to 16%. It was concluded that the precision was sufficient and the analytical technique (GC-MS) was suitable for the analysis of the compounds.

The surrogate standard mesterolone is spiked into the filtered samples at a concentration of 100 ng/L. Steroid hormones are then pressure extracted from the filtrate by using preconditioned 90-mm Empore C-18 SPE disks. Acidic drugs are extracted by using ENVI-18 SPE resin followed by derivatization and GC/MS/MS. The surrogate standard fluriprofen is spiked into the filtered samples at a concentration of 500 ng/L. Acidic drugs are then extracted by pumping the filtrate (10 mL/min) via a peristaltic pump through the extraction columns containing preconditioned ENVI-18 SPE resin. These methods employ electron impact ionization (EI), which typically yield limit of detections for these compounds in the higher ng/L concentration range. These detection limits may be suitable for many wastewaters after primary or secondary treatment but not be sufficiently sensitive to quantify all these compounds in the broad range of reclaimed wastewaters. GC-MS techniques have been used that employ negative chemical ionization (NCI), which allows detection of these chemicals at concentrations in the low ng/L range, which is in the range of detection limits of enzyme-linked immunosorbent assay detection (ELISA), but has significantly better specificity than ELISA (Huang and Sedlak, 2001).

3.2.3 Liquid chromatography

The use of LC-tandem MS (LC-MS/MS) for environmental analysis allows the determination of a wide range of compounds. LC-MS/MS can give a slightly higher limit of detection (LOD) than can be achieved with the GC-MS. Increased use of liquid chromatography – mass spectrometry (LC-MS) has provided a new analytical tool that allows identification of highly polar organic pollutants in the environment down ng/L levels without derivatization. LC-MS techniques can be coupled with on-line devices for sample preparation and pre-concentration methods, such as SPE. PPCPs can be analysed with LC-MS without derivatization. The use of LC-tandem (LC-MS/MS) in environmental analysis resulted in the determination of a wide range of contaminants, therefore paved the way to extensive assessment of environmental pollutants. Acetonitrile with methanol is used as organic mobile phases for the LC separation, the use of a buffer in the eluent or acidification of the mobile phase is also recommended, in order to achieve sufficient retention for acidic drugs and reproducible retention times. Volatile compounds such as ammonium acetate, ammonium formate or formic acid are the most preferred mobile phase additives for the analysis of acidic analgesics or anti-inflammatory drugs and antiphlogistics.

Atmospheric chemical pressure ionization (APCI) sensitivity is generally less than obtainable with electrospray ionization (ESI) and has been described to be less susceptible to matrix effects. Lindsey et al. (2001) analysed antimicrobials (six sulfonamide and five tetracyclines) using multiple LC-MS ionization methods (positive and negative mode) under optimized conditions. Both ESI and APCI in the positive modes worked well. ESI was chosen over APCI because it was more sensitive towards chrotetracycline. QqTOF is mainly used as an unequivocal tool for confirmation of detected pollutants. It possesses unique

characteristic of generating full scan and production scan spectra with exact masses which makes it excellent for the removal of false positives and avoiding interpretation uncertainties. QqTOF possesses a lower linear dynamic range (over two orders of magnitude) compared to QqQ instruments (characteristically greater than four orders of magnitude) for quantitative analysis. Nonetheless, when the application requires a high degree of certainty analysis of unknowns, the use of QqTOF can be a viable option when the analysis require a high degree of certainty or is aimed at multiple tasks (to target analysis combined with qualitative).

A study by Nurmi and Jukka (2011) involving optimization and testing the multi-residue method for analysis of emerging contaminants in wastewater using ultra performance liquid chromatography – time of – flight, quantification of pharmaceuticals was done based on the standard addition method. Furosemide (diuretic) was the most abundant compound with concentrations of 2200±180 and 2100±110 ng/L. Trimethoprim (antibiotic) level was 780±22 ng/L, and 330±2.9 ng/L for atenolol. The multi-residue screening method allows analysis of a wide range of organic compounds in wastewater within one analytical run. Shraim et al. (2012) demonstrated application of tandem LC-MS to detect and quantify the presence of some frequently dispensed pharmaceuticals in the sewage treatment plant of Almadinah Almunawara in Saudi Arabian. The average concentrations (ng mL-1) of the drugs in the influent were acetaminophen (38.9), atenolol (2.04), and cephalexin (1.88), metformin (15.2), and norfluoxetine (7.07). A slightly lower concentration average of 3.12, 0.545, 1.53, 3.19, and 7.25 (ng mL-1) for acetaminophen, atenolol, cephalexin, metformin and norfluoxetine respectively were detected in the effluents.

Farre et al. (2001) monitored some selected acidic and highly polar analgesics such as Diclofenac, Gemfibrozil, Ibuprofen, Naproxen, Salicylic acid and Ketoprofen) in surface water and wastewater using LC-(ESI)-MS and GC-MS (after BF3-MeOH derivatization). The results obtained were compared and a good correlation between the used techniques was shown, except for Gemfibrozil, for which derivatization was not completely attained in some samples. Furthermore, the use of two SPE sorbent materials for sample pre-treatment in order to strengthen the extraction of different compounds is essential for accurate multi residue screening. In a study by Aufiero et al. (2012), three methods (Fluorescence spectroscopy, gas chromatography, and high-pressure liquid chromatography) were tested for detection of triclosan in water before and after adsorption onto zeolite and activated carbon. High pressure liquid chromatography (HPLC) was considered the best technique. It was concluded that that fluorescence spectroscopy is not a suitable method for determining triclosan concentrations. Inconsistence peaks where noticed when samples were run repetitively, even when run in close succession. Furthermore, no clear trend with respect to fluorescence reading and concentration was observed when generating the calibration curve.

3.2.4 Capillary electrophoresis technique

Capillary electrophoresis technique (CE) is another technique employed for analyzing PPCPs in aqueous solution. Separation takes place in fused silica capillaries and in order to achieve separation, a high voltage is often applied through buffer field capillaries. CE has gained a huge recognition because of its high efficiency and analysis speed; low reagent uses and sample consumption and fast method development. CE has been found to be less selective compared to HPLC technique. Nonetheless, it may be used as complimentary or alternative technique due to the fact that its separation selectivity can be similar to that of HPLC (Wolfgang, 2011). CE has the highest potential when combined with MS. Ultra-performance liquid chromatography electrospray tandem mass spectrometry (UPLC-ESI/MS/MS) was employed for simultaneous analysis of pharmaceuticals, anti-inflammatory drugs, antibiotics, personal care products, anti-epileptics and illicit drugs in both surface water and waste water. This method offer improvement in resolution, speed and sensitivity at low level (0.1 ng/l), good analyte separation in short period of time was also achieved. Extremely low column calibration and low mobile phase flow rate of <4 min and 0.05-0.7 ml/min respectively were achieved.

3.2.5 Bioanalytical techniques

Because EDCs represent a broad variety of compounds, it is important to define which EDCs one seeks to analyse. It is widely accepted that DDT and other organochlorine pesticides can act as EDCs. Methodologies for these "classic" contaminants, as well as various endocrine-disrupting metals, are well established with standardized protocols used in drinking and wastewater regulations. The majority of novel analytical work is focused on trace levels of less-characterized contaminants with greater polarity than many of the "classic" contaminants. Several classes of EDCs and PPCPs have acidic or basic moieties, large molecular weights, and/or polar functional groups. No standard methods are currently available for these compounds, and few commercial laboratories analyse these compounds. A further complication is the desire to quantitate these compounds at ultratrace concentrations (sub-ng/L), which may have toxicological relevance (e.g. EE2). Bioanalytical techniques are important tools for monitoring certain EDCs and PPCPs. These techniques employ a biological end point that is related to a type of toxicity or a class of compounds. The simplest methods are receptor binding assays and cellular bioassays that have rapid response times, high sensitivity, and relativity low cost. *In vivo* bioassays are also used to detect various classes of EDCs. Although each instrumental and bio-analytical technique has advantages and disadvantages, a combination of these methods is most likely to detect and quantify EDCs. This approach is often referred to as toxicity identification evaluation, and may use bioassay-directed fractionation to guide instrumental analyses towards elucidation of toxic compounds.

ELISA is a simple, sensitive tool for detecting environmentally relevant concentrations of many pesticides and other chemicals of concern (Vanderlaan, 1991). Antibodies for many endocrine disrupting compounds have recently been developed and are now commercially available in ELISA kits. Currently, kits exist for many steroid hormones (17β-estradiol, estriol, testosterone), several nonylphenols, and bisphenol A. Chemical identification with GC-NCI-MS was used in conjunction with ELISA, as ELISA proved to be an inexpensive, novel tool useful to water utility personnel with little training in or access to more traditional chemical analysis methods. However, natural organic material present in wastewater effluents does interfere with commercially available ELISA kits; therefore, a cleanup step using HPLC is necessary prior to analysis (Huang and Sedlak, 2001).

Because endocrine disruption is a biological endpoint, bioassays are used to identify compounds with endocrine disrupting potential. The major concern regarding endocrine disrupting compounds in wastewater effluent has been estrogen receptor agonists. Receptor agonists are chemicals that bind with the hormone receptor and elicit a response. Receptor-mediated transcription assays rely on cells that are transfected with reporter gene constructs inducible by the receptor of interest. Reporter gene constructs are made up of a promoter region (a region of DNA that is responsive to the receptor), which is linked to a reporter gene. Reporter genes often include a gene encoding an enzyme that can be assayed spectrophotometrically (such as β-galactosidase) when the gene is expressed.

3.3 CURRENT SURROGATES USED IN POTABLE WATER REUSE

The following surrogates as recommended by Drewes et al. (2006) would be valuable for inclusion in South African potable water reuse water quality analysis programmes, as they indirectly quantify a number of pollutants and micro-pollutants found in wastewaters:

3.3.1 Organic bulk surrogates

Organic matter in municipal wastewater is referred to as effluent organic matter (EfOM). EfOM consists of (a) NOM derived from drinking water sources, (b) organic chemicals of anthropogenic origin, and (c) SMPs

generated during biological wastewater treatment by the decomposition of organic matter. Different approaches have been proposed to distinguish between nature- and wastewater-derived organics by using differences in functional groups, structural properties, molecular size distribution, aromaticity, reactivity, or acid/base solubility (Drewes et al., 2006). The following parameters/analysis should be considered for organic bulk surrogates:

- Total Organic Carbon (TOC)

TOC is a useful parameter that can quantify EfOM in wastewater effluents. TOC consists of particulate organic carbon (POC) and dissolved organic carbon (DOC) (operationally defined as 0.45 µm filtered). TOC has been proposed as a surrogate for water quality concerns. TOC is used as a surrogate to assess the removal of wastewater-derived contaminants of concern. Unfortunately, TOC is somewhat limiting, since it cannot be used to differentiate between biologically oxidizable matter and inert organic matter.

- Biodegradable Dissolved Organic Carbon (BDOC)

BDOC quantifies the dissolved biodegradable organic matter. The latter consists of organic compounds that undergo microbial biotransformation and mineralization. BDOC in conjunction with DOC serves as a surrogate for the presence of organic compounds that are not derived from humic substances.

- Colour

Colour mainly results from dissolved materials, most often organics. Colour typically indicates the presence of organic debris, such as leaves and wood in various stages of decomposition. Tannins, humic acid, and humates from the decomposition of lignin are considered the principal sources of colour in natural waters.

- Chemical Oxygen Demand (COD)

COD measures the gross amounts of organic carbon and is widely used for determining the strength of wastewaters. COD has been proposed as a surrogate for TOC as well as for BDOC.

- Biological Oxygen Demand (BOD)

BOD is the amount of oxygen consumed by living organisms (mainly bacteria) while utilizing the organic matter present in the wastewater sample. BOD can be used as a surrogate for BDOC in conventional and advanced wastewater-treated effluents. The BOD and COD parameters can be used together to indicate toxic conditions and the presence of biologically resistant organic substances.

- UV Spectrometry

The absorbance spectrum at wavelengths of 200 to 400 nm is associated with the aromaticity of NOM. Most researchers use a single UV absorbance (UVA) at 254 or 272 nm to monitor UV-absorbing components of NOM. To better compare the UVA at 254 nm for different waters, the UVA is normalized by the DOC concentration of the sample, expressed in units of litres per milligram-meter. This is defined as the specific UVA (SUVA). It was found that SUVA was a good indicator of the humic content of raw waters.

- Fluorescence Spectrometry

The fluorescence of NOM is due to the presence of fluorophores that absorb photons, followed by the excitation to a higher electronic energy state. Fluorescence spectrometry can be used to distinguish humus-like organic matter from protein-like organic matter.

- Molecular Weight (MW)

The MW for a heterogeneous mixture of organic matter is represented by an average MW or an MW distribution. It can be measured by the size exclusion chromatography (SEC) method using UV detection and/or DOC detection.

- TOX

TOX, sometimes referred to as adsorbable organic halides, is a bulk parameter that measures the total organically bound halogens. TOX has been used to describe mainly halogenated organics of anthropogenic origin in water as well as the formation of halogenated species during chlorination. If one couples TOX with ion chromatography, the halogens can be distinguished into chlorinated (TOCl), brominated (TOBr), and iodinated (TOI) organics. TOX can be used to monitor the breakthrough of some synthetic organic compounds in water treatment processes and/or to estimate the level of formation of chlorinated organic by-products after disinfection.

3.3.2 Other bulk surrogates (Drewes et al., 2006)

- Turbidity

Turbidity is used to assess the clarity of water and is caused by a wide variety of suspended materials, which range in size from colloidal to coarse dispersions. Turbidity can serve as a surrogate to assess the system performance and integrity of membranes, such as ultrafiltration, NF, and RO types.

- Hardness

Hardness is caused by multivalent metallic cations. The principal hardness-causing cations are the divalent calcium, magnesium, strontium, ferrous iron, and manganous ions.

- Alkalinity

The alkalinity of water is a measure of its capacity to neutralize acids. The alkalinity is caused primarily by the salts of weak acids. Alkalinity is used to a great extent in wastewater treatment practice for determining the buffering capacity.

- Nitrogen

In aquatic systems the dominant nitrogen forms are ammonia, nitrogen (N_2), nitrite, nitrate, and organic nitrogen. Organically bound nitrogen is usually associated with amino acids, amines, amides, imides, nitro

derivatives, and a number of other compounds. Ammonia and organic nitrogen analyses are important in determining whether sufficient available nitrogen is present for biological treatment (i.e. SAT and BAC).

- Phosphorus

In wastewater the dominant phosphorus forms are the inorganic phosphorus forms, orthophosphates and polyphosphates, and organically bound phosphorus. Phosphorus is important in determining whether sufficient available phosphorus is present for biological treatment.

- Conductivity

The conductivity of a solution is a measure of its ability to carry an electrical current and varies both with the number and type of ions the solution contains. Conductivity can serve as a surrogate to assess the system performance and integrity of membranes, such as UF, NF, and RO types.

- Total Dissolved Solids (TDS)

TDS is the dissolved portion of solid matter in aqueous samples. In water, TDS consists mainly of inorganic salts, a small amount of organic matter, and dissolved gases. The operational definition is the matter that remains as residue upon evaporation and drying at 180°C. The TDS correlates well with hardness. So, like conductivity, TDS can serve as a surrogate to assess the system performance of membranes, such as UF, NF, and RO types.

3.4 SITUATIONAL ANALYSIS OF WATER QUALITY LABORATORIES IN SOUTH AFRICA

3.4.1 Overview

A previous investigation (Balfour et al., 2011) found that there are a limited number of laboratories that undertake water quality testing in the country. It was further found that many of these laboratories have capacity limitations. Until recently there has been little focus on the quality control of the laboratories utilized in the testing of water. This has resulted in municipalities and the Department of Water Affairs (DWA) using both centres of excellence and those with little evidence of being able to produce reliable results. The process and cost of ISO 17025 accreditation with SANAS has been highlighted as a stumbling block for many laboratories. As a result, DWA is currently in the planning stages of implementing a laboratory strategy for ensuring the credibility of results from drinking water quality laboratories, based on a pared down version of ISO 17025, and focusing on technical competency. Nearly 200 laboratories were identified and 50% of these completed the survey. The geographic spread of the laboratories correlated to their testing capability has provided useful information in establishing whether there are sufficient laboratories across the country, and where additional credible laboratories need to be established. A holistic gap analysis has been portrayed, providing a base for improvement in the water quality testing sector and thus improving water service delivery.

Generally, findings from this study showed a high occurrence of financial reasons for non-accreditation (25%). The initial financial implications of attaining ISO 17025 accreditation are severe, as a management system needs to be put in place. The maintenance of equipment, procurement of stock, method validation, technician competency per method, and record keeping are vital in achieving ISO 17025 accreditation. It appears that training is a priority for the majority of laboratories A total of 79% of laboratories conduct training needs assessments, but the main concern lies with those laboratories with little or no training at all. A total of 77% of laboratories acknowledge the availability of assistance both internally and externally and 79% stated that their organisation is in a position to train personnel from their facilities to assist them

in methodology training. The basic laboratory information is useful to determine geographic spread, in order to analyse where there are sufficient laboratories and where additional laboratories should be established. It is also useful to look at the geographic spread of the laboratories that have SANAS accreditation in order to establish the number of accredited labs per province as well as any trends regarding accreditation or participation in proficiency testing schemes. This will also assist in the laboratory classification structure which requires certain knowledge of the location of laboratories and their accreditation status.

The following were identified by laboratories as “areas of concern” (in no specific order):

- Accreditation requirements
- Method validation
- Estimation of uncertainty of measurement
- Proficiency testing schemes and inter laboratory comparisons
- Skills shortage, development of staff and how to retain skilled people,
- Quality control and quality assurance
- Water quality (chemical, organic and microbiology)
- Calibration of water lab equipment
- Laboratory safety and waste disposal
- Equipment, including calibration and maintenance.

When analysing the requirements for SANS 17025, the training categories identified as important for a laboratory doing water quality testing were:

- Accreditation
- Laboratory Techniques
- Statistical methods and method validation
- Laboratory Safety
- Sampling

A workshop that was held by the project team with key industry stakeholders identified the following issues as the Top 10 Challenges with laboratories at the time (Chapman et al., 2011):

- Human resources
- Sector leadership
- Quality/credibility of results
- Sample integrity
- Financial constraints
- Supplier role and responsibility
- ISO 17025 accreditation
- Insufficient laboratories
- Water quality testing undervalued
- Communication.

To begin to address the human resources challenge, it is recommended that in-service training for new graduates is promoted and practiced throughout the laboratories; regional training courses should be regularly held to make training more affordable and accessible; willing retirees could be contracted to train and mentor junior staff; and technicians and managers should be required to obtain registration/approval based on a set of competence criteria.

DWS is the sector leader and as such needs to set the tone regarding the importance of credibility in water

quality testing results. Strategy and policy for regulation and support needs to be generated; a regulatory tool to influence municipal budgeting relating to water quality testing needs to be developed; DWS staff need to be capacitated to understand and interpret results submitted to them; and strategic partnerships with SANAS, the NLA, the NHLS and water boards need to be established. (Balfour et al., 2011).

Lastly, a communication strategy that includes the general public, laboratories, municipalities and relevant government departments is needed to raise the profile of water quality testing. Once there is a better understanding and a demand for credible water quality results, many of the current challenges will become priorities, and hopefully resolved/improved.

3.4.2 Accredited laboratories

Table 3-2 shows accredited water laboratories in South Africa (SANAS website, February 2014).

Table 3-2: Accredited water laboratories in South Africa (SANAS, 2014)

Name	Location (City)	Province	Status	Disciplines
AL Abbott and Associates (Pty) Ltd	Cape Town	The Western Cape	Accredited	Chemical and Microbiological Analysis
Amatola Water	East London	The Eastern Cape	Withdrawn	Chemical and Microbiological Analysis
Buckman Laboratories (PTY) Ltd	New Castle	KwaZulu-Natal	Accredited	Chemical Analysis
City of Cape Town, Water and Sanitation, Scientific Services Department	Cape Town	The Western Cape	Accredited	Chemical and Hydrobiology Analysis
CSIR Water Laboratories: Stellenbosch	Stellenbosch	Gauteng	Withdrawn	Chemical Analysis & Microbiological Testing: Water
eThekwini Water & Sanitation – Scientific Services	Durban	KwaZulu-Natal	Accredited	Chemical & Microbiology Analysis
Integral laboratories (Pty) Ltd	Empangeni	The Western Cape	Accredited	Chemical and Microbiological Analysis
Johannesburg Water (Pty) Ltd	Houghton	Gauteng	Accredited	Chemical Analysis
Mhlathuze Water	Richards Bay	KwaZulu-Natal	Accredited	Chemical & Microbiological Analysis
Midvaal Water Company Laboratory	Klerksdorp	North West	Accredited	Chemical and Microbiological Analysis
National Health Laboratory Service (NHLS)	Parktown	Gauteng	Suspended	Testing Laboratory: Microbiology
SABS Commercial (Pty) Ltd	Secunda	Mpumalanga	Withdrawn	Chemical & physical analysis

Name	Location (City)	Province	Status	Disciplines
Sedibeng Water – Quality Control Laboratory	Bothaville	The Free State	Accredited	Chemical & Biological Analysis
Talbot Laboratories (Pty) Ltd	Pietermaritzburg	KwaZulu-Natal	Accredited	Chemical and Microbiological Analysis
Umgeni Water – Amanzi	Pietermaritzburg	KwaZulu-Natal	Accredited	Chemical, Hydrobiology & Microbiological Analysis
Water Analytical Laboratory cc	Stellenbosch	The Western Cape	Accredited	Microbiological Analysis

3.5 INVENTORY OF LABORATORIES FOR SPECIALISED WATER QUALITY ANALYSIS IN SOUTH AFRICA

3.5.1 Western Cape

The presence of emerging micro-pollutants in various water sources has caused increasing environmental and public health concern. It is a well-established fact that large numbers of contaminants of concern are present in South Africa. In the last couple of years, there has been tremendous progress in analytical techniques for analysing emerging micro-pollutants. However, the identification and perhaps quantification of these xenobiotics in the environment depends solely on the availability and accessibility of advanced analytical facilities. These analytical facilities include: high performance liquid chromatography (HPLC), high performance liquid chromatography coupled with mass spectrometry (HPLC-MS), liquid chromatography mass spectrometry (LC-MS), liquid chromatography mass spectrometry coupled with mass spectrometry (LC-MS/MS), gas chromatography mass spectrometry, Nuclear Magnetic Resonance (NMR), amongst others.

Good analytical facilities are essential ingredients of research and overall rating of a University. Research involving emerging micro-pollutants is relatively new and as such modern analytical facilities are required for method development and identification in water samples. The recalcitrant toxic contaminants in wastewater are present in µg/L to ng/L level and therefore require good analytical facilities to be able to detect them in environmental samples. Presently, in Western Cape Province, there are insufficient analytical facilities and skilled personnel that are based at the universities laboratories in Western Cape. Some universities in Western Cape Province; University of Stellenbosch (Central analytical facilities division) and Cape-Peninsula University of Technology, Cape Town campus, have one or more of the above-mentioned facilities in their laboratory to conveniently analyse wastewater containing contaminants of concern (CECs). At the moment, three students of the University of the Western Cape who are working on CECs utilize the mentioned analytical facilities. However, there are associated challenges such as availability of the facilities and the contact person during analysis, which are highlighted in this report. Table 3-3 shows costs for selected analysis in 2015.

Table 3-3: 2015 Prices

Item	Academic Rates (R)	Internal Rates (R)	Industrial Rates (R)
ESIM direct injection high resolution	342/injection	300/injection	428
ESIM direct injection low resolution	246/injection	200/injection	326
Low res GCMS, LCMS and LCMSMS	514/injection	450/injection	963
High res LCMS, LCMSMS analysis and low res GCMSMS	738/injection	650/injection	1204
Amino acid analysis, excluding hydrolysis	678/injection	600/injection	1075
Method development/Training/Data analysis and reporting/ Setting up of equipment for special application, excluding consumables	5211/ 8hours	4550/ 8hours	8014
Hourly Rates	690/ hour	600/hour	942
1g HLB Solid Phase Extraction tubes	3 packs	R 2,918.54 per pack	8, 755.62

3.5.1.1 CSIR, Stellenbosch

CSIR Consulting and Analytical Services (CAS) has environmental laboratories in Durban, Stellenbosch and Pretoria equipped with sophisticated instruments and competent technicians in environmental analytical chemistry (Table 3-4).

Table 3-4: List of CSIR CAS laboratories

CSIT CAS Environmental, Food And Beverage Laboratories Pretoria		Chemical And Microbiological Analysis
ENVIRONMENTAL LABORATORY: INORGANIC CHEMISTRY Drinking Water, Surface Water, Wastewater, Ground Water, Effluent Water	Aluminium, Antimony, Barium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Gold, Iron Lead, Lithium, Magnesium, Manganese, Molybdenum, Nickel, Potassium, Silicon, Silver, Sodium, Strontium, Titanium, Vanadium, Zinc & Zirconium Arsenic, Selenium (low level) Mercury (low level) Total hardness (calculation) pH value Colour Turbidity Electric conductivity at 25°C Total dissolved solids at 180°C Total suspended solids at 103-105°C Alkalinity Fluoride Chemical oxygen demand Oxygen absorbed Kjeldahl nitrogen	CMP 1 – Varian – ICP OES CMP 2 – Hydride generation by AA CMP 3A – Cold vapour by AAS CMP 4 – Calculation CMP 11 – Electrometric CMP 12 – Pt – Co method comparison CMP 13 – Nephelometric CMP 14 – Conductimetric CMP 15 – Gravimetric CMP 16 – Gravimetric CMP 17– Potentiometric Titration CMP 21 – Ion selective electrode CMP 24 – Colorimetric CMP 25 – Titrimetric CMP 26 (a) – Colorimetric, FIA CMP 26 (f) – Colorimetric, FIA CMP 26 (j) – Inline distillation CMP 27(9.1-9.9) – Discrete Analysis by Gallery Plus

CSIT CAS Environmental, Food And Beverage Laboratories Pretoria		**Chemical And Microbiological Analysis**
	Total phosphorus	CMP 30 – DPD, Spectrophotometric
	Total Cyanide & Free Cyanide	CMP 29 – IR-Spectroscopy
	Ammonium nitrogen, nitrate + nitrite nitrogen, nitrite nitrogen, nitrate nitrogen, ortho-Phosphate as P, Chloride, Sulphate, Total Phenolic Compounds, Hexavalent Chromium	CMP 11, 14, 17 and 21 – Automated analysis by Mantech Automax 197
	Total and Free Chlorine	CMP 21 – ION 570 Radiometer
	Total and Dissolved Organic Carbon	
	pH, Conductivity, Alkalinity & Fluoride	
	Fluoride	
	Determination of volatile organic compounds (including THM and BTEX components) In water samples by GC-MS	
ENVIRONMENTAL LABORATORY ORGANIC CHEMISTRY Ground Water, Waste Water, Drinking Water, Effluent Water, Surface Water	Determination of Total Petroleum Hydrocarbons (TPH) in soil and water samples by GC-FID	GC 050
	Gasoline range organics (GRO) by purge and trap GC-MS	AM 194
	Moisture (105°C) and Ash (550°C) determination	OMP 3
	Carbohydrates (Glucose, Sucrose, Fructose, Maltose, Lactose, Trehalose, Galactose)	FCMP 1-Gravimetric
	Determination of Fat and Cholesterol	FCMP 2-HPLC-RID
	Glycaemic Carbohydrates and Total Dietary Fibre analysis	FCMP 3-GC-FID, GC-MS
	Determination of Sodium content	FCMP 4-Spectrophotometric, Gravimetric
	Determination of Nitrogen	FCMP 5-AAS
	Total Starch Analysis	FCMP 6-Dumas (LECO)
		FCMP 7-Spectrophotometric
ENVIRONMENTAL LABORATORY: MICROBIOLOGY Ground Water, Waste Water, Drinking	Heterotrophic Plate Count	
	Total coliforms	MMP 1 – Pour plate
	Faecal coliforms	MMP 2 – Membrane Filtration
	Detection of *Salmonella* spp.	MMP 3 – Membrane Filtration
	Escherichia coli	MMP 6 – Presence/Absence

CSIT CAS Environmental, Food And Beverage Laboratories Pretoria		**Chemical And Microbiological Analysis**
Water, Effluent Water, Surface Water All Water, Soil, Sewage, Sludge	Enumeration of Total Aerobic Microorganisms Enumeration of Total Yeast and Moulds Detection and Confirmed Quantification of Coliforms and *Escherichia coli* Horizontal Method for the enumeration of Coagulase Positive *Staphylococci* (*Staphylococcus aureus*) Horizontal Method for the enumeration of Presumptive *Bacillus cereus* Horizontal Method for the enumeration of *Clostridium perfringens* Enumeration of *Listeria monocytogenes* Horizontal Method for the detection of *Salmonella* spp. Detection of *Escherichia coli* O157/H7 Horizontal method for the detection of *Campylobacter* spp. Horizontal methods for the enumeration of mesophilic lactic acid bacteria	MMP 8 – Indole Test FMP 1-SimPlate Colour Indicator Method FMP 2-SimPlate Colour Indicator Method FMP 3-SimPlate Colour Indicator Methods FMP 4-Baird Parker Agar at 37°C FMP 5-Colony count at 30°C FMP 6-Colony count at 37°C FMP 7-Oxoid Listeria Precis Method, colony count at 37°C FMP 8-Present/Absent FMP 9-Du-Pont Lateral Flow System FMP-10-Detection method FMP 11-Colony count at 30°C
PARASITOLOGY LABORATORY Ground Water, Waste Water, Drinking Water, Effluent Water, Surface Water	*Cryptosporidium* oocysts and *Giardia* cysts	PMP 1 – Filtration, IMS, FA

3.5.1.2 Stellenbosch University Central Analytical Facilities

The aim of the Central Analytical Facilities (CAF) is to ensure optimal utilisation of expensive multi-user research equipment in the service of the research community of Stellenbosch University, and the South African research and development sector in general. To this end, CAF consists of operational units built around logical clusters of equipment and managed by a Staff Scientist, who provides advice to potential users on relevant analytical and sample preparation techniques, perform analyses for clients, train users to perform their own analyses and ensure good maintenance, calibration and performance of the equipment. The ICP-MS laboratory perform inorganic analysis on samples ranging from water samples that are analysed directly, to waste, plant, animal and soil samples that are first prepared using microwave acid digestion; the Mass Spectrometry Unit identify and quantify organic molecules. Solution State NMR unit specializes in the 2D and 3D structure determination of natural products and other molecules from plant and other extracts like aloe. The analytical instruments in Mass Spectrometry Unit at Central Analytical Facilities (CAF) laboratory, Stellenbosch, Western Cape, South Africa include:

- Liquid Chromatography/Mass Spectrometry Ionization (ESI) or Atmospheric Pressure Chemical Ionization (APCI).
- Liquid chromatography/ quadrupole mass spectrometer (LC-MS/MS)
- Liquid chromatography/ Time of flight (LCMS/TOF)

- Gas Chromatograph/Photoionization Detector (GC-FID).
- Gas Chromatograph/ Mass spectrometry (GC-MS).

The UWC students in the project team of the current WRC project were able to develop an analytical method for identification and quantification of perfluorinated compounds (PFCs) in water in the CAF laboratory. Perfluorinated compounds were separated with a Waters Acquity UPLC system fitted to a Waters Xevo triple-stage quadrupole mass spectrometer (MS/MS). This is a powerful technique with high sensitivity and selectivity (capable to measure compounds at trace level). Challenges encountered include:

1. Long queue on the instrument: these facilities are used by University of Stellenbosch students, students from other Universities and Researchers from different companies such as wine and food additive companies. We are unable to plan our analysis base on our own timing but on the availability of the instrument. Instrument booking can take as long as 3 months. This can cause delay in analysis and also reduce output per year.
2. Distance: Long distance and transportation difficulties are another challenge we face with our work. It is always advisable to analyse as soon as possible after sampling in other to avoid the loss and change in the chemical composition of analytes before analysis.
3. High Cost of analysis: the cost of analysis for 8 hours was R5550.09 as at November 2014. This has increased drastically in 2015. Below is the 2015 price for the LCMS and GCMS analysis in CAF laboratory. The list price is excluding Tax. External users also pay 7% administration fee to the University of Stellenbosch.

3.5.1.3 Stellenbosch University Tygerberg campus

University of Stellenbosch Tygerberg campus, has two German-made Agilent 1100 series and one 1260 infinity series High performance liquid chromatography (HPLC) facilities in their analytical laboratory. In addition to these, they also have one mass spectrometry device (MS) that is not working due to a faulty component that requires R100 000 to replace. These facilities are managed by Dr Qiling Ying. Although these analytical facilities are able to detect emerging contaminants such as triclosan and their intermediate by-products, method development for analysing, detecting and quantification of compounds and intermediates is a major challenge.

The following difficulties have been encountered by students.

1. Limited access to the instruments
2. High charging rate (R150 per sample) when using the instruments, especially when you are not a student of the University of Stellenbosch.
3. Late analysis of sample, collection of data and presentation of results due to the increased number of students using the facilities at the same time.
4. Difficulty in using the desired type of column as a result of changes in method developed for a specific pollutant. These contaminants are column dependent.
5. Finding and funding the appropriate standards
6. Problem of tubes and valves blockages resulting from improper sample pre-treatment. This in-turn has led to high pressure output in the system resulting in wrong data presentation and results.
7. Too many samples have to be analysed and there are limited number of facilities for such analyses.

3.5.1.4 Cape Peninsula University of Technology (CPUT)

The laboratory has the following facilities: high performance liquid chromatographic, Waters Chromatograph equipped with a Waters 1525 binary HPLC pump, Waters 2487 dual λ absorbance detector, Waters 2707 auto-sampler and running on the Breeze software. Also, a liquid chromatograph coupled with a mass spectrometer (Agilent 6230 TOF LC-MS) is readily available at CPUT. The Agilent 1260 infinity series used comprise a binary pump, an auto-sampler and an 1100 diode array detector (DAD). Some of these facilities are new and functioning well. However, preference is always given to their internal students.

3.5.1.5 City of Cape Town Scientific Services

The City's Scientific Services laboratory was established in the 1920s to monitor the operation processes of Cape Town's sewage works. Later its scope of work was extended to include water treatment plants. The laboratory became a fully-fledged department under the Water & Sanitation's chemical branch in the 1940s and soon afterwards was named the Scientific Services Department (SSD). It included Trade Waste, Hydrobiology, Wastewater, Water, Microbiology, Water Pollution Control and the Air Quality Monitoring Unit. The department currently has three laboratories: Water, Analytical and Biological Sciences with the Air Quality Unit as part of its secondary business. The need for testing the impact of polluted waters on the environment increases as regulations become demanding. Through the hydrobiology and microbiology laboratories, the range of analyses consists of:

- Marine water quality monitoring
- Nutrients
- Metals and organics
- Microbial analysis of dams, rivers, streams, vleis
- Macro invertebrates and algae to determine the health of our streams and lakes

3.5.2 Gauteng

3.5.2.1 Rand Water Scientific Services

Water is tested for compliance prior to supplying to municipalities. Rand Water Analytical Services is fully accredited by the South African National Accreditation System (SANAS) and demonstrates the organization's acceptance of international quality standards (Table 3-5). The laboratory participates in national and international proficiency testing schemes to continuously monitor the quality of its data. Data in hydrobiology, microbiology and chemistry are produced. The **hydrobiology** laboratory performs a diverse range of tests on source and drinking water, including aquatic toxicity testing, aquatic invertebrate assessment, algae and algal toxin monitoring and aquatic biomonitoring. The **chemistry** laboratories perform extensive testing in organic and inorganic chemistry to monitor water quality for parameters such as pesticides, disinfection by-products, hydrocarbons, trace metals, surfactants, ions, taste and odour. The **microbiology** laboratory performs analyses to determine for the presence of indicator organisms (*E.coli,* coliforms, coliphages, etc.) and analyses various sample matrices for an array of pathogens including Cryptosporidium and Giardia.

Table 3-5: Rand water analytical services

Rand Water Analytical Services Vereeniging	
HYDROBIOLOGY Drinking water Surface water Waste water Ground water	Chlorophyll-a Chlorophyll-665 (total pigment) Phytoplankton Identification and Enumeration Daphnia pulex acute toxicity test Mycrocystine total screening test (ELISA Technique) SASS Invertebrate Assessment Invertebrate Identification Enumeration Vibrio Fischeri Vibrio Fischeri AGI (Algae Growth Inhibition)
MICROBIOLOGY Drinking Water Ground Water Waste water Surface water	Standard Plate Count Faecal Coliform Count Determination of Coliphages Isolation and detection of Cryptosporidium oocysts and Giardia cysts Detection and enumeration of Escherichia coli and coliform bacteria by Colilert Real-time Polymerase Chain Reaction Assay for ctxA gene of Cholerae
INORGANIC CHEMISTRY **Drinking water** **Ground water** **Surface water** **Waste water**	Determination of pH, Conductivity and Automated Method Turbidity Nitrite by Aquakem NH3 as N by AQ2 PO4 as P by AQ2 Chemical oxygen demand Nitrate by Aquakem PO4 as P by Aquakem Recoverable Cyanide TKN by Aquakem Analysis of Na and K by flame Atomic Absorption (Part 1) Analysis of arsenic, Selenium and Antimony by AA using Graphite Furnace (Part 2) Multi-element Analysis by ICP-MS Active Silica by Aquakem Determination of anions (F, Cl, Br, NO3, && SO4) by Ion Chromatography – High range Determination of anions (F, Cl, Br, NO3 & SO4) by Ion Chromatography – Low range Dissolved Solids Suspended Solids Colour Free Cyanide
ORGANIC CHEMISTRY **Drinking water** **Surface water**	Calcium, Magnesium, Sodium, Potassium, Cadmium, Chromium, Cobalt, Copper, Iron, Manganese, Lead, Zinc, Nickel, Vanadium, Molybdenum, Boron, Aluminium, Silicon, Phosphorus, Sulphur by ICP No2 + No3 by AQ2 Chloride by AQ Total Trihalomethanes (µg / l) -Chloroform -Bromodichloromethane -Dibromochloromethane -Bromoform Geosmin (µg / l) Determination of BTEX's in water samples Determination of Total Organic Carbon (TOC) TOC and DOC by Wet oxidation Determination of total phenols ultraviolet oxidation Determination of organochlorins and riazinet Pesticides in water by GC-MS Hydrocarbons Determination of Phenol by GC Determination of Oil and Grease

3.5.2.2 East Rand Water Care Company (ERWAT)

ERWAT Laboratory services, a SANAS 17025 accredited laboratory, offers the water industry a wide variety of services in the fields of chemical and microbiological analyses, as well as expert advice on water-related problems. ERWAT Laboratory services, a SANAS 17025 accredited laboratory, offers the water industry a wide variety of services in the fields of chemical and microbiological analyses.

Microbiological

- Total Coliforms
- Faecal Coliforms
- Heterotrophic Plate Count
- Salmonella
- *E. coli*
- Faecal Streptococcus
- Pseudomonas aeruginosa (quantitative)
- Sulphur Reducing Bacteria (SRB)
- Milk analysis
- Yeast and mold

Sludge and soil

- Volatile Fatty Acids
- Kjeldahl Nitrogen
- Total Phosphorus
- Metals
- % Water
- % Total solids
- % Volatile matter
- Sludge classifications according to sludge guidelines
- Helminth ova
- Activated sludge (microscopic analysis)

GC-MS Analysis

- Gas chromatography/mass-spectrometry (GC-MS) applications on a variety of liquid and solid sample matrices.
- GC-MS analysis (organic determinants-based on EPA method specifications):
- Volatile organic compounds (VOC's) including BTEXN; components
- Semi-volatile organic compounds (SVOC's) including PAH's and Phenols
- Polychlorinated Biphenyls (PCB's)
- Organochlorine Pesticides (OCP's)
- Organophosphorous Pesticides (OPP's)
- Total Petroleum Hydrocarbons (TPH-GC) including Gasoline Range Organics (GRO's and Diesel Range Organics (DRO's)
- Organics fingerprinting (GC-MS Scans)

PCR Analysis

- Specialised services – pathogen detection
- Rapid detection of waterborne pathogens using real-time Polymerase Chain Reaction (PCR):
- SANAS (ISO 17025) accredited real-time PCR assays
- Highly specific and rapid results (available within 24-48 hours)
- Qualitative (present/absent) PCR analyses currently available include:
- *Salmonella enterica*
- *Shigella species and/or entero-invasive E. coli (EIEC)*
- *Toxigenic Vibrio cholerae (cholera causing)*
- Serotyping of Salmonella by means of PCR also available:
- *Salmonella Typhimurium*
- *Salmonella Enteritidis*
- *Salmonella Typhi*
- *Salmonella Group B screen*

Automated Photometric Analysis

- Low range potable; and borehole specialised analysis

3.5.2.3 Waterlab

Waterlab (Pty) Ltd was established in 1983 as a service company specialising in Analytical Chemistry, providing services in the various disciplines of water, being potable water supply, sewage treatment, industrial effluents, acid mine drainage or underground water. With the arrival of legislation governing environmental impacts by industry, mining and other activities, the range of services supplied by Waterlab were expanded to include the following:

- Full chemical and microbiological analyses of potable- and underground water, treated
- sewage industrial- and mining effluents
- Liquid extraction (acid rain, TCLP, etc.) of soil materials, solid industrial- and mining
- Waste and waste site materials and analyses of extracts to determine potential risk
- Geochemical analyses of rock materials, and tailings (waste rock) from mining operations.
- Analyses include acid base accounting, XRD, XRF, ICP (metals), humidity cells, etc.

3.5.3 KwaZulu-Natal

3.5.3.1 Umgeni Water

Table 3-6: Umgeni Water Services (Pty) Ltd

Umgeni Water Services (Pty) Ltd Co. Reg. No.: 1997/007705/07 Amanzi Laboratory Services Department		**Chemical, Hydrobiology And Microbiological Analysis**
CHEMICAL **Water** **Water and raw water** **Wastewater**	Alkalinity Anions – (Chloride, Nitrite, Nitrate and Sulphate) Colour Conductivity at 25˚C Hardness (Total) pH at 25˚C Suspended Solids at 105˚C Total Solids and Total Dissolved Solids at 105˚C Trihalomethanes Total Solids and Total Dissolved Solids at 105˚C Fe, Mn, Cu, Zn, Si, Ca, Mg, K, Na Cd, Ni, Pb, Cr, Al, Co, Mo, V Total As, Se, Sb Turbidity Fluoride Total organic carbon and dissolved organic carbon (DOC)	Internal Specifications 1 (Auto-titrator) 5 Jon Chromatography 19 (UV-Vis Spectrophotometer) 21 (conductivity Meter) 27 (Calculation) 46 (pH Meter) 59 (Gravimetric) 61 (Gravimetric) 67 (Gas Chromatograph – ECD) 61 (Gravimetric) 30 (ICP-OES) 102 (ICP-OES) 154 (ICP-MS) 69 (Turbidimeter) 94 (Ion-selective electrode) 151 (TOC-analyser)
HYDROBIOLOGICAL **Water**	Oxygen Absorbed Algae Chlorophyll a Rapid Bioassessment (pH, Dissolved Oxygen & Electrical Conductivity) Toxicity – Algae Toxicity – Daphnia Toxicity – Guppies	45 (Titration) 77 (Membrane Filtration) 78 (UV-VIS Spectrophotometer) 99 (South African Scoring System) (SASS) 103 LC_{50} 104 LC_{50} 105 LC_{50}
MICROBIOLOGICAL **Potable Water** **Raw Water** **Effluents**	Heterotrophic Plate Counts @ 37^{o}C and 21^{o}C Detection of *Vibrio Cholerae* Detection of *Salmonellae spp*. Coliphages assay Enumeration of Total Coliforms and *E.coli*	80 (Pour Plate) 82 (Moore Rad) 83 (Moore Pad) 85 (Double agar layer plaque Assay) 121 (Colilert)

3.5.4 Free State

LiquidTech™ is a cutting-edge biotechnology enterprise that is being incubated by the Advanced Biomolecular Research Cluster at the University of the Free State (UFS). The LiquidTech™ laboratory is physically located in the Biotechnology Building on the UFS main campus in Bloemfontein. LiquidTech™ is headed by two established research scientists, Dr. Gabre Kemp and Prof. Hugh Patterton, assisted by support personnel. LiquidTech™ is currently in the process of acquiring SANAS certification as a Chemical Testing Laboratory. The secure LiquidTech™ laboratory is separated into a sample preparation area and a sample analysis area. Sample preparation allows detection of minute quantities (ng/L or 10^{-9}g/L) of organic pollutants, including endocrine disruptors, algal toxins such as microcystins as well as pesticides in water. Samples are analysed by tandem mass spectrometry. At LiquidTech™ we make use of highly sensitive, ultra-modern small molecule discovery equipment, including triple hybrid-quadrupole 4000QTRAP and 3200QTRAP mass spectrometers that are housed in the facility. Routine chemical and bacteriological analyses of water, to test for legal compliance, are performed in dedicated laboratories on the campus of the UFS. An advanced, in-house computational biology facility is used for analysis and identification of small molecules. All analysis results are stored securely to guarantee confidentiality of client data.

At LiquidTech™, organic compounds are analysed using either GC/MS to detect and quantitate non-polar compounds, while the more polar compounds are detected and quantitated using LC/MS/MS in either the positive or negative ionization modes. Two types of liquid analyses can be performed. When the client has no idea as to the identity of the contaminant in the liquid, a *Qualitative* screen can be performed. These screens provide you an insight into the presence or absence of a vast number of compounds, but provide no information on the concentration at which a compound may be present. Once one or more contaminants have been identified (either from our qualitative screen or otherwise), a *Quantitative* analysis follows a more focused approached using the previously gained knowledge. This analysis gives you accurate contaminant levels in the liquid, but *only* for the compounds included in the analysis method.

3.6 SUMMARY

A number of developments in both direct and indirect water reuse have taken place during the last two decades, of which the most important one is the gradual increase in the concern regarding emerging contaminants of concern in reuse water, which have accelerated during the past three years. These contaminants and chemicals include endocrine disrupting compounds (EDCs), and pharmaceuticals and personal care products (PPCPs). If water reclamation is to become a commonplace on a municipal level in South Africa, or any country, there will have to be competent laboratories that can perform the analyses required to ensure that WRPs are performing as intended and that the water supplied to the public is, in fact, safe and complies with the relevant water quality standards.

The costs of advanced water quality analysis, such as EDCs and emerging contaminants relevant to both water purification and, in particular, water reclamation is limiting for proper monitoring and risk management at such plants. Furthermore, only a few laboratories are able to perform the specialized analyses required for monitoring of treatment process efficiency to minimize risks and health impacts. There is, therefore, a need for the establishment of such a national laboratory network laboratory, to be funded by central government (Department of Water and Sanitation).

CHAPTER 4: SELECTION AND PRIORITIZATION OF CHEMICALS OF EMERGING CONCERN

4.1 INTRODUCTION

There is some evidence that certain emerging contaminants could affect human and environmental health. For example, the veterinary use of diclofenac, which is a human pharmaceutical used as an anti-inflammatory treatment, was found to be responsible for the massive decline in populations of vulture species in certain areas of Asia (Oaks et al., 2004); the veterinary drug ivermectin, which is used to treat parasitic infections in livestock, has been shown to affect the growth of aquatic invertebrates at concentration lower than those that are expected to occur in the aquatic environment (Garric et al., 2007); ethinylestradiol, one of the active ingredients in the contraceptive pill, has been associated with endocrine disruption in fish (Lange et al., 2001); and there is concern that long-term exposure to antibiotic pharmaceuticals, used in human and veterinary medicine, may be contributing to the selection of resistant bacteria in the environment which may have significant implications for human health (Boxall et al., 2003). For this reason, the USEPA has developed a CECs Removal Database consisting of published scientific studies on the removal of CECs from water and wastewater. The database is available at http://water.USEPA.gov/scitech/swguidance/ppcp/results.cfm. A report on Treating Contaminants of Emerging Concern: A Literature Review Database (August 2010) is also available at the website, providing examples for municipal wastewater and treated effluent.

Table 4-1 shows a list of about 112 emerging pollutants marked as priority in North America. Table 4-2 shows a list of 52 compounds considered to be useful indicators of trace organic chemicals in water based on detection frequency and levels in North American surface waters where compounds that did not occur at a frequency above 80% or were not present in secondary- or tertiary-treated wastewater at concentrations at least five times higher than their respective limits of quantification were eliminated (Dickenson et al. (2011). In the European Union a list of 58 chemical compounds was included as priority (Table 4-3).

In 2010, the Californian State Water Resources Control Board convened a panel of experts to address the monitoring strategies for CECs in recycled water providing recommendations for monitoring reclaimed water (Anderson et al., 2010). The panel provided a conceptual framework for assessing potential CEC targets for monitoring and used the framework to identify a list of chemicals that should be monitored (Anderson et al., 2010). The chemicals the panel recommended for monitoring are those found in recycled water at concentrations with human health relevance. In addition to risk-based priority chemicals, the panel recommended monitoring both the performance of treatment processes to remove CECs using selected "performance indicator CECs," and surrogate/operational parameters to verify that treatment units are working as designed. Surrogates include turbidity, DOC, and conductivity. Health-based CECs selected for monitoring included caffeine, 17β-estradiol, NDMA, and triclosan. Performance-based indicator CECs were selected by the panel, each representing a group of CECs: caffeine, gemfibrozil, n,n-diethyl-meta-toluamide (DEET), iopromide, NDMA, and sucralose. Caffeine and NDMA serve as both health and performance-based indicator CECs.

Table 4-1: US-EPA priority pollutants

Benzo(a)pyrene	4.4-DDD	Chlorine	Methyl Chloride
Bis(2-choroethyl) ether	4.4-DDE	Chlorobenzene	Methylene Chloride
Chloroethane	4,4-DDT	Chlorodibromomethane	Naphthalene
1,1,1-trichloreothane	4,6-dinitro-o-cresol	Chloroform	Nitrobenzene
1,1,2,2-tetrachloroethane	4-bromophenyl phenyl ether	Chrysene	N-nitrosodimethylamine
1,1,2-trichloroethane	4-chlorophenyl phenyl ether	Delta-BHC	N-nitrosodi-n-propylamine
1,1-dichloroethane	4-nitrophenol	Dibenzo(,h) anthracene	N-nitrosodiphenylamine
1,1-dichloroethylene	Acenaphthene	Dichlorobromomethane	Parachlorometa cresol
1,2,4-trichlorobenzene	Acenaphthylene	Dieldrin	PCB-1016 (Arochlor 1016)
1,2-dichlorobenzene	Acrolein	Diethyl Phthalate	PCB-1221 (Arochlor 1221)
1,2-dichloroethane	Acrylonitrile	Dimethyl phthalate	PCB-1232 (Arochlor 1232)
1,2-dichloropropane	Aldrin	Di-N-Butyl Phthalate	PCB-1242 (Arochlor 1242)
1,2-diphenylhydrazine	Alpha-BHC	Di-n-octyl phthalate	PCB-1248 (Arochlor 1248)
1,2-trans-dichloroethylene	Alpha-endosulfan	Endosulfan sulfate	PCB-1254 (Arochlor 1254)
1,3-dichlorobenzene	Anthracene	Endrin	PCB-1260 (Arochlor 1260)
1,3-dichloropropylene	Benzene	Endrin aldehyde	Pentachlorophenol
1,4-dichlorobenzene	Benzidine	Ethylbenzene	Phenanthrene
2,3,7,8-TCDD	benzo(a) anthracene	Fluoranthene	Phenol
2,4,6-trichlorophenol	Benzo(b) fluoranthene	Fluorene	Pyrene
2,4-dichlorophenol	Benzo(ghi) perylene	Gamma-BHC	Tetrachloroethylene
2,4-dimethylphenol	Benzo(k) fluoranthene	Heptachlor	Toluene
2,4-dinitrophenol	Beta-BHC	Heptachlor epoxide	Toxaphene
2,4-dinitrotoluene	Beta-endosulfan	Hexachlorobenzene	Trichloroethylene
2,6-dinitrotoluene	Bis(2-chloroethoxy) methane	Hexachlorobutadiene	Vinyl chloride
2-chloroethyl vinyl ethers	Bis(2-chloroisopropyl) ether	Hexachlorocyclopentadiene	
2-chloronaphthalene	Bis(2-ethylhexyl) phthalate	Hexachloroethane	
2-chlorophenol	Bromoform	Indeno (1,2,3-cd) pyrene	
2-nitrophenol	Butyl benzyl phthalate	Isophorone	
3,3-dichlorobenzidine	Carbon tetrachloride	Methyl bromide	

Table 4-2: Potential organic indicator compounds (52 compounds) found in North American treated wastewater effluents. (Dickenson et al., 2011)

COMPOUND	TYPE	COMPOUND	TYPE
Hexyl salicylate	Fragrance	Musk ketone	Fragrance
Diphenhydramine	PhAC	Methyl dihydrojasmonate	Fragrance
NDMA	Disinfection byproduct	Benzyl salicylate	Fragrance
Isobornyl acetate	Fragrance	Ibuprofen	Pharmaceutical
Hexylcinnamaldehyde	Fragrance	Hydrocodone	Pharmaceutical
Benzophenone	UV absorber	Ofloxacin	Pharmaceutical
Terpineol	Fragrance	Sulfapyridine	Pharmaceutical
Codeine	PhAC	Nonylphenol	Surfactant
Fluoxetine	PhAC	Dilantin	Pharmaceutical
Musk xylene	Fragrance	Clarithromycin	Pharmaceutical
TDCPP	Flame retardant	Carbamazepine	Pharmaceutical
Methyl salicylate	Fragrance	Galaxolide	Fragrance
Bisphenol A	Plasticiser	Primidone	Pharmaceutical
Propylparaben	Biocide	Erythromycin	Pharmaceutical
g-Methyl ionine	Fragrance	Iopromide	X-ray contrast agent
Propranolol	Beta Blocker	Naproxen	Pharmaceutical
Metoprolol	Beta Blocker	Indol-3-butyric acid	Plant Hormone
Caffeine	Stimulant	Trimethoprim	Pharmaceutical
Oxybenzone	UV absorber	Meprobamate	Pharmaceutical
Dibutyl phthalate	Plasticizer	Triclosan	Biocide
Acetyl cedrene	Fragrance	Gemfibrozil	Pharmaceutical
OTNE, ethanone	Fragrance	Tonalide (AHTN)	Fragrance
TCEP	Flame retardant	DEET	Insecticide
Benzyl acetate	Fragrance	Triclocarban	Biocide
Diclofenac	PhAC	Sulfamethoxazole	Pharmaceutical
p-t-Bucinal	Fragrance	EDTA	Chelating agent

Table 4-3: EU Directive 2008/105/EC Water Framework directive – 58 priority compounds

Alachlor	Endosulfan	Pentachlorophenol	Cybutryne
Anthracene	Fluoranthene	Polyaromatic Hydrocarbons	Perfluorooctane sulfonic acid (PFOS)
Atrazine	Hexachlorobenzene	(Benzo(a)pyrene)	Hexabromocyclododecane (HBCDD)
Benzene	Hexachlorobutadiene	(Benzo(b)fluoranthene)	Dioxin
Brominated Diphenyletheriv	Hexachlorocyclohexane	(Benzo(g,h,i)perylene)	PCBs
Pentabromodiphenyleth er (congener numbers 28, 47, 99, 100, 153 and 154)	Isoproturon	(Benzo(k)fluoranthene)	17 alphaethinylestradiol (EE2)
Cadmium and its Compounds	Lead and its compounds	(Indeno(1,2,3cd)pyrene)	Diclofenac
Chloroalkanes, C10-13 iv	Mercury and its Compounds	Imazine	17 beta-estradiol (E2)
Chlorfenvinphos	Naphthalene	Tributyltin compounds	Bifenox,
Chlorpyrifos	Nickel and its Compounds	(Tributyltin-cation)	Cypermethrin,
(Chlorpyrifos-ethyl)	Nonylphenols	Trichlorobenzenes	Dicofol
1,2-Dichloroethane	(4-nonylphenol)	Trichloromethane (chloroform)	Quinoxyfen
Dichloromethane	Octylphenols	Trifluralin	Aclonife
Di(2-ethylhexyl)phthalate (DEHP)	(4-(1,1',3,3' tetramethylbutyl)-phenol)	Terbutryn	
Diuron	Pentachlorobenzene	Dichlorvos	

Some of the more comprehensive databases for contaminants of concern are:

- IRIS (Integrated Risk Information System) database, with more than 550 compounds, available at http://cfpub.USEPA.gov/ncea/iris /indexcfm fuseaction=iris.showSubstance List.
- SIN (Substitute It Now) list with 406 compounds available at http://www.chemsec.org/ what-we-do/sin-list.
- HSDB (Hazardous Substances Data Bank) database, with information on 5 756 compounds available at http://sis.nlm.nih.gov/enviro/hsdbchemicalslist.html.
- Country lists. Many countries have drawn up their own lists of CECs. A reference to some of these lists is available at http://ec.europa.eu/environment/archives/ document/pdf/bkh_ annex_ 02_03.pdf.
- TEDX (The Endocrine Disrupting Exchange) database, with more than 1000 compounds available at http://endocrinedisruption.org/endocrine-disruption/tedx-list-of-potential-endocrine-disruptors/overview.
- The Household Products database with information and ingredients on 14 000 consumer brands in the USA, available at http://hpd.nlm.nih.gov.

4.2 SOUTH AFRICAN PERSPECTIVES

South Africa is a water scarce country with increasing demand on its natural resources. Increasing attention has therefore been given to the reclamation of water from wastewater sources for direct potable reuse to augment the national water supply. As wastewater reuse acts as a possible exposure pathway to a high number of emerging contaminants and their metabolites, monitoring of CECs is essential to determine its fitness for use. In 2012 (Ncube et al., 2012) suggested a protocol for the selection and prioritisation of contaminants in drinking water in which Rand Water, RSA, was used as a case example. A priority list of organic contaminants was identified which could then be used by Rand Water to optimise their resources and efficiency without compromising of public health. The priority list is given in Table 4-4, and was derived from primary lists of organic pollutants of concern which was based on occurrence criterion in both international and national literature.

Table 4-4: The priority list of organic contaminants for monitoring in the drinking water value chain (Ncube et al., 2012)

Industrial Chemicals	Dieldrin*	Dibromochloromethane*
Benzene	Atrazine and metabolites*	Formaldehyde
Chlorobenzene	Chlorpyrifos	Trichloroacetaldehyde
1,2-Dichlorobenzene	Cyhexatin	Monochloroacetic acid
1,2,4-Trichlorobenzene	DDT*	Trichloroacetic acid
1,4-Dichlorobenzene	DDD	Dichloroacetic acid
Pentachlorobenzene	DDE*	Bromoacetic acid
2-Chlorophenol	Diquat	Dibromoacetic acid
2,4-Dichlorophenol	Endosulphan	Bromochloroacetic acid
2,4,6-Dichlorophenol	Endosulphan sulphate	Nitrosodimethylamine
Pentachlorophenol	β-Endosulphan	THMs*
Di-2-(ethylhexyl)phthalate	Endrin	***Polymer residues***
Di-n-butylphthalate	Heptachlor*	Acrylamide
Di-2-(ethylhexyladipate (DEHA)	Heptachlor epoxide	Epichlorohydrin
2,3,7,8-Tetrachlorodiphenyldioxin	Lindane	Diallyldimethylammonium chloride
Nitrilotriacetic acid (NTA)	Metolachlor*	Dimethylamine
Benzo[a]pyrene	Methoxychlor	1,3-Dichloro-2-propanol
Bisphenol A	Paraquat	2,3-Dichloro-1-propanol
Ethylbenzene	Simazine*	3-Chloro-1,2-propanediol
p-Octylphenol	Terbutylazine*	***Cyanotoxins***
p-Nonylphenol	Acetochlor ethanesulphonic acid	Geosmin*
Polychlorinated biphenyls	Acetoclor	2-MIB*
(Aroclor 1016; Aroclor 1248	Acetochlor oxanilic acid	Anatoxin-a
Aroclor 1254; Aroclor 1260)	Metolachlor ethanesulphonic acid	Homoanatoxin-a
Toluene	Metolachlor oxanilic acid	Anatoxin-a(S)
Xylene isomers	Aldicarb*	Microcystin-LR
Dibutyltin	Deltamethrin*	Saxtoxin
Dimethyltin	Vinclozolin	Cylindrospermopsin

4.3 DEVELOPMENT OF A FRAMEWORK FOR SELECTION AND PRIORITIZATION OF CHEMICALS OF EMERGING CONCERN

4.3.1 Approach

The health and environmental risk for individual chemicals of emerging concern must be assessed to prioritise chemicals which should be included in monitoring programs. A risk-based screening framework was used, which includes a few principal steps:

- Establishing which chemicals of emerging concern have been detected in either environmental and drinking waters from international literature
- Establishing which chemicals have been detected in either environmental and drinking
- waters in South Africa (prevalence)
- Quantity of drugs prescribed in South Africa – to represent exposure potential
- Identifying those chemicals known to be persistent and not easily removed in treatment processes
- Identifying those chemicals with an established analytical detection method as well as relevant detection limit

The criteria described above was applied to a representative group of CECs complied from literature. Figure 4-1 is a schematic representation of the framework used for selection and prioritisation of CECs for South Africa. The list of representative groups of CECs is shown in Appendix 1 and 2. This list was compiled using the studies carried out throughout the world, and consisted of the USEPA (112 compounds), the EU (58 compounds) the NRC potential organic indicator compounds (52 compounds), the Australian drinking water quality guideline compounds (129 compounds) and relevant South African chemical compounds. From a local context point of view, both studies by Ncube et al. (2012) and Osunmakinde et al. (2013) involved compiling a priority list of target analytes relevant to South Africa were also considered. The prescription volume of drugs was considered, and in some cases the stability of the drugs was also considered. The compounds were often the same as those commonly detected in water systems worldwide. The target compounds from a South African perspective can be grouped into different classes, namely hypertension, analgesics, antiretroviral, antibiotics, hormones and anti-diabetic drugs. Using the prescription data, an estimate can be made relating to the amounts in which these contaminants may be found in wastewater. Developing the CEC prioritisation list also required a significant review of guidelines and developments in the field of water reuse, CECs and quantitative South African data.

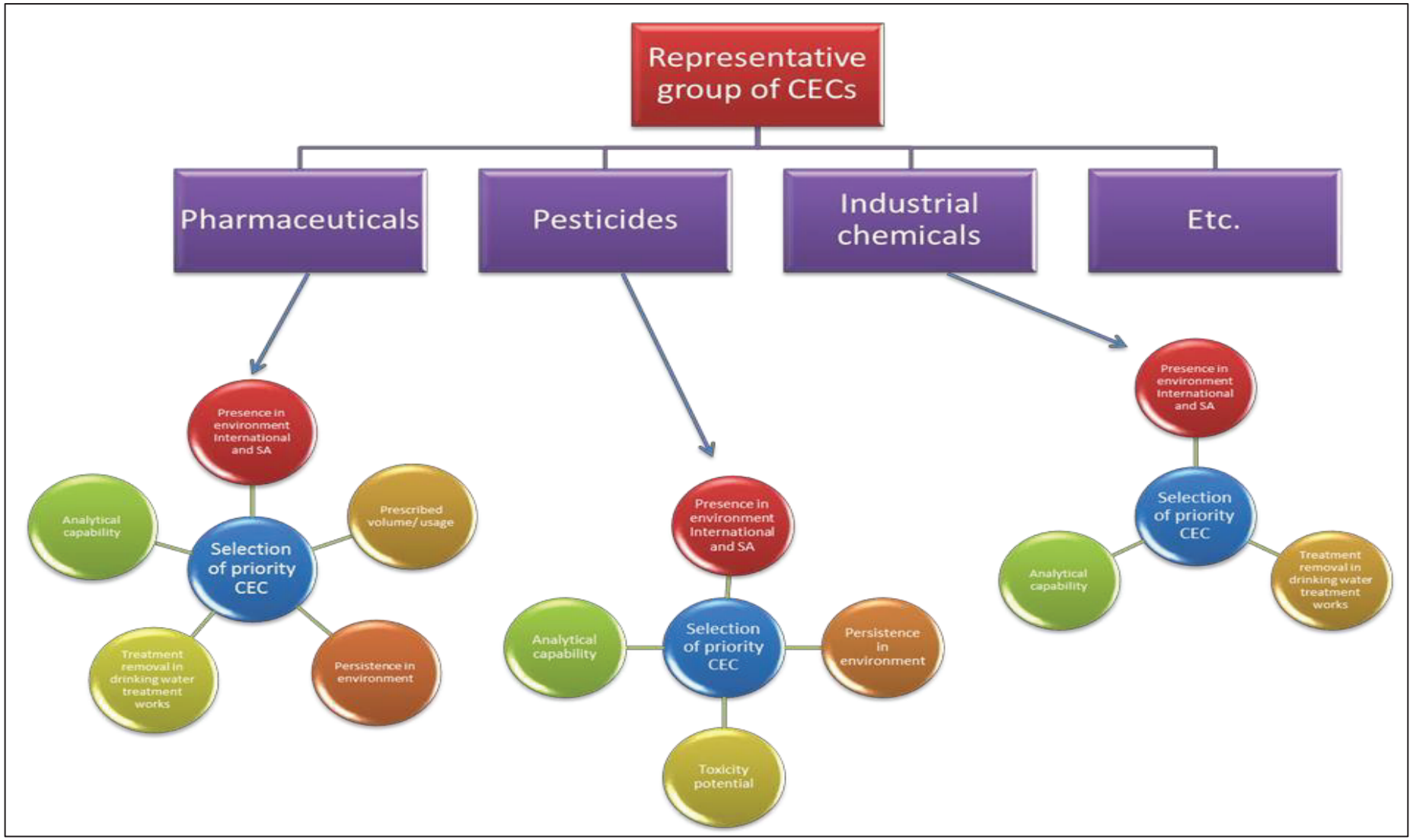

Figure 4-1: Process for inclusion in identifying priority CECs for monitoring water reuse

4.3.2 Recommended Priority List of chemicals of concern

A restricted priority list representing the different groups of chemicals of emerging concern based on best-available knowledge, South African prevalence, potential for exposure and other criteria such as analytical ability to detect is presented in Table 4-5 and forms a framework for discussion for potential monitoring for reclaimed potable water. It is important to note that the priority list cannot be seen as an exhaustive list as each reclaimed potable water reuse project should interrogate the relevance according to the specific area to consider whether extra chemicals might need to be added to the priority list. Indicator compounds representing different groups of compounds and present in large amounts in wastewater such as caffeine, the hormone, 17 beta estradiol, the plasticiser, bisphenol-A, the biocide triclosan, the X-ray contrast fluid Iopromide, flame retardants TDCPP and TCEP are found more frequently in water at detectable levels that may cause harmful effects to the ecosystem or human health and thus can play an important role in reclaimed water quality monitoring.

Table 4-5: Recommended Priority List of chemicals of concern to be included in water quality assessment with direct reuse

Industrial chemicals	Flame retardants: TDCPP and TCEP, X-ray contract fluid: Iopromide, PAH: Benzo(a)pyrene
Pesticides, biocides and herbicides	Atrazine, Terbutylazine, Imidacloprid and Simazine
Natural chemicals	Caffeine, 17 beta estradiol
Pharmaceuticals and metabolites	Antiretroviral drugs Lamivudine and Stavudine Anti-epileptic, Carbamazepine Anti-malarial drugs, Cinchonidine and Cinchonine Analgesic, Paracetamol Antibiotic, Sulfamethoxazole
Personal care products	Anti-microbial, Triclosan
Household chemicals and food additives	Plasticiser, Bisphenol-A
Transformation products	By-product, N-Nitrosodimethylamine (NMDA)

4.4 HEALTH RISKS ASSOCIATED WITH SELECTED PRIORITY CHEMICALS OF EMERGING CONCERN

4.4.1 Industrial chemicals

4.4.1.1 Tris (1,3-dichloro-2-propyp) phosphate (TDCPP)

TDCPP is a widely distributed chemical and is used in flame retardants, pesticides, plasticizers, and nerve gases. Although TDCPP had been banned from use in children's clothing since 1977, frequent detection of TDCPP was reported in a study of children's products, including car seats, changing table pads, portable mattresses, nursing pillows, and high chairs (Stapleton et al., 2011). TDCPP is the most frequently detected flame retardant which is not readily degraded in sewage sludge. Studies have demonstrated limited degradation of TDCPP in natural waters and it is rapidly metabolized by fish (WHO, 1998). TDCPP and its metabolites are considered carcinogenic (Cal. US EPA, 2012). Evidence of carcinogenicity includes increased incidence of liver and kidney tumors in male and female rats, and testicular tumors in male rats (CAL EPA, 2011). TDCPP is associated with other health effects including: kidney and testicular abnormalities, changes in blood parameters, and an increase in thyroid, kidney, and liver weights in rodents (US DHH, 2012). The MRL for TDCPP is 0.05 mg/kg/day (< 364 days) and 0.02 (>365 days) (ATSDR, 2009). No slope factor has been derived for TDCPP.

4.4.1.2 Tris(2-chloroethyl) phosphate (TCEP)

TCEP, is a flame-retardant primarily found in furniture containing polyurethane foam. It is also used as a flame retardant in many other applications such as electronics, textiles, and carpet (ECA, 2009). TCEP was added to the California list of carcinogens in 1992 (Miller, 2011). In 2010, the European Union listed TCEP as a Substance of Very High Concern due its reproductive toxicity and potential to impair fertility (ECA, 2009). Oral studies found that TDCPP as well as TCEP can easily pass from the stomach and intestines into the blood stream. TCEP given to rats caused lesions in the brain (short term exposure) as well as in the kidneys (> 2 years). TCEP also decreased the fertility and induced tumors in the kidney, liver, and stomach, and also induced leukaemia (ATSDR, 2012). Supporting studies found that exposure to TCEP increased tumors in the kidneys, brain damage (Matthews et al., 1993) as well as learning impairments (Tilsen et al., 1990). The International Agency for Research on Cancer (IARC) has classified TCEP as a Group 3 carcinogen (not classifiable as to carcinogenicity to humans) (IARC 2009). The National Institutes of Health's National Toxicology Program has, however, included TCEP as a cancer-causing agent. The MRL for TCEP (<364days) is 0.6 mg/kg/day and 0.2 mg/kg/day for chronic-duration oral exposure (ATSDR, 2009).

4.4.1.3 Iopromide

Iopromide is an iodinated contrast medium used to image internal body organs and blood vessels by x-ray or computerised tomography (CT) scan. Iopromide is consumed at g/L concentrations and is excreted within 24 hours (urine) (Steger-Hartmann et al., 2002). Due its high hydrophilicity (log Kow = -2.33) it may be quite persistent in the environment. Iopromide and trimethoprim are frequently detected pharmaceuticals in effluents of wastewater treatment plants and in surface waters due to their persistence and high usage. The ADI (Acceptable Daily Intake) or maximum amount of iopromide considered safe for a lifetime of exposure is 21 µg/kg/day (NYC, 2010). Unintentional over exposure to iopromide may result in anaphylaxes and severe kidney problems. Iopromide is also included as a performance indicator for injection operations and for surface spreading of CECs in water reuse and groundwater recharge

operations (Anderson et al., 2010). Municipal wastewater is often elevated in nitrogen, iodine, and bromine constituents as compared with ambient waters (NRC, 2012; Teijon et al., 2010). Chlorination of wastewater may therefore lead to increased levels of nitrogenous, iodinated, and brominated disinfection products. Recent studies indicate that iopromide and other ICMs can form toxic iodinated disinfection by-products during oxidation and disinfection water treatment processes (Kormos et al., 2011, Schultz et al., 2008) which will also need to be considered in a health risk assessment.

4.4.1.4 Benzo[a]pyrene

Benzo[a]pyrene is a polycyclic aromatic hydrocarbon (PAH) which is not produced commercially, but occurs as a result of incomplete combustion of organic (carbon-containing) materials such as cigarettes, wood, and coal (ATSDR, 1995). In water, it will absorb strongly to sediment and solids in the water column, where it can be degraded by light near water surfaces, or metabolized by microorganisms in some natural water bodies. Benzo(a)pyrene is listed number 9 on the 2005 Priority List of Hazardous Substances for the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (US EPA, 2007). Subchronic dietary administration of benzo[a]pyrene resulted in in hematopoietic effects (bone narrow depression) in a certain strain of mice (Robinson et al., 1975). In utero exposure to benzo[a]pyrene has produced adverse developmental/reproductive effects in mice, reducing fertility and reproductive capacity in offspring (Mackenzie and Angevine, 1981). Higher doses (120 mg/kg/day) during gestation caused stillbirths, resorptions, and malformations (Legraverend et al., 1984). Neither a reference dose nor a reference concentration has been derived for benzo[a]pyrene by any organization. Dietary administration of benzo[a]pyrene has produced papillomas and carcinomas of the forestomach in mice (Neal and Rigdon, 1967), and treatment by gavage has produced mammary tumors in rats (McCormick et al., 1981) and pulmonary adenomas in mice (Wattenberg and Leong, 1970). Benzo[a]pyrene is classified as a complete carcinogen and also an initiator of skin tumors (EPA, 1991). U.S. EPA Cancer Oral Slope Factor for benzo(a)pyrene is 7.3 per (mg/kg)/day, with a US EPA MCL (drinking water) of 0.0002 mg/L (US EPA 1984). The critical effects of benzo(a)pyrene were reproductive difficulties and an increased risk of cancer.

4.4.2 Pesticides

4.4.2.1 Atrazine

Atrazine is a selective triazine herbicide. It is highly persistent in soil and degrades slowly in water, it has a high potential for groundwater contamination despite its moderate solubility in water (Wauchope et al., 1992). In mammalian studies, atrazine is rated as having low acute toxicity. Atrazine product formulations can be mild skin sensitizers and irritants. Chronic high dose toxicity observed in animals have demonstrated decreased body weight, myocardial muscle degeneration, liver toxicity, developmental ossification defects, impaired fertility, altered estrus cycles, increased pituitary weight, delayed onset of puberty, and reduced levels of luteinizing hormone, prolactin, and testosterone (Eldridge et al., 1994; Laws et al., 2003; Rayner et al., 2004; U.S.EPA, 2003b). Atrazine is not considered genotoxic and not classified as a human carcinogen (IARC and US EPA) The US-EPA has set a NOAEL of 3.5 mg/kg/day and a LOAEL of 25 mg/kg/day based on a 2-year long study showing cardiac toxicity and moderate to severe dilution of the right atrium. The reference dose for the oral consumption of atrazine is 0.035 mg/kg/day. Atrazine has been classified as a category 1 EDC with evidence of ED activity in animal and human cell studies (Matisová and Hrouzková, 2012, EC Document, 1999). It has also been reported to be an androgen inhibitor with a weak oestrogenic effect and also disrupts the hypothalamic control of lutenising hormone and prolactin levels. Other ED complications include damaging of the adrenal glands and impairment of steroid hormone metabolism (summarised by McKinlay et al., 2008).

4.4.2.2 Terbutylazine

Terbuthylazine is an algaecide, microbicide and microbiostat used to control slime-forming algae, fungi, and bacteria. In a few years, terbuthylazine became a chemical of concern, together with its main metabolite desethylterbuthylazine (DET), because of alerting detections in surface and groundwater resources. Terbuthylazine generally is of relatively low acute toxicity, classified as a Group D carcinogen, (inadequate evidence to determine carcinogenicity in humans). There is currently no reference dose or Maximum Concentration Levels (MCL) for terbuthylazine. In a study using rats, maternal toxicity was observed as reduced body weight gain and food intake, and developmental toxicity was observed in the litter with chronic exposure to terbuthylazine. Available studies indicate that terbuthylazine is not mutagenic, however, it is associated with developmental toxicity in a study using rats. (USEPA, 1995). The ED activity of concern with regards to terbuthylazine is activity around the Human pregnane X receptor (hPXR) agonist. From structural similarities to atrazine, it is likely that a weak EDC activity for terbuthylazine may be due to the increase in aromatase, increasing estrogen production (Sanderson et al., 2000). Terbuthylazine is classified (US EPA, 1995) to be practically non-toxic to birds, moderately toxic to vertebrates and highly toxic to aquatic species (Plhalova et al., 2012).

4.4.2.3 Imidaclorprid

Imidacloprid is a systemic, chloro-nicotinyl insecticide. Based on its high water solubility (0.5-0.6 g/L) and persistence, it is highly likely to leach into ground water. Consumption of imidacloprid results in decreased body weight and skeletal abnormalities and changes in chromosomes in human lymphocytes. Imidacloprid also tested positive for causing genotoxicity in Chinese hamster ovary cells. Imidacloprid is considered non-carcinogenic (Gervias et al., 2010). U.S. EPA has derived a chronic RfD for imidacloprid of 0.057 mg/kg/day and an acute RfD of 0.14 mg/kg/day. It is not listed for reproductive or developmental toxicity. A developmental neurotoxicity screening study in rats (Sheets 2001) suggests that imidacloprid may cause neurotoxicity in offspring born to imidacloprid-exposed mothers at doses which do not cause maternal toxicity. Study conducted on rats suggests that the neonicotinoids may adversely affect human health, especially the developing brain (Gervias et al., 2010). Imidacloprid is included in the draft list of initial chemicals for screening under the U.S. EPA Endocrine Disruptor Screening Program (EDSP) (US-EPA, 2007). The list of chemicals was generated based on exposure potential, not based on whether the pesticide is a known or likely potential endocrine disruptor. Imidacloprid caused degenerative changes in the thyroid in various animal studies (summarised in USDA, 2005). Imidacloprid was also found to alter the levels of Luteinizing hormone, follicle stimulating hormone and progesterone in female rat studies (Upasana et al., 2011). Exposure to sublethal dosages of imidacloprid affects the reproductive organ of male rats by fragmenting seminal DNA and by increasing apoptosis of spermatogenic cells (Bal et al., 2012). The adverse effect of imidacloprid on the reproduction of male rats appeared to be due to the induction of oxidative stress in testis.

4.4.2.4 Simazine

Simazine is a selective triazine herbicide. Simazine is persistent and does not adsorb strongly to soil particles and is likely to contaminate the groundwater table. Observed effects in test animals include tremors, damage to the testes, kidneys, liver, and thyroid, disturbances in sperm production, and gene mutations (US EPA, 1988). Long term exposure to simazine has the potential to cause tremors; damage to testes, kidneys, liver and thyroid; gene mutations. Simazine is likely either non-mutagenic or weakly mutagenic and does not appear to be teratogenic. Although initial evaluations indicated that there may be a cancer risk to humans exposed to Simazine had been classified as “unlikely to be carcinogenic to humans” in 2006 (US-EPA, 2006). After subchronic and chronic exposure to simazine, a variety of species were shown to exhibit neuroendocrine effects resulting in both reproductive and developmental

consequences that are considered relevant to humans. Simazine is genotoxic and has been shown to have immunosuppressive (Kim et al., 2002) and have endocrine disrupting activities (Orton et al., 2009). There is direct evidence that simazine is associated with neuroendocrine disruption which is the primary toxicological effects of regulatory concern for simazine. The NOAEL determined for short-term exposure is 6.25 mg/kg/day. The MOE level of concern includes an uncertainty factor of 100X which includes 10X each for Category 2 EDC (US-EPA, 2006).

Simazine is an inducer of aromatase and may thereby act as an endocrine disrupter by increasing cellular estrogen levels (Rakitsky et al., 2000; Sanderson et al., 2000). Significant association between prostate cancer risk and exposure to simazine (1.89-fold excess risk for those highly exposed compared with those not exposed) was observed among 1516 prostate cancer cases and 4994 age-matched controls in a population-based case-control study in British Columbia, Canada (Band et al., 2011). Since simazine appears to be genotoxic, it has been proposed that chlorotriazine (atrazine and simazine) administration promotes the development of mammary gland tumors by inducing a premature reproductive senescence and thus creating an endocrine milieu conducive to tumor growth (Stevens et al., 1994; Rakitsky et al., 2000).

4.4.3 Natural chemicals

4.4.3.1 Caffeine

Caffeine is a central nervous system and metabolic stimulant. The principal mode of action is as a nonselective antagonist of adenosine receptors. An adverse effect level of 3 mg/kg bw/day is based on observations of increased anxiety (NZFSA, 2012). No studies have reported the potential chronic effects of caffeine consumption by children. Toxic doses are found at greater than 10 grams for an average adult, which is greater than typically consumed doses of less than 500 milligrams. Ordinary consumption has low health risks, even when carried on for years. The Australian guideline value for caffeine has been recommended as 0.35 µg/L which was calculated based on a predicted Threshold of Toxicological Concern (TTC) of 1.5 µg/kg/d (NRMMC, 2008). The system used in deriving the predicted TTC assigns organic chemicals to one of three ‘classes’ based on their chemical structure, presence of structural alerts for toxicity and known metabolic pathways.

4.4.3.2 17-alpha-estradiol

The ADI for 17-alpha-estradiol of 0.05 µg/kg/d is recommended by the Australian Guidelines for Water Recycling Augmentation of Drinking Water Supplies (2008) which leads to a drinking water quality guideline of 0.0015 µg/l (or 1.5 ng/ℓ). The South African recommended target value has a lower value of <1.0 ng/ℓ for estrogenic activity specifically provided in estrogenic equivalency factor or quotients (or EEQs/ℓ) (Genthe and Steyn, 2009). The guideline value was based on an acceptable daily intake of 50 ng/kg body weight per day. The trigger value of 0.7 ng EEQ/L is based on the World Health Organisation’s value for an acceptable daily estradiol equivalent intake of 50 ng/kg of body mass, also taking into consideration that exposure through water intake probably accounts for only about 10% of the total exposure to oestrogenic activity. Furthermore, in calculating the trigger value, an average body mass of 65 kg and daily water intake of 2 L were assumed with allowance made for a safety factor of 1 000 to compensate, among others, for sensitive populations. Studies carried out in South Africa have found that although river waters generally contained above trigger value levels of estrogenic activity, conventionally treated drinking waters were found to be below the recommended trigger value (Genthe and Steyn, 2009).

4.4.4 Pharmaceuticals and metabolites

4.4.4.1 Carbamazepine

Carbamazepine was included as it has been detected in South African drinking waters, is prescribed in abundant quantities, and is persistent. Paracetamol and Carbamazepine are both used as indicators of removal efficiency, are risk exemplar contaminants, recommended in the Australian drinking water quality guidelines and detected in treated wastewater and should therefore be included on a priority list. The calculated Reference Dose (RfD) for carbamazepine is 0.013 mg/kg/d, based on the human minimum therapeutic dose for children and accounting for uncertainty is (MDH, 2013) whereas the Australian Guidelines for Water Recycling Augmentation of Drinking Water Supplies (NRMMC, 2008) have a lower recommended reference dose of 2.8 µg/kg/d (or 0.0028 mg/kg/d). The RfD is based, in part, on endocrine effects observed in humans at therapeutic dose levels. Nervous system effects have been reported in various human studies (drowsiness, vision disturbances, and equilibrium disturbances). In addition, reduced body weight gain in offspring in laboratory animals during lactation has been observed. Developmental effects in humans include spinal bifida, head and facial deformities and heart defects. Endocrine effects include decreased thyroid hormones and reduced free oestrogen and testosterone. Decreased fertility was reported in animals at 8 times higher than the human LOAEL (lowest observed adverse effect level) and over 3,000 times higher than the RfD. Carbamazepine may affect the pituitary gland. Some clinical studies have shown immunosuppression. Human developmental effects have been reported at therapeutic doses in many prospective studies of epileptic women who have taken carbamazepine while pregnant. Most developmental effects in animal studies have occurred at doses near or above 200 mg/kg/d, with a human equivalent dose > 44 mg/kg/d which is over 8 times higher than the human LOAEL and over 2,000 times higher than the RfD. Carbamazepine has produced decreased fertility in animal studies at human equivalent doses of 52 mg/kg-day or more (over 10 times higher than the human LOAEL and over 2500 times higher than the RfD). Effects on testes and spermatogenesis in animals occurred at human equivalent doses from 7.3 to 23 mg/kg/d (within the human therapeutic maintenance dose range) and decreased fertility was reported in animals at human equivalent doses of over 8 times higher than the human LOAEL and above the “not to exceed” dose level of approximately 17 mg/kg/d for human adults.

4.4.5 Antimalarial drugs

4.4.5.1 Cinchonidine and Cinchonine

As antimalarial drugs are not normally included in the European, Australian and North American priority lists, cinchonidine and cinchonine are prescribed and have been detected so should therefore be included in a South African priority list of chemicals of concern. No acceptable daily intake or reference dose for long-term exposure has been calculated for these drugs. In some cases, side effects have occurred at therapeutic doses of 1,6 mg/kg. These side effects include tinnitus, dizziness, headaches, sight disorders, hearing loss, nausea and diarrhoea. (IMEA, 2009).

4.4.5.2 Paracetamol

Paracetamol is an analgesic prescribed in high volumes and available over-the-counter in South Africa. A paracetamol guideline value of 175µg/l is recommended by the Australian Guidelines for Water Recycling Augmentation of Drinking Water Supplies (NRMMC, 2008) based on an ADI (Acceptable Daily Intake) of 50µg/kg/d.

4.4.5.3 Sulfamethoxazole

A guideline for the antibiotic sulfamethoxazole in drinking water made from recycled water has been established at 35µg/l by applying the lowest acceptable daily intake for sulphonamides established by the NRA (namely 0.01 mg/kg bw/day [NRA 2000]).

4.4.5.4 DDT

Total DDT may need to be included in areas where DDT usage is known to occur. DDT was not included in the prevalence screening as the extraction process focussed on polar water-soluble compounds and was not present in the library of compounds selected for.

4.4.6 Antiretroviral drugs – Lamivudine and Stavudine

Lamivudine and Stavudine, the antiretroviral drugs were included in the list as they are regularly prescribed and may be persistent in the environment. No acceptable daily intake or reference dose for long-term exposure has been calculated for these drugs, and as for the antimalarial drugs side effects at therapeutic doses (average of 2 mg/kg) have been observed and include the following: anorexia, nausea, abdominal pain, joint pains, burning sensation in the feet, itching of skin or skin rash, dizziness, jaundice, vomiting, confusion, and convulsions. A surrogate ADI can be used as described in the section Pharmaceuticals with no reference dose values or acceptable daily intakes

4.4.7 Personal care products

As representatives of personal care products; either Triclosan or 5-Chloro-2-(2,4-dichlorophenoxy) phenol should be considered. The Minnesota Department of Health has determined a reference dose for triclosan to be 0.067 mg/kg/d based on animal studies and accounting for uncertainty (MDH, 2013). The adverse effect measured was decreased total thyroxine (tT4). Additional health effects observed in the study were increased liver weights in pregnant animals, decreased foetal body weight, and decreased serum estradiol.

4.4.8 Household chemicals and food additives

Bisphenol-A (BPA) is a widely studied organic chemical used in the production of polycarbonate (PC) and epoxy-phenolic resins and can be found in infant feeding bottles, storage containers, refillable water and other liquid containers as well as water pipes (EU, 2003). BPA results in changes in tissue enzymes and hormone receptors, and interacts with other hormone-response systems, such as the androgen and thyroid hormone receptor signalling systems. (Chapel Hill Panel, 2007). Those most vulnerable to problems resulting from BPA exposure are pregnant mothers and new-borns (FDA 2008). Studies have shown that BPA in very low (pico- and nanomolar) concentrations exerted multidirectional effects on physiological functions of cells and tissues by binding with receptors present out of the nucleus. BPA can block both androgen and thyroid hormone receptors resulting in negative impacts on sex hormones in men (Jiang et al., 2013). Adverse effects include [1] decreased androstenedione levels, [2] decreased free testosterone levels, [3] decreased free androgen index, [4] increased sex hormone-binding globulin levels. A reference dose of 0.05 mg/kg/d (UF 1000) is based on the reduced body weights in rats. Both the FDA (2008) and EFSA (2006) have accepted the appropriate no observed adverse effect level (NOAEL) for its assessment of BPA to be 5 mg/kg bw/day derived from two multigenerational rodent studies (EU, 2003). The FDA set a TDI of 0.05 mg BPA/kg bw, derived by applying a 100-fold uncertainty factor to the overall NOAEL of 5 mg/kg bw/day, whereas the EFSA (2006) derived a temporary TDI of 0.01 mg/kg bw, applying a 500-fold

uncertainty factor. An anti-androgenic (AA) reference dose (RfD) based on the decreased testosterone levels in male offspring was derived for BPA for use in cumulative health risk assessments (Kortenkamp and Faust, 2010). The RfD for anti-androgenic activity for BPA is 12.5 µg/kg/day, with a point of departure of 1.25 mg/kg/day and an uncertainty factor (UF) of 100.

4.4.9 Transformation by-product – N-Nitrosodimethylamine (NMDA)

NDMA is an industrial by-product of several industrial processes and is used in the manufacturing of unsymmetrical dimethylhydrazine (UDMH) used for rocket fuel. NDMA can be an especially challenging contaminant for water reuse applications because chlorination has been linked to NDMA formation. Chlorination of secondary wastewater effluent typically results in the formation of between 20 and 100 ng/L NDMA (Mitch and Sedlak, 2002). NDMA is also not well rejected by reverse osmosis membranes (Mitch et al., 2003) and must be removed by subsequent photolysis. NDMA is included in a group of extremely potent carcinogens, the N-nitrosamines (U.S. EPA, 2002). Their cancer potencies are much higher than those of the trihalomethanes. The US EPA has calculated the one in one million cancer risk from drinking water to occur at approximately 0.7 ng/L. Although NDMA is listed as a priority pollutant, a federal maximum contaminant level (MCL) has not been established for drinking water. The U.S. EPA established a clean-up level of 0.7 ng/L for NDMA in groundwater, based on a risk assessment target of an increased lifetime cancer risk of 10-6 in drinking water (U.S. EPA, 2002). The oral slope factor for NDMA in water is 5.1, yet no reference dose has been derived for this compound.

4.4.10 Other compounds

In some cases, for certain chemical compounds and pharmaceuticals with no reference dose values or acceptable daily intakes, the World Health Organisation recommends the use of a surrogate ADI, which is derived by dividing the lowest daily therapeutic dose by safety factors ranging from 1000 to 10 000 (WHO, 2012). The use of the lowest daily therapeutic dose as a starting point for deriving guideline values or assessing risk has been adopted by others (Webb et al., 2003; Schwab et al., 2005; DWI, 2007; Versteegh, Van der Aa & Dijkman, 2007). For most pharmaceuticals, a safety factor of 1000 is applied to the lowest daily therapeutic dose. The Australian drinking water guidelines make use of a very similar approach based on the structure of a compound called the Threshold of Toxicological Concerns (TTC) approach where chemicals are grouped into three general toxicity classes:

- Class I – Simple chemicals, efficient metabolism, low oral toxicity
- Class II – May contain reactive functional groups, slightly more toxic than Class I
- Class III – Substances that have structural features that permit no strong initial presumption of safety or may even suggest significant toxicity

Human exposure thresholds of 1800, 540, and 90 µg/person/day were proposed for the 3 classes of chemicals which represents dosages of 30, 9, and 1.5 µg/kg body weight/day, respectively assuming a human body weight of 60 kg, and a safety/uncertainty factor of 100 (Munro et al., 1996). Using these TTC human exposure thresholds, an acceptable level of each chemical in reclaimed water was derived as follows:

$$\text{Acceptable Level in recycled water (µg/L)} = \frac{x\ \mu g\ per\ person\ per\ day \times \text{proportion allocated to water}}{2L\ per\ person}$$

Where X = 1800 µg/day for class I compounds, 540 µg/day for class II compounds, and 90 µg/day for class III compounds;

Proportion exposure allocated to water is 0.2 (20% from water intake and rest from food and other exposures) and drinking water intake = 2 L/day.

Therefore, the TTC approach assigns acceptable levels for these three classes of chemicals in reclaimed water as follows:

- 180 µg/L for Class I compounds,
- 54 µg/L for Class II compounds, and
- 9 µg/L for Class III compounds.

It is important to note that the TTC approach was meant solely as a method to derive relatively rapid conservative estimation of risk for compounds without detailed risk assessment or with limited datasets.

4.5 SUMMARY

Many lists of contaminants of emerging concern have been compiled internationally and locally. In this project, a priority list for CECs in direct potable reuse was developed. Developing the CEC recommended prioritisation list involved using compounds detected in South African potable waters which also represents those compounds which are persistent and are not removed by water treatment processes, pharmaceuticals prescribed in the largest volumes, pesticides identified as high-risk priority pesticides in South Africa, and chemicals representing each of the groups of CECs. Other chemicals were included as indicator compounds known to occur in high concentrations in wastewaters to illustrate process efficiencies. Chemicals representing the different groups of contaminants of emerging concern based on best-available knowledge, South African prevalence, potential for exposure and other criteria such as analytical ability to detect are included in the recommended list.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

With the rise in utilisation of chemical compounds on a daily basis, thousands of regulated and unregulated emerging contaminants have been discharged and detected in the aquatic environment. If not adequately treated, reclaimed water can serve as an exposure route for emerging contaminants. In order to conduct a thorough risk assessment of emerging micro-pollutants for humans, there is a need to put in place appropriate facilities for analysis and to assess the exposure rate and the actual dose in order to predict the associated adverse health effects. During wide discussions within the water sector in the course of carrying out this project, including and in particular also the DWS, the conclusion was reached that it is imperative that a national (virtual) centre for analysis of contaminants of concern (including all specialised chemical and microbiological analyses) be established, consisting of a network of laboratories. More specifically, the following is recommended:

- That a national laboratory network for advanced water quality analysis be established, and that it will have the framework of a virtual centralised facility, but consisting of regional laboratory networks in four of the provinces, namely Western Cape, Gauteng, KwaZulu-Natal and Free State.
- It is the intention that the national laboratory network for advanced water quality analysis will:
  - Facilitate regional cooperation between the laboratories.
  - Propose validated, standard operating procedures.
  - Provide competitive analysis costs (different packages) for WSPs.
  - Develop regional capacity and expertise that can again be made available nationally through the NCWRA.
  - Promote the exchange of scientific data and technical knowledge.
- Support (financial and institutional) by the Department of Water and Sanitation (DWS) will be crucial in ensuring the success and sustainability of the water reuse RLNs. DWS is the sector leader and as such needs to set the tone regarding the importance of credibility in water quality testing results. Private-public partnerships (PPP) could also be a viable option for this purpose, either as part of the Strategic Water Partners Network (SWPN) or similar thereto.

A further important factor, and one that needs to be addressed from the outset, is the need for well-trained and experienced personnel and managers for the regional laboratory networks (RLNs). Follow-up projects by the WRC, WISA, Universities, Water Boards and EWSETA will be required to create and enabling climate for planning the staffing and career development in the RLNs. Capacity building initiatives in current WRC projects are already driving this strongly.

Many lists of contaminants of emerging concern have been compiled internationally and locally. In this project, a priority list for CECs in direct potable reuse was developed. It is recommended that each reclaimed potable water reuse project interrogate the relevance of these chemicals according to the specific area, to consider whether additional chemicals might need to be added to the priority list. Using the framework described in this Chapter above and lists of chemical compounds included in the spreadsheets, an appropriate list should be developed. For example, total DDT where DDT use is known to occur, or metals, if a metallurgic industry occurs in the catchment. In addition, a review of current guidelines and developments in the field of water reuse, CECs and quantitative South African data is required. Screening tests looking at the quality of the wastewaters should initially be carried out on a frequent and regular basis, to establish which compounds are found or are consistently absent, before the more expensive quantitative tests be used on a routine basis to monitor removal of CECs.

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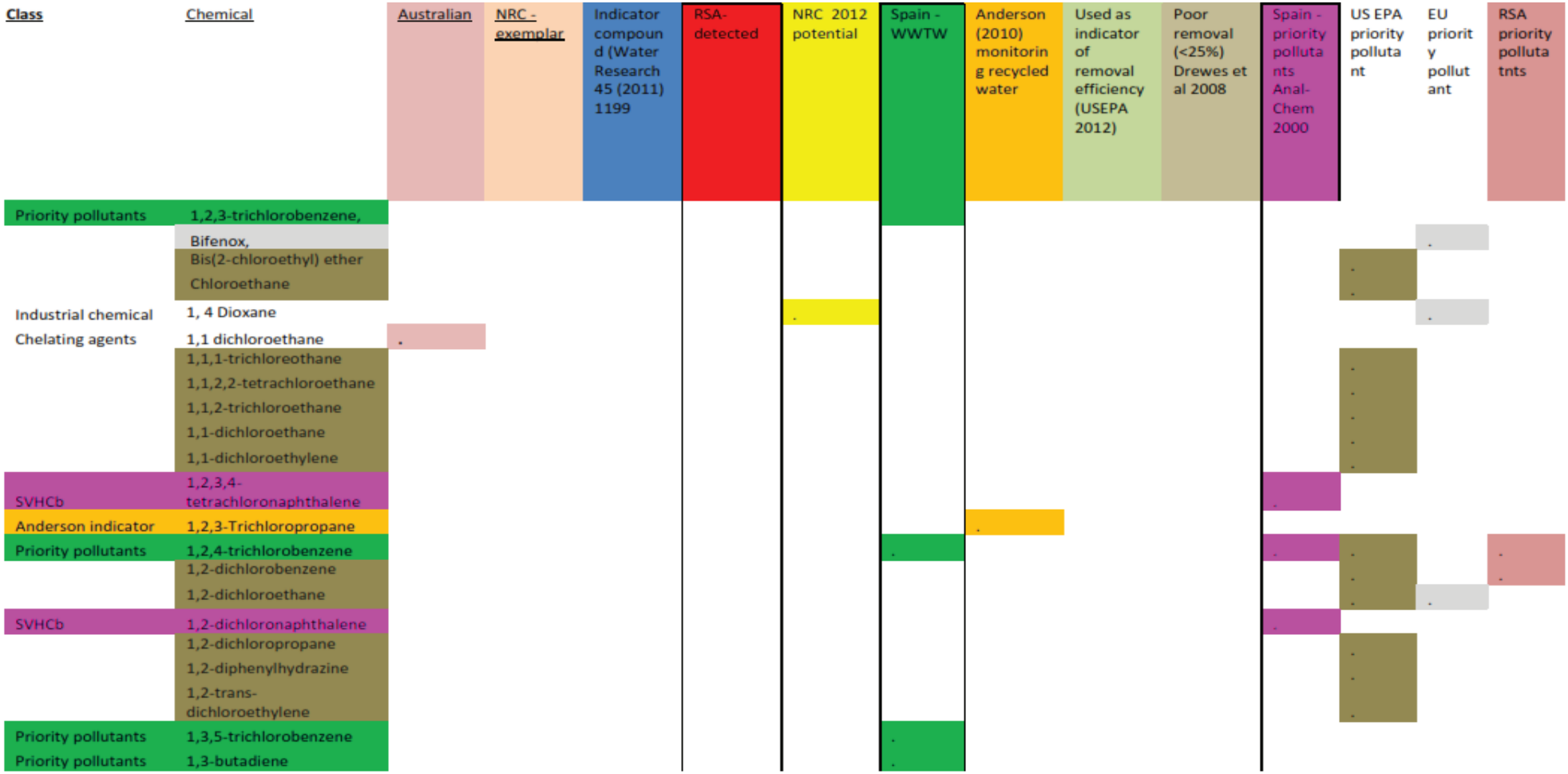
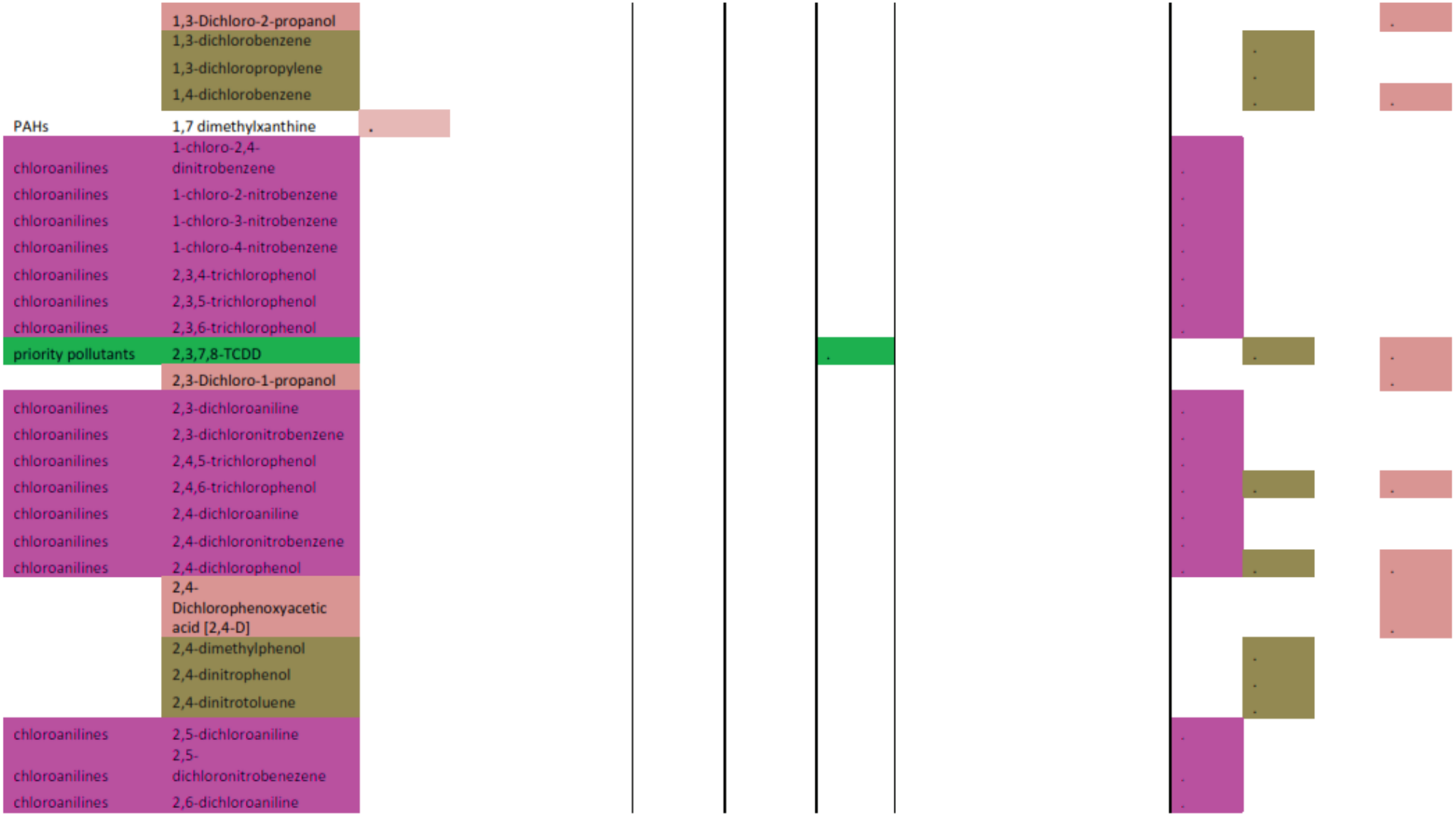
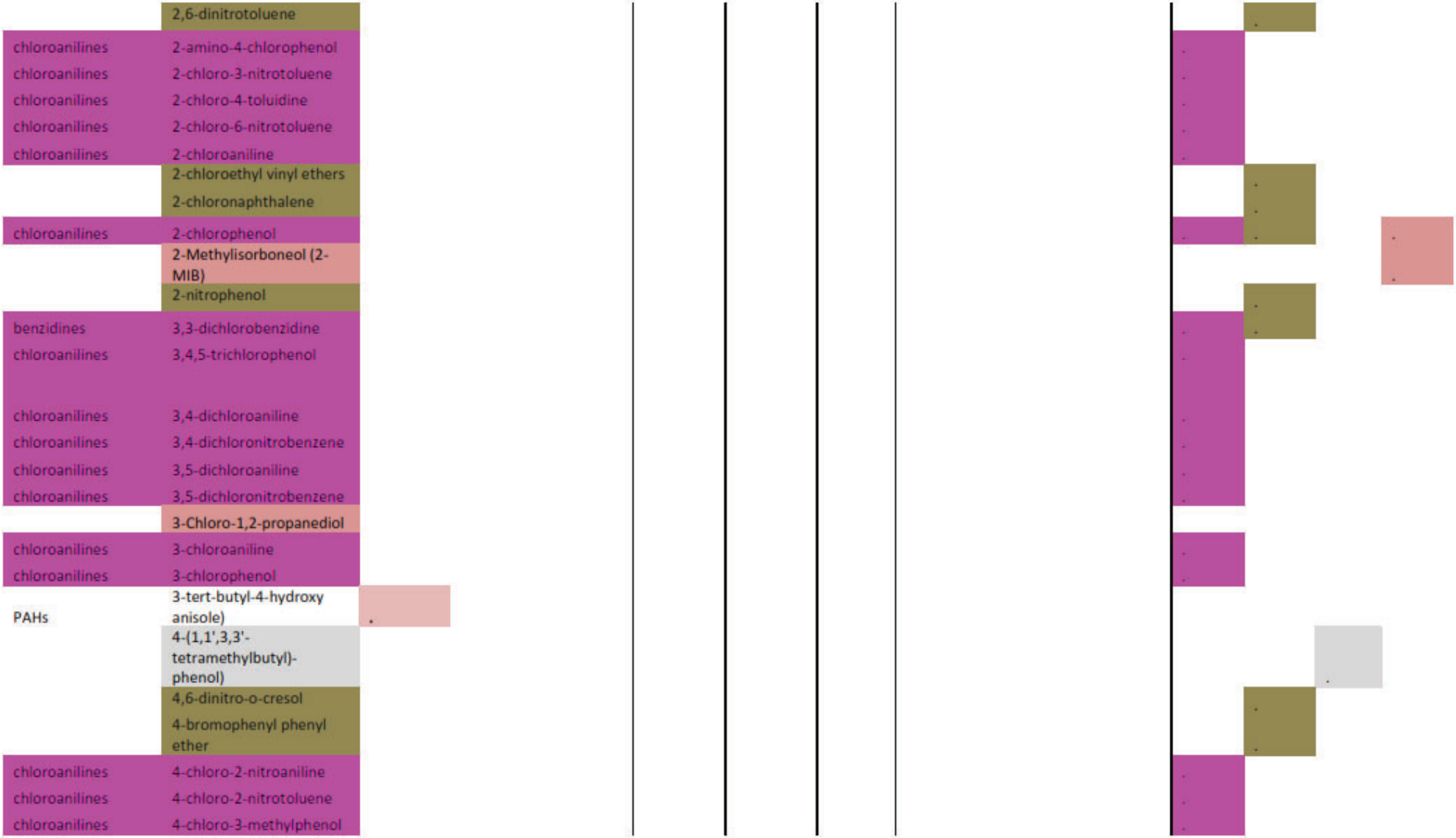
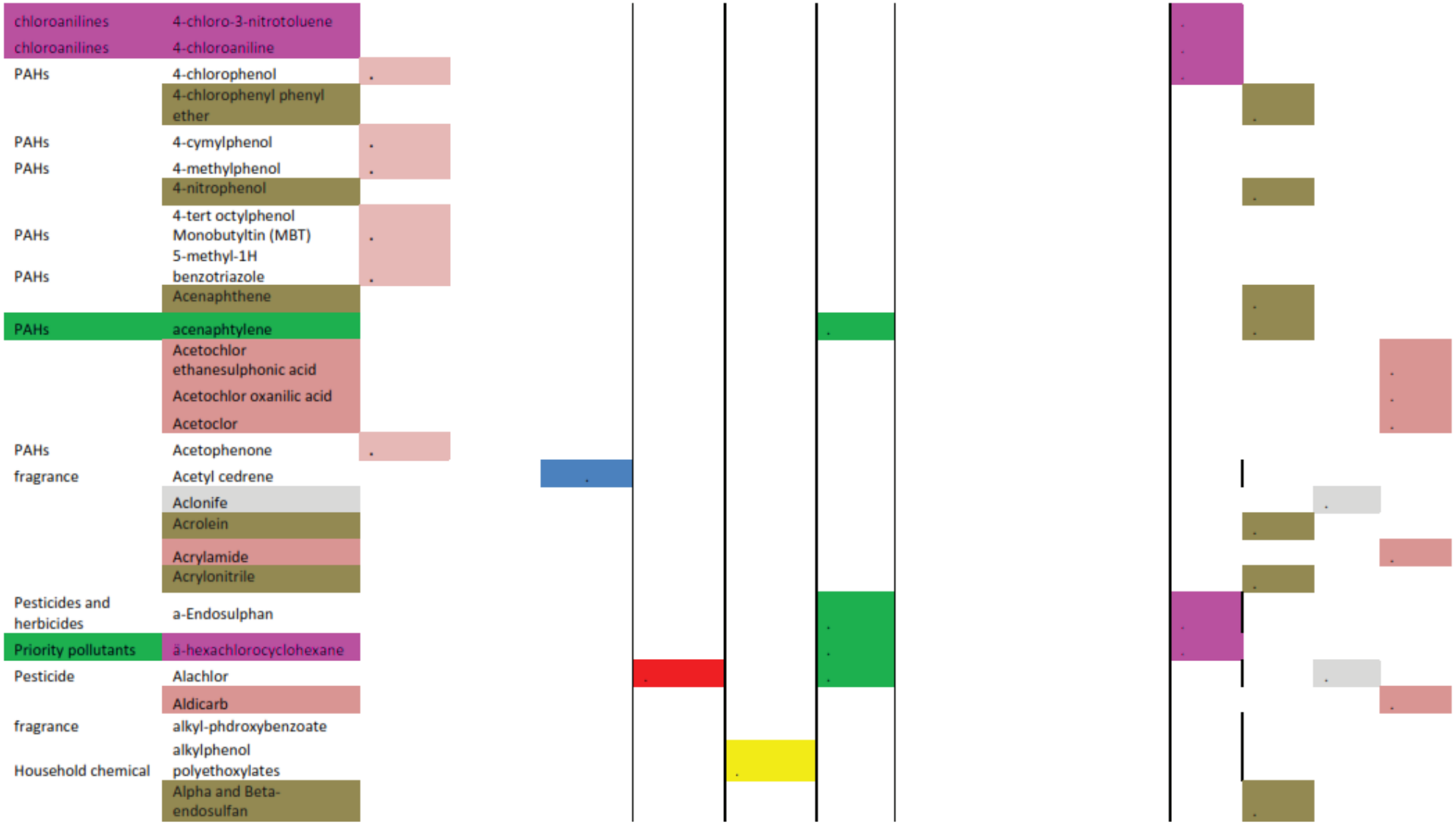
APPENDIX 1: PRIORITY LIST OF INDUSTRIAL CHEMICALS

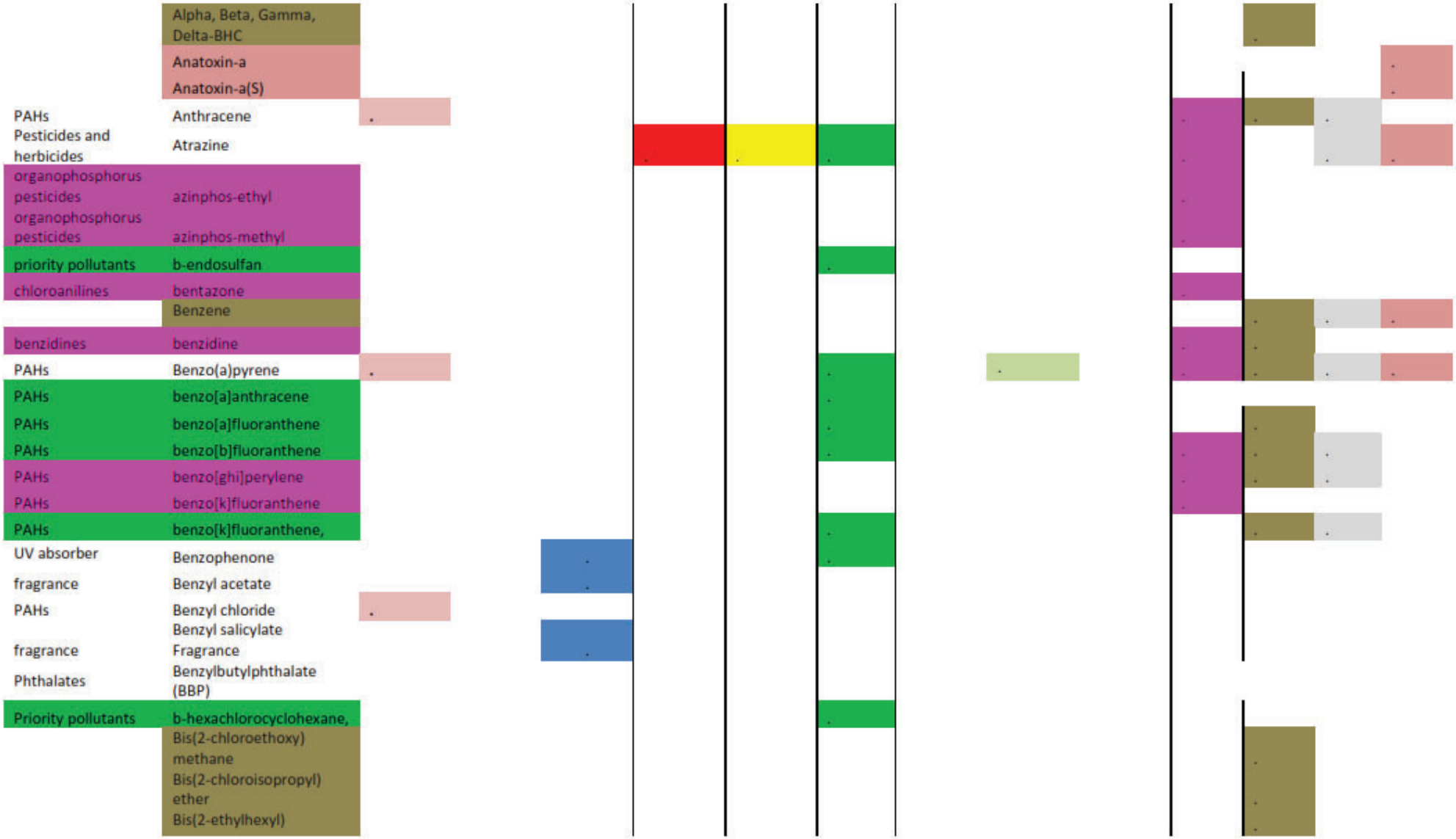


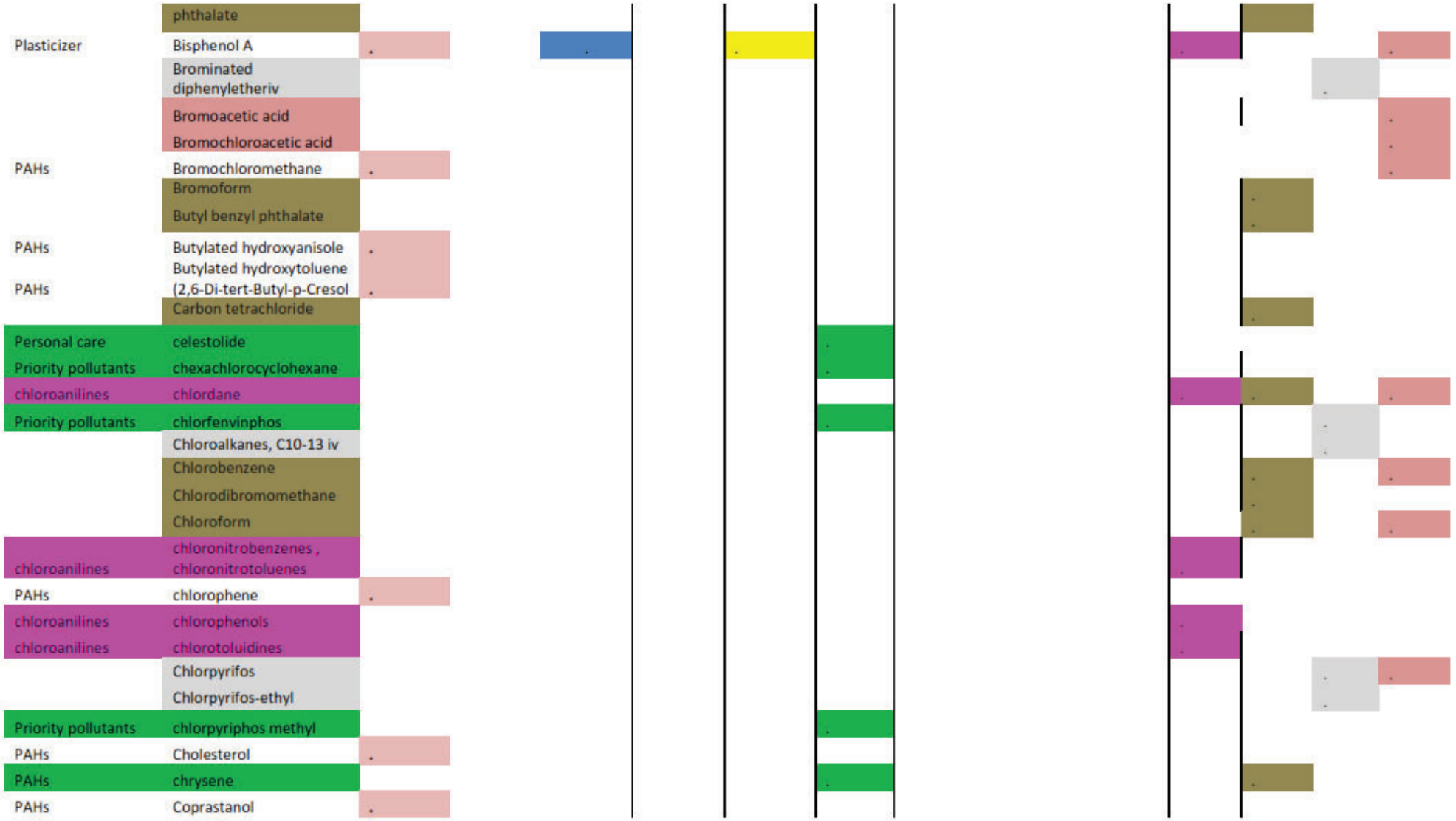
Class	Chemical	Australian	NRC - exemplar	Indicator compound (Water Research 45 (2011) 1199	RSA-detected	NRC 2012 potential	Spain - WWTW	Anderson (2010) monitoring recycled water	Used as indicator of removal efficiency (USEPA 2012)	Poor removal (<25%) Drewes et al 2008	Spain - priority pollutants Anal-Chem 2000	US EPA priority pollutant	EU priority pollutant	RSA priority pollutants
Priority pollutants	1,2,3-trichlorobenzene,													
	Bifenox,												.	
	Bis(2-chloroethyl) ether											.		
	Chloroethane											.		
Industrial chemical	1, 4 Dioxane					.							.	
Chelating agents	1,1 dichloroethane	.												
	1,1,1-trichloreothane											.		
	1,1,2,2-tetrachloroethane											.		
	1,1,2-trichloroethane											.		
	1,1-dichloroethane											.		
	1,1-dichloroethylene											.		
SVHCb	1,2,3,4-tetrachloronaphthalene										.			
Anderson indicator	1,2,3-Trichloropropane							.						
Priority pollutants	1,2,4-trichlorobenzene						.				.	.		.
	1,2-dichlorobenzene											.		.
	1,2-dichloroethane											.	.	
SVHCb	1,2-dichloronaphthalene										.			
	1,2-dichloropropane											.		
	1,2-diphenylhydrazine											.		
	1,2-trans-dichloroethylene											.		
Priority pollutants	1,3,5-trichlorobenzene						.							
Priority pollutants	1,3-butadiene						.							

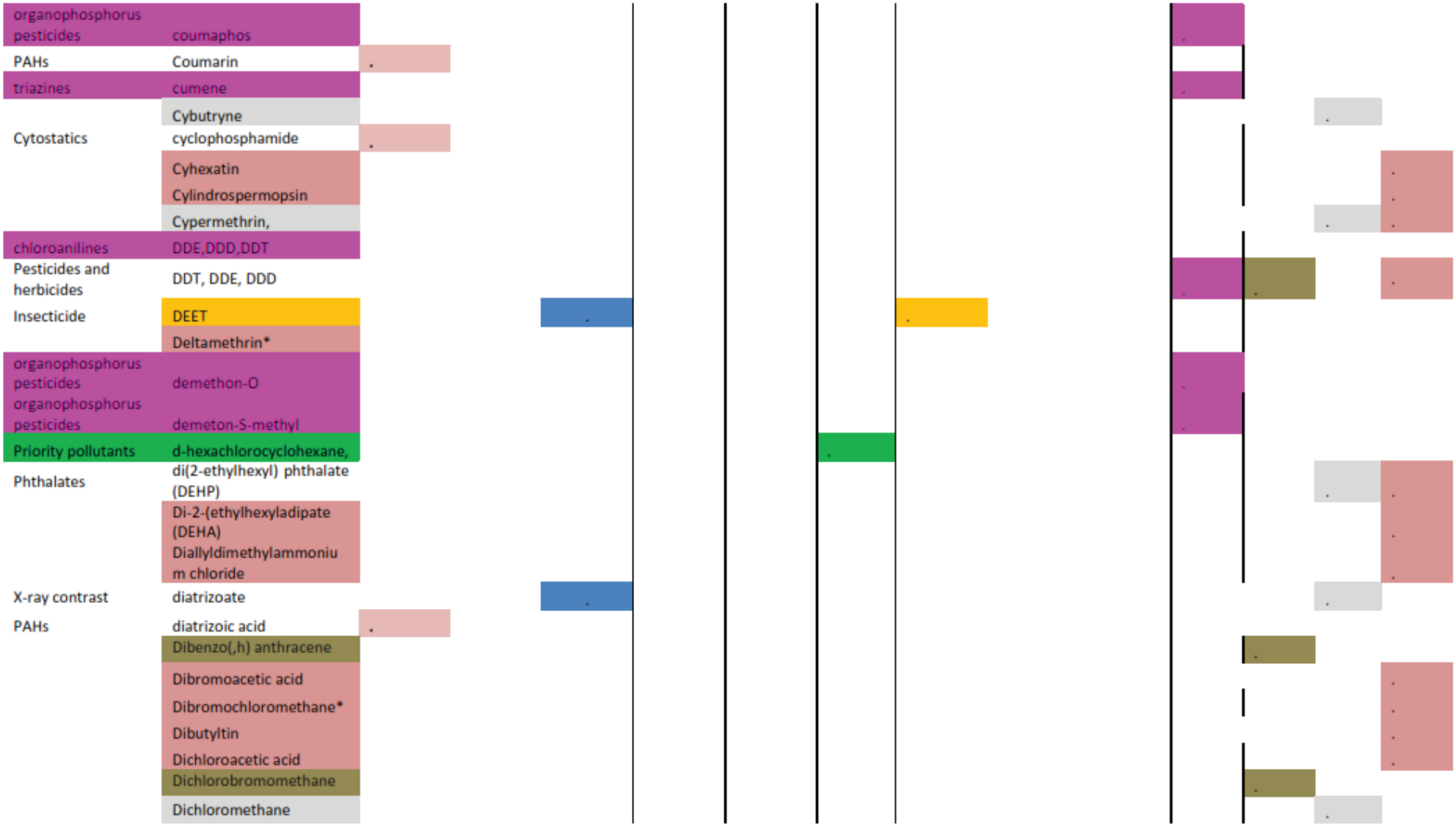

1,3-Dichloro-2-propanol
1,3-dichlorobenzene
1,3-dichloropropylene
1,4-dichlorobenzene
PAHs
1,7 dimethylxanthine
chloroanilines
1-chloro-2,4-dinitrobenzene
chloroanilines
1-chloro-2-nitrobenzene
chloroanilines
1-chloro-3-nitrobenzene
chloroanilines
1-chloro-4-nitrobenzene
chloroanilines
2,3,4-trichlorophenol
chloroanilines
2,3,5-trichlorophenol
chloroanilines
2,3,6-trichlorophenol
priority pollutants
2,3,7,8-TCDD
2,3-Dichloro-1-propanol
chloroanilines
2,3-dichloroaniline
chloroanilines
2,3-dichloronitrobenzene
chloroanilines
2,4,5-trichlorophenol
chloroanilines
2,4,6-trichlorophenol
chloroanilines
2,4-dichloroaniline
chloroanilines
2,4-dichloronitrobenzene
chloroanilines
2,4-dichlorophenol
2,4-Dichlorophenoxyacetic acid [2,4-D]
2,4-dimethylphenol
2,4-dinitrophenol
2,4-dinitrotoluene
chloroanilines
2,5-dichloroaniline
chloroanilines
2,5-dichloronitrobenezene
chloroanilines
2,6-dichloroaniline

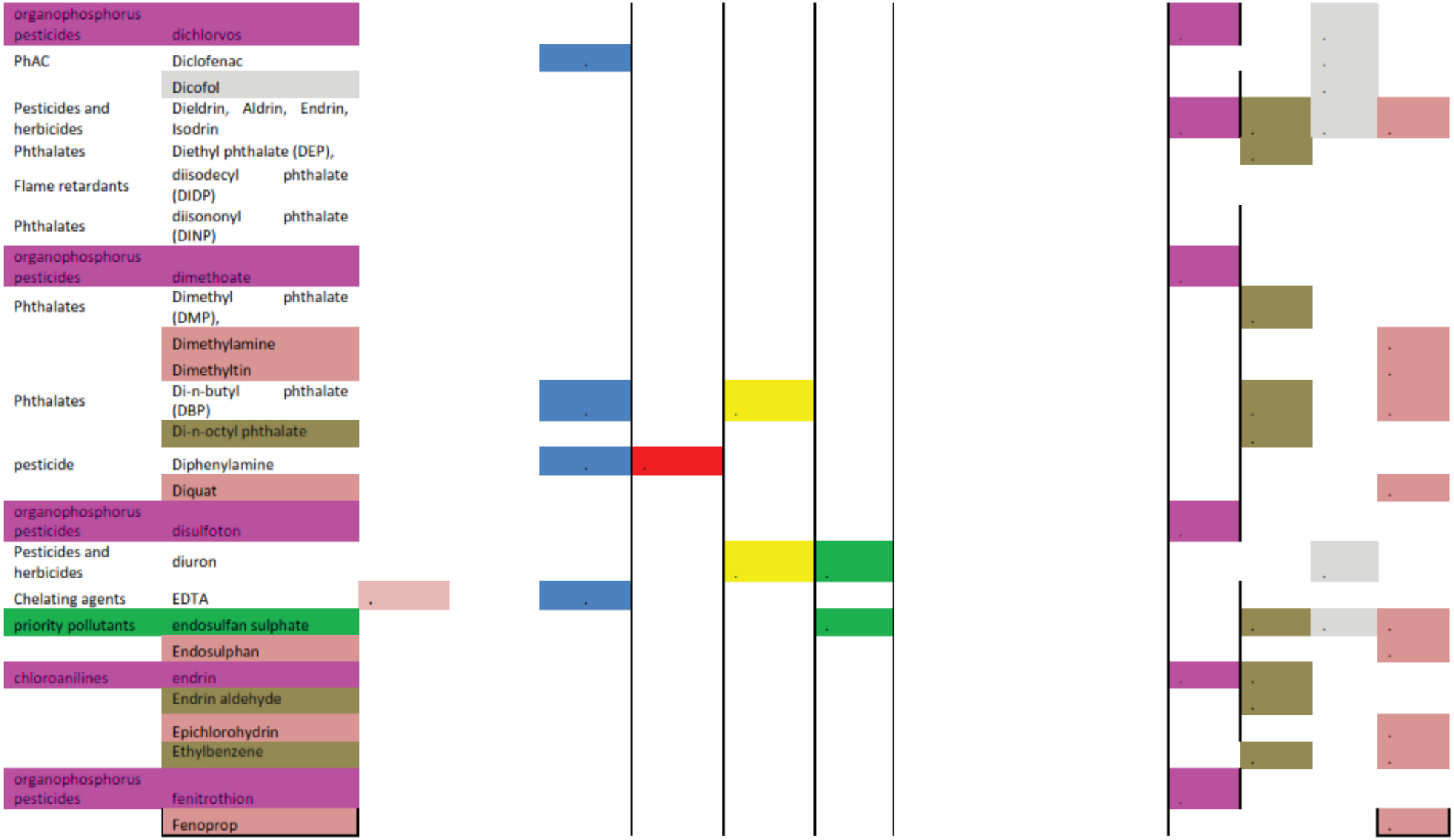

2,6-dinitrotoluene
chloroanilines 2-amino-4-chlorophenol
chloroanilines 2-chloro-3-nitrotoluene
chloroanilines 2-chloro-4-toluidine
chloroanilines 2-chloro-6-nitrotoluene
chloroanilines 2-chloroaniline
2-chloroethyl vinyl ethers
2-chloronaphthalene
chloroanilines 2-chlorophenol
2-Methylisorboneol (2-MIB)
2-nitrophenol
benzidines 3,3-dichlorobenzidine
chloroanilines 3,4,5-trichlorophenol
chloroanilines 3,4-dichloroaniline
chloroanilines 3,4-dichloronitrobenzene
chloroanilines 3,5-dichloroaniline
chloroanilines 3,5-dichloronitrobenzene
3-Chloro-1,2-propanediol
chloroanilines 3-chloroaniline
chloroanilines 3-chlorophenol
PAHs 3-tert-butyl-4-hydroxy anisole)
4-(1,1',3,3'-tetramethylbutyl)-phenol)
4,6-dinitro-o-cresol
4-bromophenyl phenyl ether
chloroanilines 4-chloro-2-nitroaniline
chloroanilines 4-chloro-2-nitrotoluene
chloroanilines 4-chloro-3-methylphenol


chloroanilines
4-chloro-3-nitrotoluene
chloroanilines
4-chloroaniline
PAHs
4-chlorophenol
4-chlorophenyl phenyl ether
PAHs
4-cymylphenol
PAHs
4-methylphenol
4-nitrophenol
4-tert octylphenol
PAHs
Monobutyltin (MBT)
5-methyl-1H
PAHs
benzotriazole
Acenaphthene
PAHs
acenaphtylene
Acetochlor ethanesulphonic acid
Acetochlor oxanilic acid
Acetoclor
PAHs
Acetophenone
fragrance
Acetyl cedrene
Aclonife
Acrolein
Acrylamide
Acrylonitrile
Pesticides and herbicides
a-Endosulphan
Priority pollutants
ä-hexachlorocyclohexane
Pesticide
Alachlor
Aldicarb
fragrance
alkyl-phdroxybenzoate
alkylphenol
Household chemical
polyethoxylates
Alpha and Beta-endosulfan

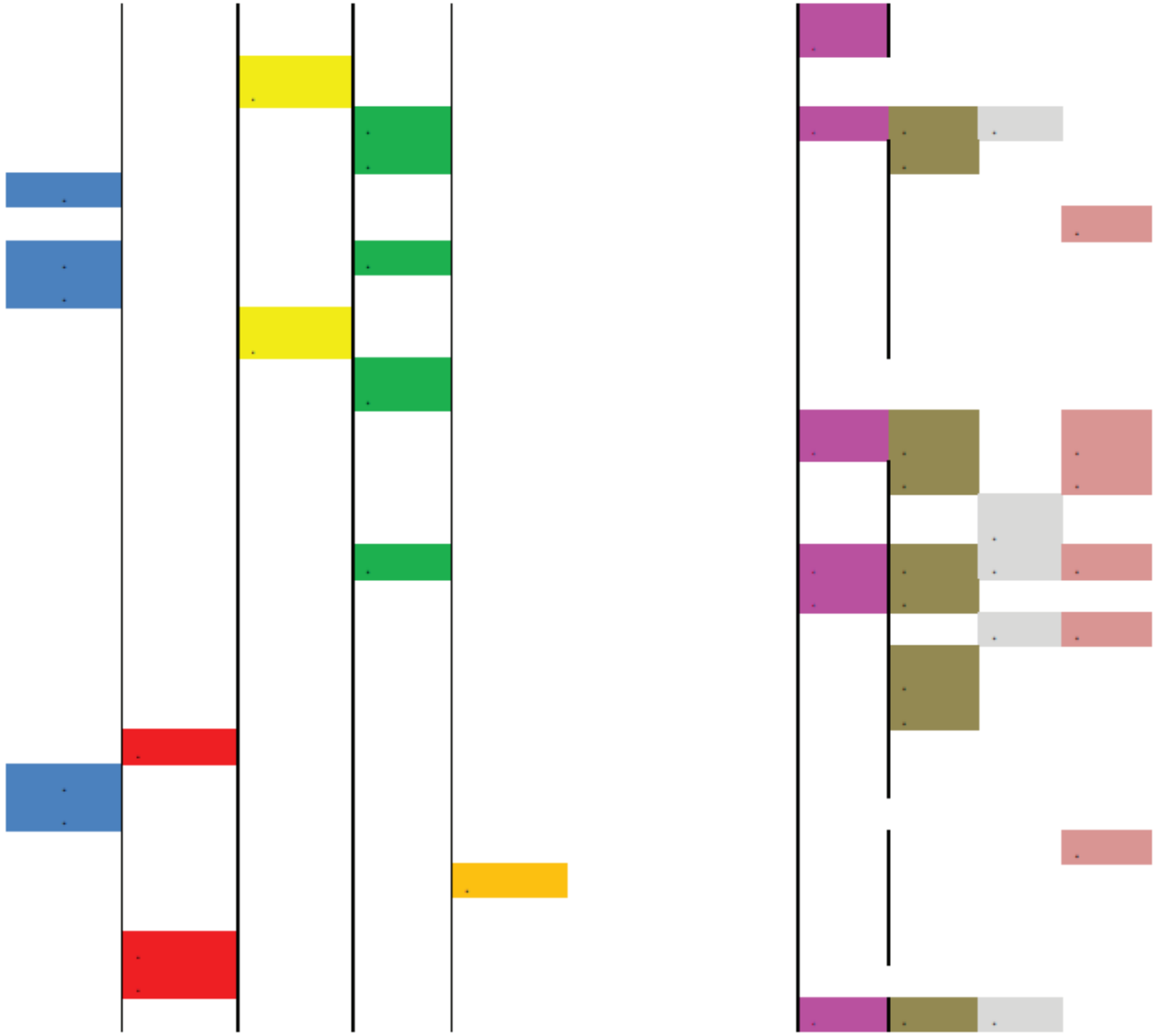

Alpha, Beta, Gamma, Delta-BHC
Anatoxin-a
Anatoxin-a(S)
PAHs
Anthracene
Pesticides and herbicides
Atrazine
organophosphorus pesticides
azinphos-ethyl
organophosphorus pesticides
azinphos-methyl
priority pollutants
b-endosulfan
chloroanilines
bentazone
Benzene
benzidines
benzidine
PAHs
Benzo(a)pyrene
PAHs
benzo[a]anthracene
PAHs
benzo[a]fluoranthene
PAHs
benzo[b]fluoranthene
PAHs
benzo[ghi]perylene
PAHs
benzo[k]fluoranthene
PAHs
benzo[k]fluoranthene,
UV absorber
Benzophenone
fragrance
Benzyl acetate
PAHs
Benzyl chloride
Benzyl salicylate
fragrance
Fragrance
Phthalates
Benzylbutylphthalate (BBP)
Priority pollutants
b-hexachlorocyclohexane,
Bis(2-chloroethoxy) methane
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl)

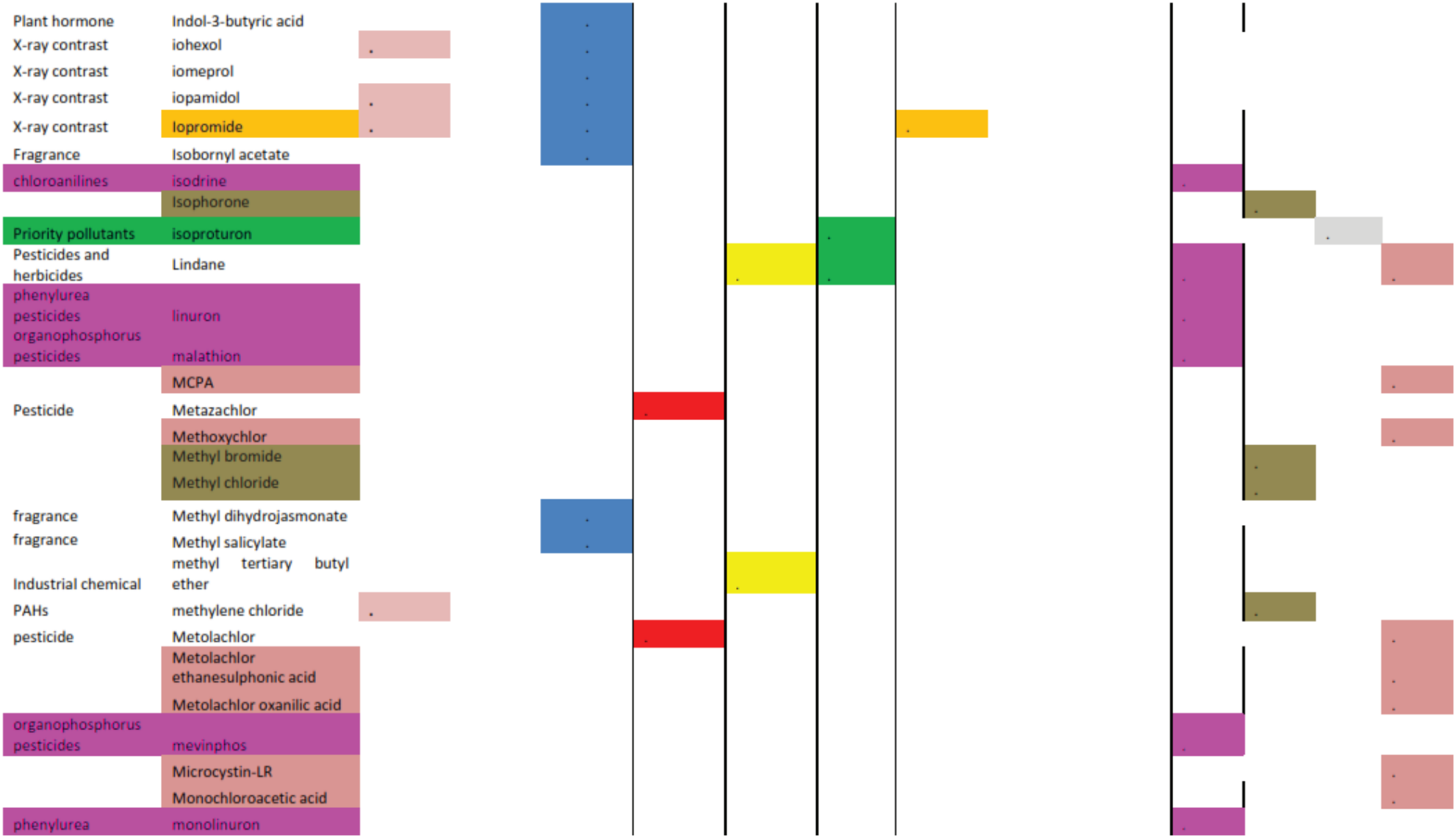

phthalate
Plasticizer
Bisphenol A
Brominated diphenyletheriv
Bromoacetic acid
Bromochloroacetic acid
PAHs
Bromochloromethane
Bromoform
Butyl benzyl phthalate
PAHs
Butylated hydroxyanisole
Butylated hydroxytoluene
PAHs
(2,6-Di-tert-Butyl-p-Cresol
Carbon tetrachloride
Personal care
celestolide
Priority pollutants
chexachlorocyclohexane
chloroanilines
chlordane
Priority pollutants
chlorfenvinphos
Chloroalkanes, C10-13 iv
Chlorobenzene
Chlorodibromomethane
Chloroform
chloroanilines
chloronitrobenzenes , chloronitrotoluenes
PAHs
chlorophene
chloroanilines
chlorophenols
chloroanilines
chlorotoluidines
Chlorpyrifos
Chlorpyrifos-ethyl
Priority pollutants
chlorpyriphos methyl
PAHs
Cholesterol
PAHs
chrysene
PAHs
Coprastanol

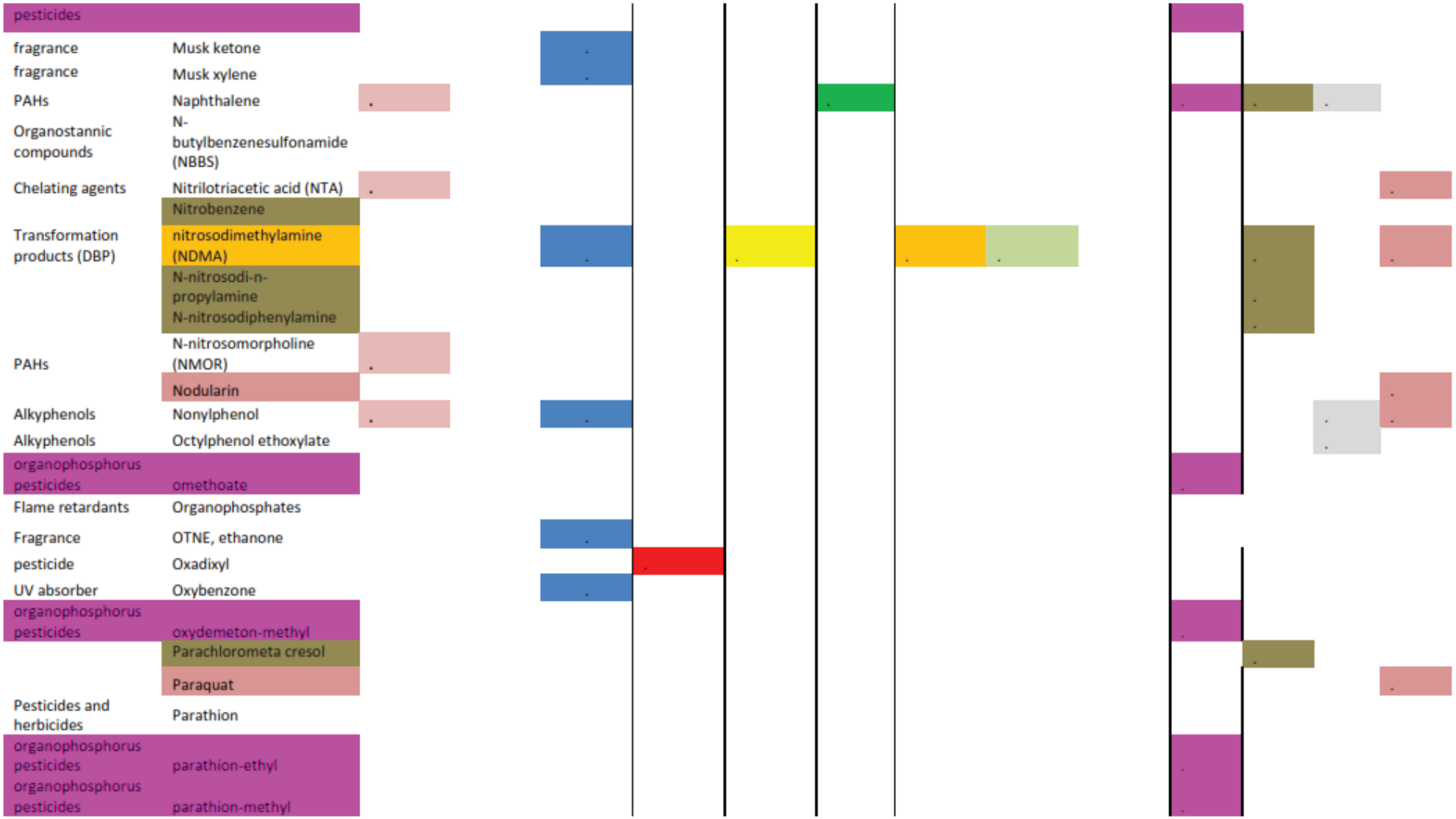

organophosphorus pesticides
coumaphos
PAHs
Coumarin
triazines
cumene
Cybutryne
Cytostatics
cyclophosphamide
Cyhexatin
Cylindrospermopsin
Cypermethrin,
chloroanilines
DDE,DDD,DDT
Pesticides and herbicides
DDT, DDE, DDD
Insecticide
DEET
Deltamethrin*
organophosphorus pesticides
demethon-O
organophosphorus pesticides
demeton-S-methyl
Priority pollutants
d-hexachlorocyclohexane,
Phthalates
di(2-ethylhexyl) phthalate (DEHP)
Di-2-(ethylhexyladipate (DEHA)
Diallyldimethylammonium chloride
X-ray contrast
diatrizoate
PAHs
diatrizoic acid
Dibenzo(,h) anthracene
Dibromoacetic acid
Dibromochloromethane*
Dibutyltin
Dichloroacetic acid
Dichlorobromomethane
Dichloromethane

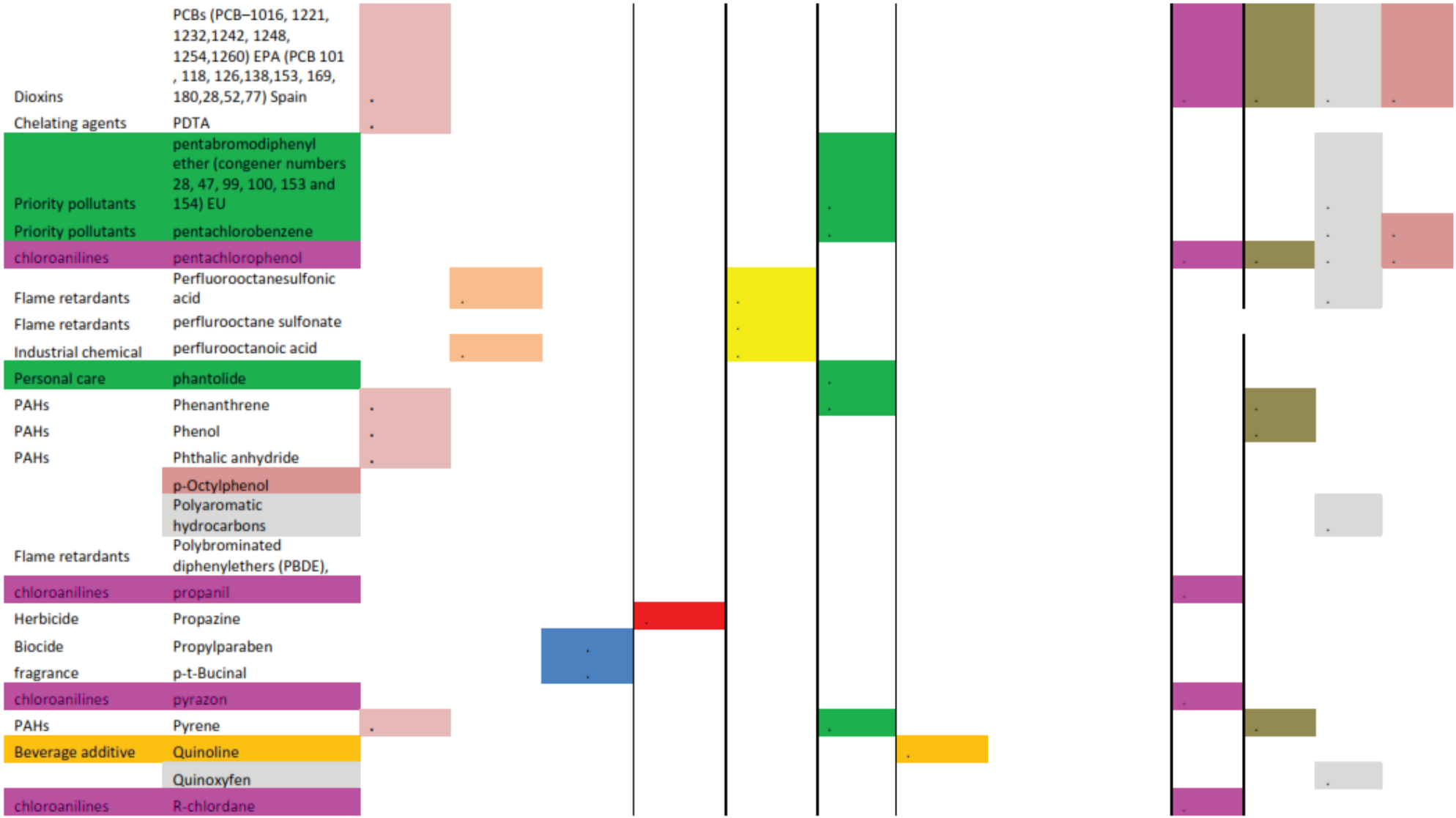

organophosphorus pesticides
dichlorvos
PhAC
Diclofenac
Dicofol
Pesticides and herbicides
Dieldrin, Aldrin, Endrin, Isodrin
Phthalates
Diethyl phthalate (DEP),
Flame retardants
diisodecyl phthalate (DIDP)
Phthalates
diisononyl phthalate (DINP)
organophosphorus pesticides
dimethoate
Phthalates
Dimethyl phthalate (DMP),
Dimethylamine
Dimethyltin
Phthalates
Di-n-butyl phthalate (DBP)
Di-n-octyl phthalate
pesticide
Diphenylamine
Diquat
organophosphorus pesticides
disulfoton
Pesticides and herbicides
diuron
Chelating agents
EDTA
priority pollutants
endosulfan sulphate
Endosulphan
chloroanilines
endrin
Endrin aldehyde
Epichlorohydrin
Ethylbenzene
organophosphorus pesticides
fenitrothion
Fenoprop

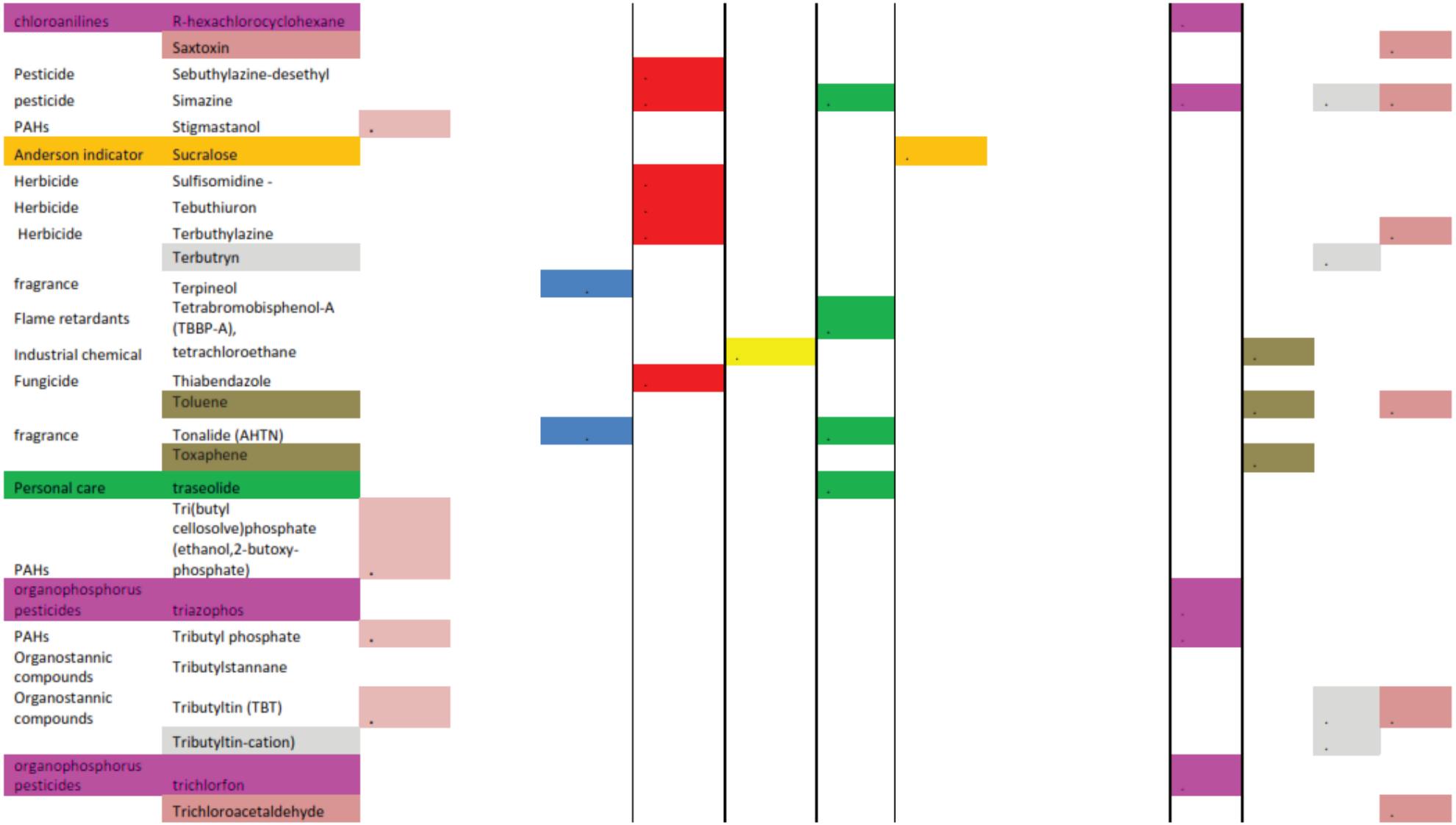
organophosphorus pesticides	fenthion
Pesticides and herbicides	fipronil
PAHs	fluoranthene
PAHs	fluorene
PhAc	Fluoxetine
	Formaldehyde
Fragrance	Galaxolide
fragrance	g-Methyl ionine
Transformation products	Halo Acetic acids (HAAs)
Priority pollutants	heptabromodiphenyl-ether
Pesticides and herbicides	Heptachlor
	Heptachlor epoxide
Flame retardants	Hexabromocyclodecane (HBCD),
chloroanilines	hexachlorobenzene
SVHCb	hexachlorobutadiene
	Hexachlorocyclohexane
	Hexachlorocyclopentadiene
	Hexachloroethane
Herbicide	Hexazinone
fragrance	Hexyl salicylate
Fragrance	Hexylcinnamaldehyde
	Homoanatoxin-a
Additive	Hydrazine
Cytostatics	ifosfamide
Fungicide	Imazalil
pesticide	Imidacloprid
PAHs	indeno [1,2,3-cd]pyrene

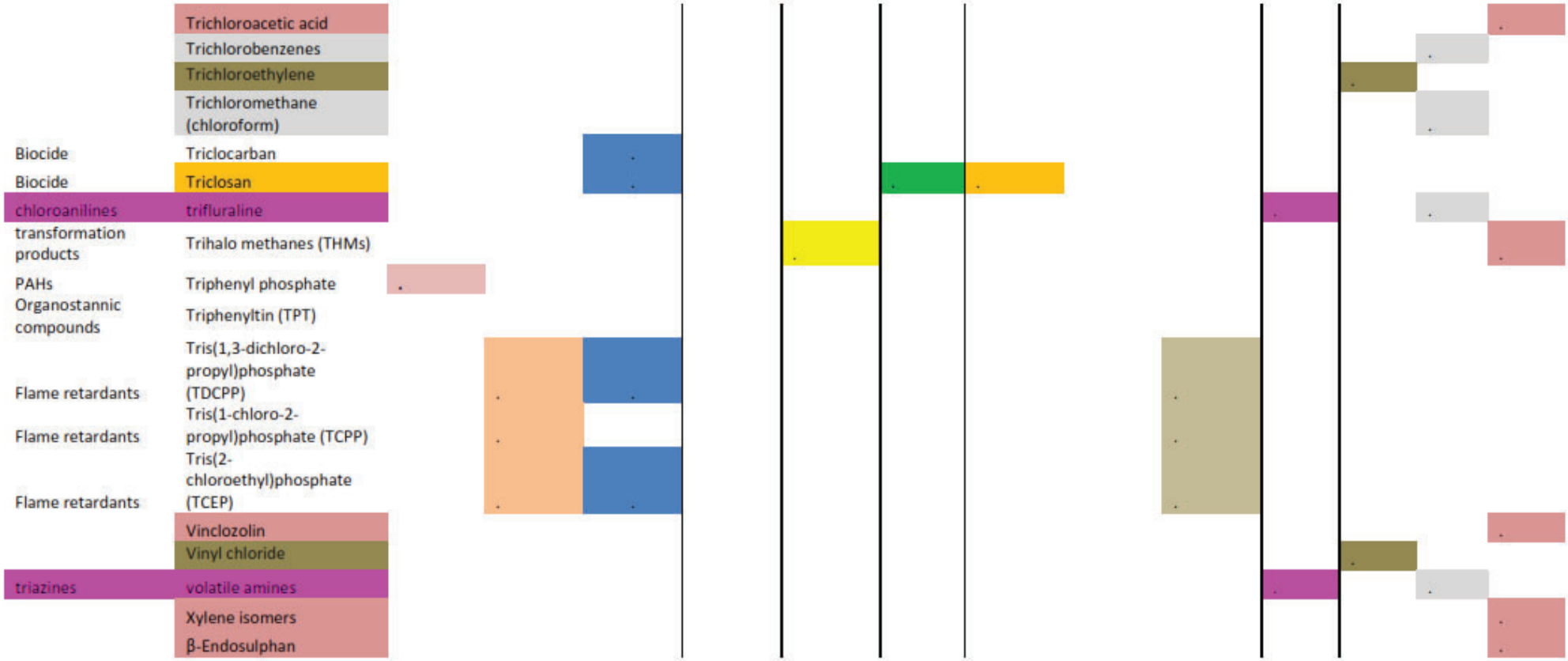



Plant hormone
Indol-3-butyric acid
X-ray contrast
iohexol
X-ray contrast
iomeprol
X-ray contrast
iopamidol
X-ray contrast
Iopromide
Fragrance
Isobornyl acetate
chloroanilines
isodrine
Isophorone
Priority pollutants
isoproturon
Pesticides and herbicides
Lindane
phenylurea pesticides
linuron
organophosphorus pesticides
malathion
MCPA
Pesticide
Metazachlor
Methoxychlor
Methyl bromide
Methyl chloride
fragrance
Methyl dihydrojasmonate
fragrance
Methyl salicylate
Industrial chemical
methyl tertiary butyl ether
PAHs
methylene chloride
pesticide
Metolachlor
Metolachlor ethanesulphonic acid
Metolachlor oxanilic acid
organophosphorus pesticides
mevinphos
Microcystin-LR
Monochloroacetic acid
phenylurea
monolinuron

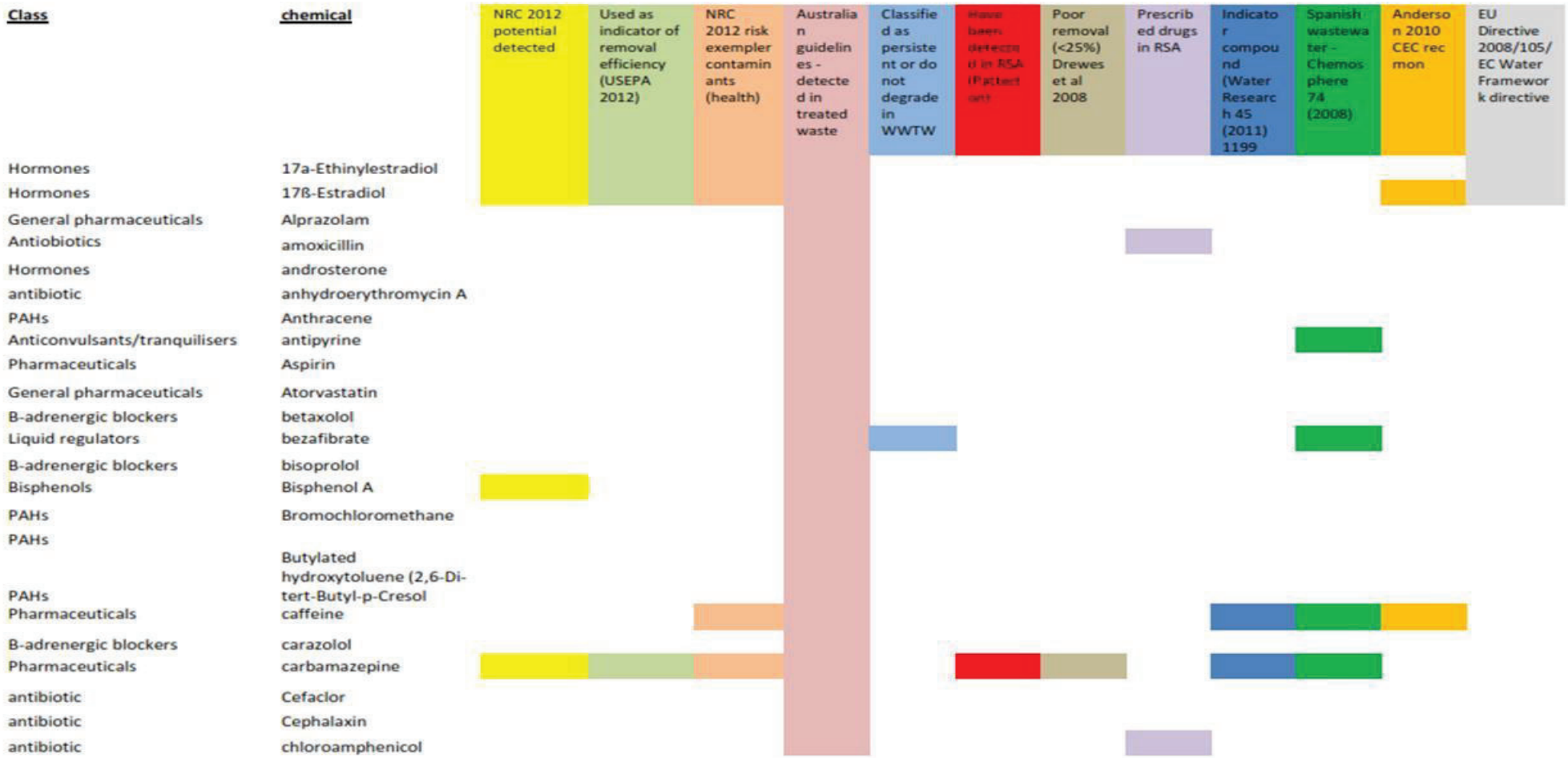

pesticides
fragrance
Musk ketone
fragrance
Musk xylene
PAHs
Naphthalene
Organostannic compounds
N-butylbenzenesulfonamide (NBBS)
Chelating agents
Nitrilotriacetic acid (NTA)
Nitrobenzene
Transformation products (DBP)
nitrosodimethylamine (NDMA)
N-nitrosodi-n-propylamine
N-nitrosodiphenylamine
PAHs
N-nitrosomorpholine (NMOR)
Nodularin
Alkyphenols
Nonylphenol
Alkyphenols
Octylphenol ethoxylate
organophosphorus pesticides
omethoate
Flame retardants
Organophosphates
Fragrance
OTNE, ethanone
pesticide
Oxadixyl
UV absorber
Oxybenzone
organophosphorus pesticides
oxydemeton-methyl
Parachlorometa cresol
Paraquat
Pesticides and herbicides
Parathion
organophosphorus pesticides
parathion-ethyl
organophosphorus pesticides
parathion-methyl


PCBs (PCB–1016, 1221, 1232,1242, 1248, 1254,1260) EPA (PCB 101 , 118, 126,138,153, 169, 180,28,52,77) Spain
Dioxins
Chelating agents
PDTA
pentabromodiphenyl ether (congener numbers 28, 47, 99, 100, 153 and 154) EU
Priority pollutants
Priority pollutants
pentachlorobenzene
chloroanilines
pentachlorophenol
Perfluorooctanesulfonic acid
Flame retardants
Flame retardants
perflurooctane sulfonate
Industrial chemical
perflurooctanoic acid
Personal care
phantolide
PAHs
Phenanthrene
PAHs
Phenol
PAHs
Phthalic anhydride
p-Octylphenol
Polyaromatic hydrocarbons
Flame retardants
Polybrominated diphenylethers (PBDE),
chloroanilines
propanil
Herbicide
Propazine
Biocide
Propylparaben
fragrance
p-t-Bucinal
chloroanilines
pyrazon
PAHs
Pyrene
Beverage additive
Quinoline
Quinoxyfen
chloroanilines
R-chlordane

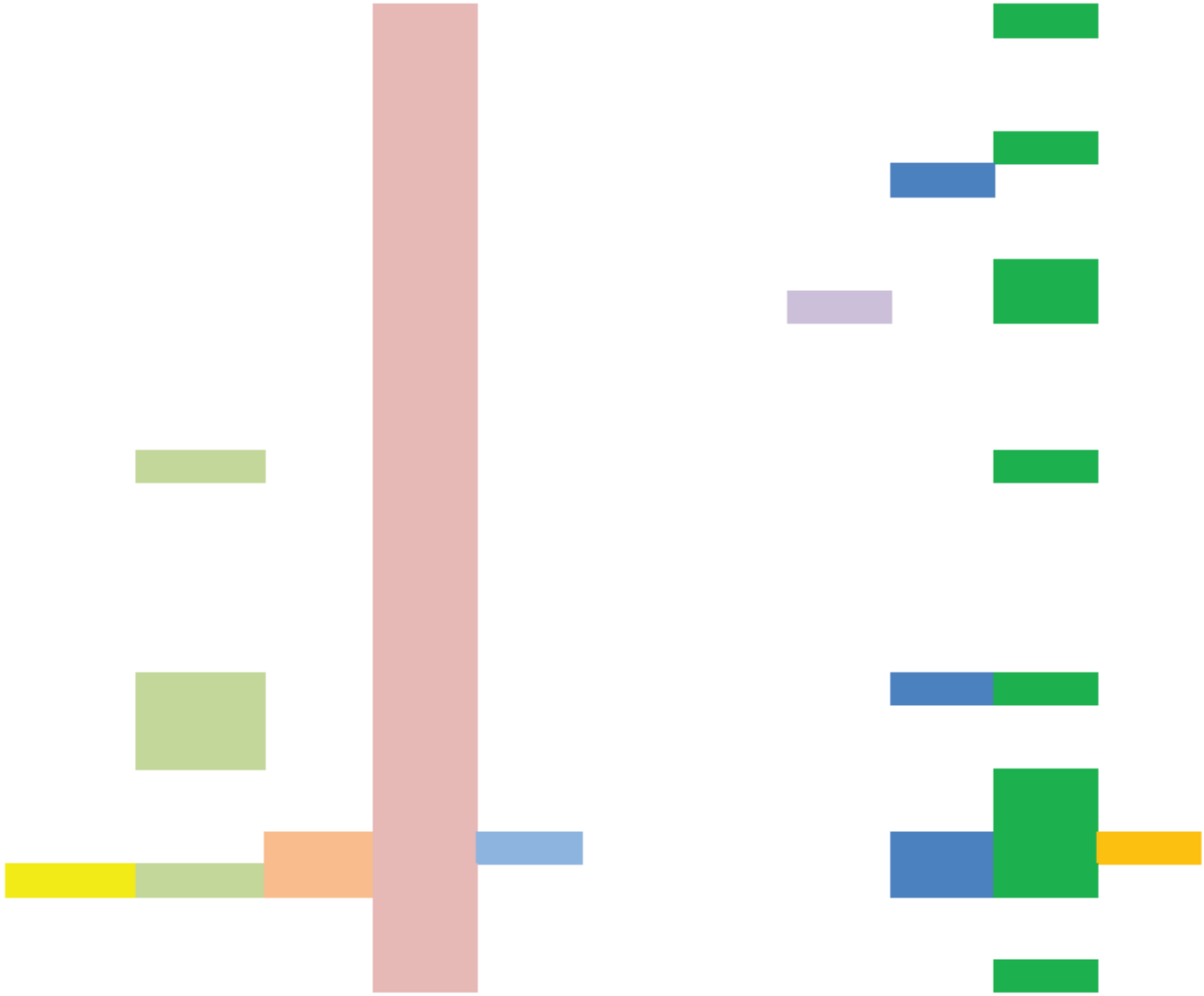

chloroanilines
R-hexachlorocyclohexane
Saxtoxin
Pesticide
Sebuthylazine-desethyl
pesticide
Simazine
PAHs
Stigmastanol
Anderson indicator
Sucralose
Herbicide
Sulfisomidine -
Herbicide
Tebuthiuron
Herbicide
Terbuthylazine
Terbutryn
fragrance
Terpineol
Flame retardants
Tetrabromobisphenol-A (TBBP-A),
Industrial chemical
tetrachloroethane
Fungicide
Thiabendazole
Toluene
fragrance
Tonalide (AHTN)
Toxaphene
Personal care
traseolide
PAHs
Tri(butyl cellosolve)phosphate (ethanol,2-butoxy-phosphate)
organophosphorus pesticides
triazophos
PAHs
Tributyl phosphate
Organostannic compounds
Tributylstannane
Organostannic compounds
Tributyltin (TBT)
Tributyltin-cation)
organophosphorus pesticides
trichlorfon
Trichloroacetaldehyde


Trichloroacetic acid
Trichlorobenzenes
Trichloroethylene
Trichloromethane (chloroform)
Biocide
Triclocarban
Biocide
Triclosan
chloroanilines
trifluraline
transformation products
Trihalo methanes (THMs)
PAHs
Triphenyl phosphate
Organostannic compounds
Triphenyltin (TPT)
Flame retardants
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)
Flame retardants
Tris(1-chloro-2-propyl)phosphate (TCPP)
Flame retardants
Tris(2-chloroethyl)phosphate (TCEP)
Vinclozolin
Vinyl chloride
triazines
volatile amines
Xylene isomers
β-Endosulphan

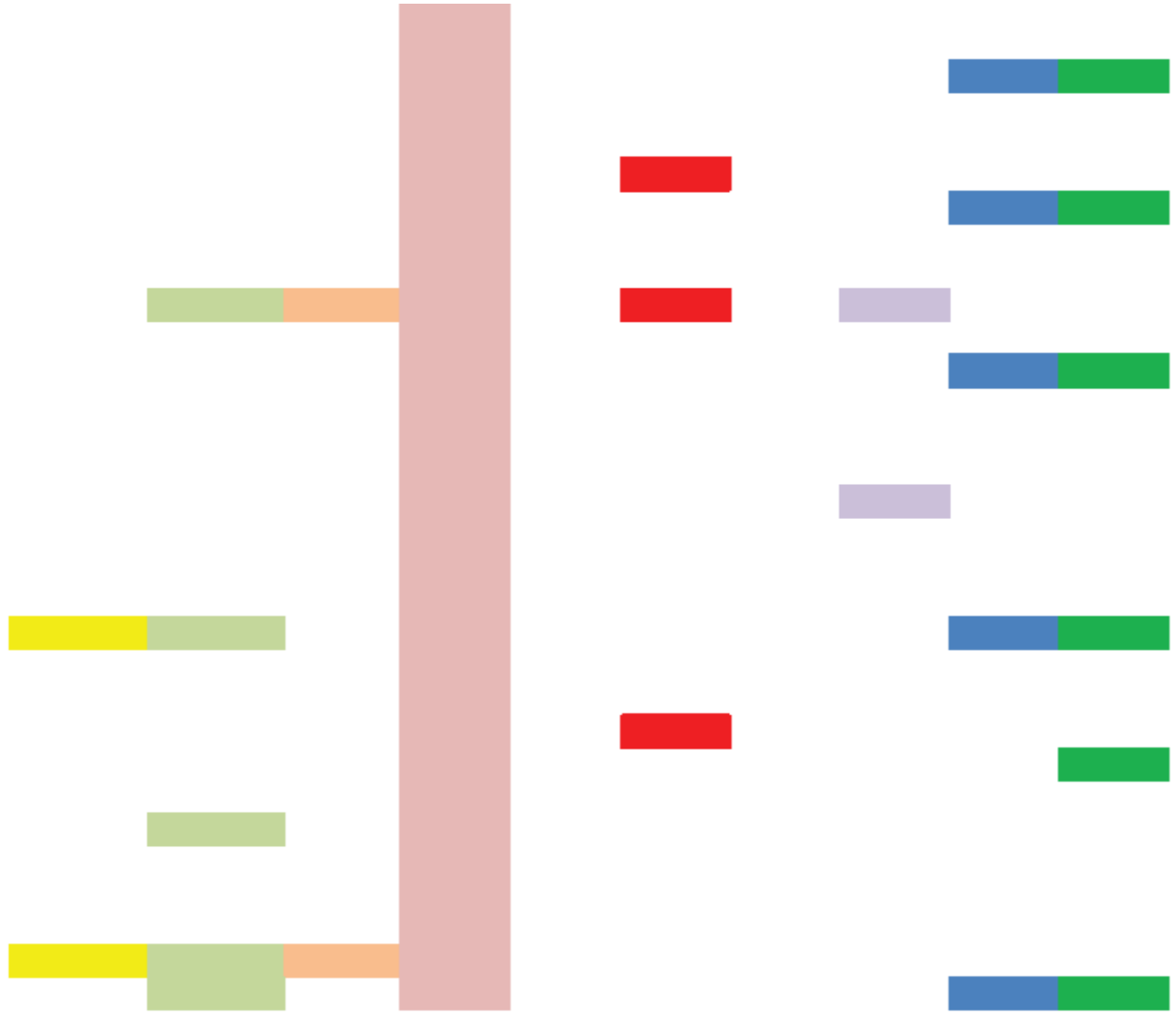
APPENDIX 2: PRIORITY LIST OF PHARMACEUTIC CHEMICALS



PAHs	chlorophene
antibiotic	Chlorotetracycline
General pharmaceuticals	Cimetidine
antibiotic	Ciproflaxin
Antiobiotics	ciprofloxacin
Antiobiotics	clarithromycin
General pharmaceuticals	clenbuterol
antibiotic	Clindamycin
Analgestic/anti-inflammatories	clofibric acid
Pharmaceuticals	codeine
General pharmaceuticals	cotinine
Antiobiotics	crythromycin
General pharmaceuticals	dehydronifedipine
antibiotic	demeclocycline
Pharmaceuticals	dichlofenac
General pharmaceuticals	diltiazem
Anti-inflammatory	dipyrone
General pharmaceuticals	enalaprilat
antibiotic	enrofloxacin
Hormones	Equilenin
Hormones	Equilin
Pharmaceuticals	erythromycin
Hormones	Estriol
Hormones	Estrone
Analgestic/anti-inflammatories	fenoprofen
General pharmaceuticals	fluoxetine (Prozac)
Lipid lowering fibrate	gemfibrozil
Analgestic/anti-inflammatories	ibuprofen
Analgestic/anti-inflammatories	indomethacine
General pharmaceuticals	Isophosphamide
Analgestic/anti-inflammatories	ketoprofen



Hormones	mestranol
General pharmaceuticals	
Liquid regulators	metoprolol
antibiotic	Monensin
B-adrenergic blockers	nadolol
antibiotic	Naladixic acid
Analgestic/anti-inflammatories	naproxen
Hormones	norethindrone
Antiobiotics	norfloxacin
Analgesic/anti-inflammatories	paracetamol
antibiotic	penicillin
B-adrenergic blockers	propranolol
PAHs	Pyrene
Antiobiotics	roxithromycin
Antiobiotics	roxithromycin
Asthma	Salbutamol
General pharmaceuticals	salicylic acid
antibiotic	sulfamethazine
antibiotic	sulfamethizole
Pharmaceuticals	sulfamethoxazole
antibiotic	sulfamethoxine
General pharmaceuticals	sulfasalazine
Pharm	Temazepam -
General pharmaceuticals	terbutaline
antibiotic	terramycin
Hormones	testosterone
Antiobiotics	tetracyclin
B-adrenergic blockers	Timolol
Anti-inflammatory	tolfenamic acid
Pharmaceuticals	triclosan
Antiobiotics	trimethoprim



antibiotic	tylosin
General pharmaceuticals	Valium (diazepam)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