



Canadian Council of Ministers  
of the Environment      Le Conseil canadien  
des ministres  
de l'environnement

# **Coordinated Science and Research on Municipal Wastewater Effluent (MWWE)**

September 2006

# TABLE OF CONTENTS

LIST OF FIGURES .....	3
LIST OF TABLES .....	3
ACRONYMS .....	5
1.0 Introduction .....	6
2.0 Overview .....	6
3.0 Current Technology for Municipal Wastewater Effluent .....	7
4.0 Substances in Municipal Wastewater Effluent .....	8
4.1 Pathogens .....	8
4.2 Conventional Substances .....	9
4.2.1 Nutrients and Organics .....	9
4.2.1.1 Background .....	9
4.2.1.2 Point and Non-Point Sources .....	10
4.2.1.3 Environmental Effects .....	10
4.2.1.4 Fate and Removal in the Liquid and Solid Treatment Trains .....	10
4.2.2. Metals .....	13
4.2.2.1 Background .....	13
4.2.2.2 Point and Non-point Sources .....	13
4.2.2.3 Environmental Effects .....	13
4.2.2.4 Fate And Removal in the Liquid and Solid Treatment Trains .....	13
4.2.3 Trace Contaminants – Legacy .....	14
4.2.3.1 Background .....	14
4.2.3.2 Point and Non-point Sources .....	14
4.2.3.3 Environmental Effects .....	14
4.2.3.4 Fate and Removal in the Liquid and Solid Treatment Trains .....	15
4.3 Emerging Trace Contaminants .....	15
4.3.1 Endocrine Disrupting Compounds and Other Priority Contaminants .....	15
4.3.1.1 Background .....	15
4.3.1.2 Point and Non-point Sources .....	16
4.3.1.3 Environmental Effects .....	16
4.3.1.4 Fate and Removal in the Liquid and Solid Treatment Trains .....	16
4.3.2 Pharmaceuticals, Personal Care Products (PPCPs) and Antimicrobial Resistance .....	16
4.3.2.1 Background .....	16
4.3.2.2 Point and Non-point Sources .....	17
4.3.2.3 Environmental Effects .....	17
4.3.2.4 Fate and Removal in the Liquid and Solid Treatment Trains .....	17
4.3.3 Brominated Flame Retardants .....	18
4.3.3.1 Background .....	18
4.3.3.2 Point and Non-Point Sources .....	18
4.3.3.3 Environmental Effects .....	18
4.3.3.4 Fate and Removal in the Liquid and Solid Treatment Streams .....	19
5.0 Existing Potential Contaminants of Concern in Wastewater .....	19
5.1 Review of Effluent Substances .....	19
5.2 Characterization List for MWW .....	20
5.3 Research Needs for Contaminants in MWW .....	23
6.0 Analysis of Municipal Wastewater and Biosolids .....	23
6.1 Nutrients and Aggregate Organics .....	23

6.2 Metals.....	24
6.3 Trace Contaminants – Legacy.....	24
6.4 Trace Contaminants – Emerging.....	24
6.5 Sampling Considerations.....	25
7.0 Summary of Issues and Data Gaps .....	25
7.1 Recommendations.....	26
7.2 Implementation Options.....	28
Appendix 1 - Analysis of Options.....	30
References.....	32

## **LIST OF FIGURES**

Figure 1. Typical tertiary WWTP showing the treatment processes.....	12
--	----

## **LIST OF TABLES**

Table 1. CAEAL Test Groups for Wastewater Characterization with Estimated Cross Canada Costs.....	22
---	----

## **Co-ordinated Science and Research Subcommittee Members**

Tim LeBlanc, Nova Scotia  
Laura Taylor, British Columbia  
Gerry Wudrich, Saskatchewan  
Michel Beland, Environment Canada  
Peter Seto, Environment Canada  
Thirunavukkarasu, Ondiveerapan , Saskatchewan  
Barbara Anderson, Ontario

## ACRONYMS

APEO	Alkylphenol ethoxylate
APEs	Alkylphenol ethoxylates
AS	Activated sludge
BFR	Bromine-based flame retardants
BNR	Biological nutrient removal
BOD	Biochemical Oxygen Demand
CAS	Chemical Abstract Service
CBOD <sub>5</sub>	Carbonaceous biochemical oxygen demand
CCME	Canadian Council of Ministers of the Environment
CEPA	Canadian Environmental Protection Act
COA	Canada-Ontario Agreement
COD	Chemical oxygen demand
CSOs	Combined sewer overflows
CWWA	Canadian Water and Wastewater Association
DBPs	Disinfection byproducts
E. coli	<i>Escherichia coli</i>
EDC	Endocrine disrupting compound
FOG	Fats, oil and grease
MWWE	Municipal wastewater effluents
NPEO	Nonylphenol ethoxylate (a type of APEO)
NPEs	Nonyl phenol ethoxylates
OSPAR	Oslo/Paris Convention for the Protection of the Marine Environment of the North-East Atlantic
PAH	Polycyclic Aromatic Hydrocarbon
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
POPs	Persistent organic pollutants
PPCPs	Pharmaceutical and personal care products
STOWA	European Foundation for Applied Water Research
TAN	Total ammonia nitrogen
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TP	Total phosphorous
TSS	Total suspended solids
WWTP	Wastewater treatment plant

## 1.0 Introduction

Coordinated science and engineering research is necessary to address the issues regarding harmful pollutants in municipal wastewater effluents (MWWEs). The science and engineering research also needs to be coordinated and complemented with policy development to ensure that viable and effective infrastructure is planned for and constructed. Policy, science and engineering gaps need to be identified and proactively investigated in a strategic coordinated scientific manner to ensure that emerging issues are adequately addressed.

The primary objectives given to the Coordinated Science and Research subcommittee were:

- review and assess the state of knowledge on MWWWE science and technology;
- assess the need for action on emerging issues related to MWWWE;
- recommend approaches to fill scientific and technology gaps in treating MWWWE; and
- recommend approaches to disseminate knowledge and experience gained.

## 2.0 Overview

Generally municipal wastewater treatment and infrastructure is designed for physical, chemical and biological degradation of readily biodegradable organic materials consisting of the conventional parameters measured as biochemical oxygen demand (BOD), total suspended solids (TSS), nitrogen (in various forms), phosphorous (as total phosphorous TP) and pathogens (measured using the surrogate parameter *E. coli*). The science and engineering behind the existing technologies and their capabilities is well established but not always optimized.

Municipal wastewater treatment plants (WWTPs) in Canada, including the most sophisticated tertiary facilities, are not designed for the removal of trace contaminants generally found at the microgram per litre ( $\mu\text{g/L}$ ) to nanogram per litre ( $\text{ng/L}$ ) concentration range. To remove trace contaminants from WWTP effluents and to eliminate the associated established or perceived risk of trace contaminants entering source water supplies, it has been reported that engineered quaternary level of treatment may be required.

It has been reported that some trace contaminants are removed from the final effluents at existing WWTP however many of the same compounds are found in municipal sludge's. What appears to be removal is in effect partitioning to the solids phase of the treatment process. True biochemical transformation or breakdown of trace contaminants has been confirmed in only a few cases.

Both the numbers and types of new substances which are introduced in new products often end up in our wastewater. Significant challenges exist for research engineers and scientists on several fronts including identifying and quantifying trace contaminants, determining toxicological impacts and assessing viable technologies or approaches to remove such substances.

With trace contaminants at micro- or nano- concentration levels, standardized, validated analytical methods are not yet available to detect the presence of these compounds in environmental matrices. To develop these selective analytical methods and verify their applicability takes considerable time and investment.

Scientific and engineering research is currently being undertaken by municipalities, universities, provincial, territorial, and federal government agencies without any significant coordination. There is no central repository of research results and there exists great difficulties in obtaining an overview of what

work is being undertaken and by whom. This is inefficient and costly both for future research and infrastructure needs.

### 3.0 Current Technology for Municipal Wastewater Effluent

The primary reason for treatment of municipal wastewaters is to reduce the impact of excessive oxygen depleting substances and nutrients on the receiving waters along with the reduction of pathogens. Pathogens are effectively eliminated by the disinfection processes employed at most WWTP. This impact of MWW on receiving water bodies is typically measured in terms of carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>), total suspended solids (TSS), total phosphorous (TP), total ammonia nitrogen (TAN) and *E. coli*. Table 1 shows a typical treatment plant processes and products and will assist in the understanding of the treatment types.

There are several levels of municipal wastewater treatment applied within Canada. They may be summarized as follows:

There are several levels of municipal wastewater treatment applied within Canada. They may be summarized as follows:

**Preliminary treatment** involves screening, shredding or grinding for the purpose of removing coarse solids such as sticks, rags and other debris from the incoming wastewater. The purpose of preliminary treatment is to protect downstream treatment components such as pumps and reduce maintenance or operational problems. Preliminary treatment is a common first step to all WWTP.

**Primary treatment** follows preliminary treatment and involves the use of primary devices that allow flows to be reduced and for solids to settle due to gravity. Commonly, sedimentation tanks that detain flows for 2 to 6 hours to allow settleable solids to settle and be drawn off for separate solids treatment. Typical BOD<sub>5</sub> and TSS removal rates in primary treatment are 30% and 60%, respectively. On stand alone primary treatment, primary effluents can be treated with chemical disinfection prior to release. Primary treatment, can also be enhanced using chemicals in which inorganic or organic flocculants are introduced into the wastewater to help improve the effluent quality over primary treatment alone.

**Secondary treatment** follows primary treatment and is specifically designed for the removal of biodegradable organic matter (in solution or suspension) and the removal of suspended solids. Secondary treatment can include nutrient removal. Typical MWW quality achieved is a CBOD<sub>5</sub> and TSS of 15 mg/L. Compliance standards are commonly set at 25 mg/l to allow for operational variations. The physical, chemical and biological processes in the process design may also fortuitously (not by design) remove other trace contaminants at unpredictable levels. The activated sludge treatment process is the most widely used form of secondary treatment in Canada and the world due to its versatility and relatively low cost

**Sewage lagoons** are one of the more common biological treatment processes used in Canada principally due to low cost and simplicity of operation. Effluent quality from lagoon systems varies depending on the type, size and configuration of the treatment cells (i.e. anaerobic cells, facultative cells and storage cells) and operational mode (i.e., seasonal or continuous discharge mode). A lagoon system with several months of storage capacity, such as systems with once a year discharge, can consistently produce very good effluent quality if the biological activity is not hindered. Recognizing that effluent quality varies with the size, type, configuration and retention time, a range of MWW effluent quality can be achieved for CBOD<sub>5</sub> of 5 to 25 mg/L and for TSS of 10 to 30 mg/L. Compliance standards are commonly set higher to allow for operational variability.

**Tertiary treatment** is defined as the additional treatment needed to remove suspended, colloidal, and dissolved constituents remaining after conventional secondary treatment (Metcalf and Eddy 2003). In Canada this term can refer to physical processes that further remove suspended solids, such as sand filtration. Tertiary treatment may include biological processes for removal of nutrients (see below). Typical tertiary effluent CBOD<sub>5</sub> and TSS values are 5 and 5 mg/L, The movement of trace contaminants and metals from the liquid to the slides streams is generally enhanced due the additional physical-chemical or extended processes which are involved.

**Nutrient Removal** refers to treatment steps used to remove nitrogen and phosphorous from MWW. Common types of nutrient removal treatment methods include nitrification (conversion of ammonia to nitrates), denitrification (conversion of nitrates to nitrogen gas) biological excess phosphorous removal and chemical phosphorous removal. Nutrient removal processes are commonly incorporated into either secondary or tertiary treatment for enhanced removal of nitrogen, phosphorous or both to protect sensitive receiving environments. Typical systems with nutrient removal can achieve MWW concentration levels of total phosphorous down to 0.1 mg/L, total ammonia-nitrogen down to 5 mg/L in winter and less than 1 mg/L in summer.

**Advanced or Quaternary treatment** refers to the treatment processes that are used to further enhance the quality of MWW beyond that produced by tertiary treatment. This level of treatment is required where enhanced source water protection is required or for water reuse applications. Advanced treatment technologies include reverse osmosis, membrane filtration, and activated carbon technologies.

**Disinfection** of MWW is typically accomplished by using appropriate dosages of chlorine, hypochlorite or ultraviolet (UV) radiation. Disinfection systems are designed to achieve low levels of indicator microorganisms such as *E. coli* in the range of 100 counts per 100 mL.

Generally treatment plants are not engineered to remove trace contaminants found at very low concentrations such as part per billion (ug/L). Recent studies have shown a reduction of some specific pharmaceuticals in tertiary (Braghetta et al 2002), lagoons (Lishman et al 2006) and secondary treatment systems (Metcalf and Eddy, 2003). However these observed reductions are not readily predictable and tend to be compound specific.

#### **4.0 Substances in Municipal Wastewater Effluent (MWW)**

Certain substances, mostly associated with human waste, are present in all sewage effluents. These include; BOD<sub>5</sub>, TSS, nutrients such as phosphorous and nitrogen-based compounds (organic nitrogen, nitrite, nitrate, ammonia, and ammonium), microorganisms and sulphides.

Residential household wastewaters are fairly consistent from place to place but the extent to which motor oil, oil-based paints, solvents and other toxic substances are dumped into drains can impact the wastewater characteristics. The kinds of contaminants in MWW depend initially on what is released into the sewer system by industries, commercial establishments and institutions in the a particular sewershed.

##### **4.1 Pathogens**

Human and animal wastes are the main sources of microbial contamination to drinking water sources. Proper treatment of wastewater, combined with treatment of drinking water reduces the potential of waterborne infections and outbreaks.

Microbial contaminants refer to bacteria, viruses, protozoan oocysts or parasites, some of which may be pathogenic (disease causing).

Two point sources that release microbial contaminants to the environment are wastewater treatment facilities and combined sewer overflows (CSOs). Non-point sources include land and road runoff, wildlife, domestic animals and birds.

Although pathogenic microorganisms occur in large numbers in raw wastewater, treatment technologies greatly reduce the number of pathogens that are released into the environment. However, treatment is not always 100% effective. During heavy rains, there may be too much water for the wastewater treatment plants to handle and some untreated or partially treated wastewater may be discharged into the receiving water. Before the final wastewater effluent is released into the receiving water, it may be disinfected to further reduce potential disease-causing microorganisms that remain after the treatment process.

A well-operated disinfection process can achieve a 99% removal of microorganisms from the wastewater. However, if high levels remain there may be a cause for concern if the receiving waters are used for activities such as swimming and shellfish harvesting that require a very low number of microorganisms to be safe. Most reported outbreaks of waterborne disease in Canada are due to the protozoa *Giardia* and *Cryptosporidium* which are generally more resistant to chlorination than the bacteria and viruses.

Ironically, another potential human health risk associated with municipal wastewater effluents results from the use of chlorine as a disinfectant in wastewater. Chlorine's potent oxidizing power causes it to react with naturally occurring organic material in water to produce chlorinated organic compounds called disinfection by-products (DBPs). To avoid excess chlorine escaping into the environment, effluent must be dechlorinated to an acceptable level prior to discharge. The use of alternative disinfectants like UV or ozone, tends to create fewer DBPs.

## **4.2 Conventional Substances**

### **4.2.1 Nutrients and Organics**

#### **4.2.1.1 Background**

Sewage or municipal wastewater contains various contaminants either dissolved in solution or associated with solids. The solids are classified as suspended solids or dissolved solids. In addition there are specific organic and inorganic compounds classified as carbonaceous (C) compounds and nutrients consisting primarily of nitrogen (N) and phosphorous (P) compounds. Nutrients and organics are relatively abundant in sewage (found in the mg/L range), along with pathogens and are commonly referred to as "conventional contaminants".

Typical strength raw sewage consists of about 200 mg/L of TSS, 170 mg/L of BOD, 430 mg/L of COD, 20 mg/L as total ammonia-nitrogen (TAN) and 7 mg/L of total phosphorous (TP) (MOE Table 1, Procedure F5-1). Typical secondary level treatment with phosphorous removal reduces the final (liquid) effluent to about 15, 15 and 1 mg/L of BOD, TSS and TP respectively.

Ammonia is a common constituent of a variety of industrial and municipal sewage effluents and is present as a mixture of unionized ammonia ( $\text{NH}_3$ ) and ionized ammonium ( $\text{NH}_4^+$ ). Aquatic toxicity due to ammonia is generally associated with the  $\text{NH}_3$  form. Therefore, conditions that favour formation of  $\text{NH}_3$ , such as increased pH and temperature, tend to increase the overall toxicity of ammonia to aquatic life.

Mathematical relationships between pH, temperature,  $\text{NH}_3$  concentration and toxicity are used to establish site-specific water quality requirements for MWW. Some effluent may contain ammonia concentrations that are lethal to aquatic biota, particularly fish; however, ammonia does not bioaccumulate or persist in aquatic environments.

Conventional contaminants have been traditional targets of sewage treatment and continue to be the primary focus in order to reduce oxygen demand on receiving water bodies from carbonaceous compounds, prevent or minimize eutrophication associated with nutrients, reduce toxicity associated with ammonia and provide adequate disinfection against pathogens.

#### **4.2.1.2 Point and Non-Point Sources**

Conventional pollutants are prevalent from both point and non-point sources. The primary point source is sewage collection leading to sewage treatment plants whereas surface urban runoff and agricultural runoff account for the major non-point sources.

#### **4.2.1.3 Environmental Effects**

Carbon compounds found in MWWE are typically quantified using a surrogate measure of chemical oxygen demand (COD) or in biological treatment methods as biochemical oxygen demand (BOD). These measures relate directly to the equivalent need of oxygen to support biochemical activity to reduce carbon compounds or, to the oxygen deficit that would be incurred in receiving waters if the sewage was not treated prior to entering the receiving waters.

Phosphorous occurs predominantly in the inorganic and soluble forms of phosphate in sewage, which is typically measured as total phosphorous (TP). Phosphorous is essential for algae growth. Due to algal blooms that occur in surface waters, the control of TP in wastewater effluents has become very important. Where MWWE are discharged into receiving waters identified as “sensitive” due to the risk of eutrophication, more stringent treatment is required which will typically include nitrogen removal in coastal waters and phosphorous removal in freshwater or in some cases both.

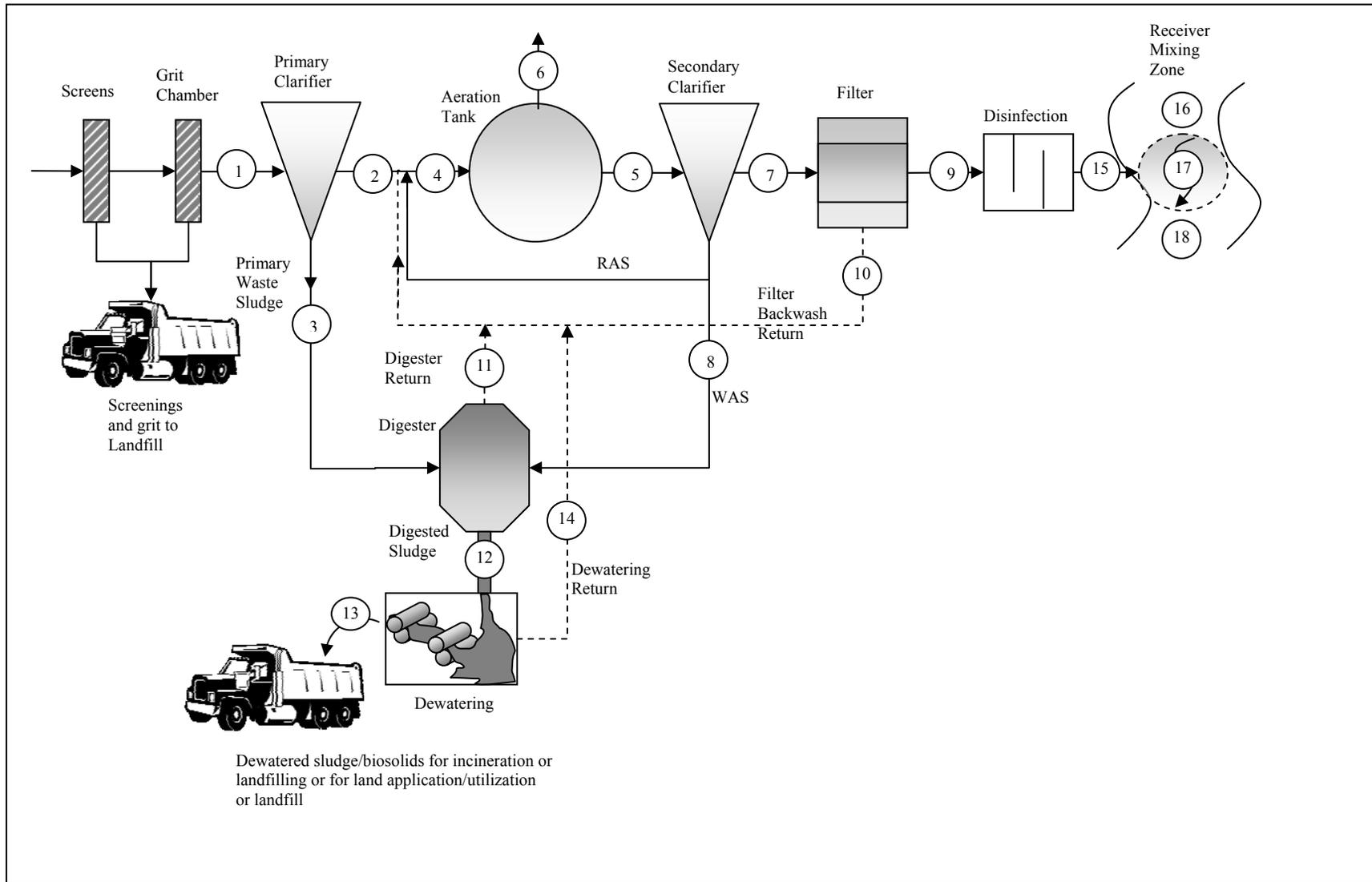
Nitrogen compounds are grouped into organic and inorganic forms. Nitrogen compounds can be organic nitrogen (Organic N), ammonia/ammonium ion forms ( $\text{NH}_3/\text{NH}_4^+$ ) or nitrite/nitrate ( $\text{NO}_2^-/\text{NO}_3^-$ ) ion forms. Nitrogen is measured as total ammonia nitrogen (TAN), as total Kjeldahl nitrogen (TKN) (Organic N + TAN), as nitrates ( $\text{NO}_3^-$ ), as nitrites ( $\text{NO}_2^-$ ) or as total nitrogen (TN) which is the sum of Organic N, TAN, nitrite and nitrate. Ammonia and total nitrogen control is important due to the fish toxicity and surface water eutrophication impacts, respectively.

#### **4.2.1.4 Fate and Removal in the Liquid and Solid Treatment Trains**

The fate and removal of nutrients and organics through the treatment process is described below, with reference to Figure:

- The separation begins with preliminary screening for large solids (> 15 mm), settling of grit in a grit chamber and followed by primary settling (settleable solids < 15 mm). The screenings and grit are typically collected and trucked to a landfill site. The primary settled solids are pumped to an anaerobic or aerobic reactor, referred to as a digester, for further reduction of associated organics and pathogens. Typically there is a 25 to 40% reduction in  $\text{BOD}_5$  and about 50 to 60 % reduction in total solids during primary treatment.
- The solids that do not settle out in the primary clarifier move to the bioreactor(s) (aerobic or anoxic reactor(s)) where a biomass (biologically active microorganisms) are actively maintained to remove the dissolved forms of carbon compounds and nutrients under aerobic conditions. Typically air and mixing controls are provided in these bioreactors.

- The bioreactor liquid effluent stream flows to a secondary clarifier for solids separation. The underflow from the secondary clarifier is separated and partly wasted to the digester and partly returned to the bioreactor. The liquid effluent from the clarifier is considered the secondary MWW. This MWW is disinfected before being discharged to the receiving water body.
- Digesters can be aerobic or anaerobic and are used to stabilize sludge's and produce biosolids. Biosolids depending on their metals to nutrient concentration are utilized on agricultural lands, disposed in landfills or incinerated according to established regulations.
- Ammonia can be removed through facilities designed for nitrification. Secondary plants are not normally designed for this purpose but this may occur under warm weather conditions or in facilities with large reserve capacity providing extended solids retention times and adequate aeration.



**Figure 1.** Typical tertiary WWTP showing the treatment processes. The numbered locations are potential sampling points for operational or research purposes. (adapted from Lee et al., 2005).

## **4.2.2 Metals**

### **4.2.2.1 Background**

Trace quantities of many metals such as aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr(III) and Cr(VI)), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), magnesium (Mg), nickel (Ni), potassium (K), selenium (Se), sodium (Na), silver (Ag) and zinc (Zn) are found in sewage from various sources including residential, groundwater infiltration, commercial, institutional and industrial discharges.

Although a few metals have been found to be essential to support biological functions, all metals are toxic at concentrations above those required or tolerated by aquatic organisms. To minimize potential toxicity it is generally desirable to have pretreatment, particularly at industrial facilities prior to discharge to municipal sewers.

Insoluble metal forms are typically concentrated in the sludge's by sorption or removed through physical-chemical processes, and also result in sludge's with high metal concentrations which increase the solids handling burden.

Some soluble metal species of As or Cr along with methylated-Pb compounds may appear in the final effluents in the order of 1 to 100 µg/L range. Metals of concern such as As, Cu, Cr and Se are typically controlled and regulated in the disposal/utilization of biosolids (stabilized sludge's) where they tend to accumulate.

### **4.2.2.2 Point and Non-point Sources**

Industrial, commercial, institutional and residential wastewater sources collected in sewers ultimately collect at WWTPs and become point sources for metals. Urban stormwater runoff and agricultural runoff which carry residuals from pesticides and herbicides are the other common non-point sources for metals.

### **4.2.2.3 Environmental Effects**

The majority of metals partition to the solids portion of the treatment stream ( i.e., sludges and ultimately biosolids (stabilized sludges). However, metals not adsorbed to solids are discharged in MWW and may cause toxic effects on aquatic organisms at trace concentrations (µg/L). Metals are persistent, continuing to cause long term effects in the environment through deposition to and remobilization from sediments. Additionally, some metals biomagnify in the food chain, thereby causing indirect effects on predators (including humans).

### **4.2.2.4 Fate and Removal in the Liquid and Solid Treatment Trains**

Metals are generally removed from the liquid train by adsorption or chemical precipitation. Typical technologies available for the removal of heavy metals include chemical precipitation, carbon adsorption, sludge adsorption, ion exchange and reverse osmosis. Of these methods sludge adsorption and chemical precipitation are the most prevalent. One common disadvantage in handling chemically precipitated sludge is that the presence of heavy metals may inhibit sludge stabilization or cause toxic effects during anaerobic digestion.

Some industrial inputs to municipal sewers contain relatively high concentrations of metals. Precipitation of these metals results in high concentrations in sludges, which then have to be disposed in secure landfill sites rather than having the beneficial use of land application. Municipal sewer use bylaws contain provisions for controlling discharge of metals to sewers.

Typical effluent concentration of important metals achievable in MWWTE vary significantly by metal and process. Metals in MWWTE range from 1 to 500 ( $\mu\text{g/L}$ ) depending on the level of industrial contribution in the sewershed.

### **4.2.3 Trace Contaminants – Legacy**

#### **4.2.3.1 Background**

The most commonly measured trace contaminants in wastewaters are volatile organic compounds (VOCs) and extractables. VOCs include low molecular weight petroleum components and brominated and chlorinated compounds, many of which have been shown to be teratogenic or carcinogenic in humans. Extractables include phenolic compounds, which have low taste thresholds and human health implications; polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) which are toxic, bioaccumulative, and stable in the environment; and pesticides (herbicides, insecticides etc.) which have the potential for a variety of toxic effects on non-target species.

Some PCBs, pesticides and PAHs are found in municipal sludge's and MWWTE and have been identified as a priority concern. The pesticides of priority concern include endosulfan, lindane, MCPA and 2,4-D. The PAHs of primary concern include anthracene, benzo(a)anthracene, benzo(a)pyrene, fluoranthene, fluorine, phenanthrene, and pyrene.

#### **4.2.3.2 Point and Non-point Sources**

The major sources of particular legacy trace contaminants to the urban environment are MWWTE. PAHs are also combustion by-products of persistent organic pollutants (POPs) (Muir et al, 2001) and through atmospheric transport, deposition and runoff become a non-point source contribution to the environment. VOCs are predominantly emitted directly to the air-shed from various industrial sources and mobile combustions sources. Pesticides tend to enter from non-point sources, most commonly runoff from agricultural and residential use.

#### **4.2.3.3 Environmental Effects**

VOCs are of great concern once released to the environment because they are most likely to volatilize, become very mobile and contribute to the reactive hydrocarbons in the atmosphere which can lead to the formation of photochemical oxidants. The presence of some of these compounds may pose a health risk as some of these compounds have a potential for tetraogenesis or carcinogenesis in humans. These VOCs are of particular concern to operators at WWTP and those that maintain the existing sanitary collection systems (Metcalf and Eddy, 2003).

PCBs generally found in municipal wastewaters primarily concentrate onto municipal sludge's during the treatment process and have been reported to be present in raw and treated sludge's in the order of 1 to 20 mg/kg. The physical-chemical properties of PCBs are complex with tendency to low water solubility, highly lipophilic and semi-volatile. PCBs tend to be very persistent in the natural environment and are strongly adsorbed by soils high in organic matter. There is minimal root uptake and minimal translocation from soil to plants (WEAO, 2001).

PAHs generally found in municipal wastewaters primarily concentrate onto municipal sludge's and have been reported to be present in raw and treated sludge's in the range of 1 to 10 mg/kg. Municipal wastewaters generally contain less than 1 µg/L in solution and PAHs have been found to be below common method detection limits in MWW. PAHs are strongly adsorbed by soils rich in organic matter and have poor foliar adsorption. If transferred to animals by soil ingestion they tend to be rapidly metabolized and do not accumulate (WEAO, 2001)

#### **4.2.3.4 Fate and Removal in the Liquid and Solid Treatment Trains**

VOCs have characteristically low boiling points (less than or equal to 100 °C) and/or vapour pressures greater than 1 mm Hg at 25 °C. The release of VOCs at WWTP is primarily due to volatilization and gas stripping. The release occurs in sewers, at the headworks, preliminary treatment and aeration tanks of WWTP (see Figure 1). The air stripping is most prevalent in aerated grit chambers, aerated biological treatment tanks and aerated transfer channels (not common in Ontario) (Metcalf and Eddy, 2003).

Stripping towers are specially designed to strip VOCs from wastewaters to the atmosphere. The stripping towers require regulatory approval and are required to comply with air emission standards.

Various control mechanisms include covering reactors of chambers and diverting the air mass to treatment or thermal units for the treatment or combustion of the off-gases containing the VOCs prior to being discharged to the atmosphere. There are problems of corrosion of mechanical parts and provision for confined space entry of personnel for equipment maintenance related to the treatment of VOCs.

Treatment and removal mechanisms for PCBs, pesticides, PAHs, and other legacy trace contaminants at WWTPs are not well understood. Survey work has shown various substances within these classes to be found in MWW, sludge's and biosolids, with a predominance in sludge's.

### **4.3 Emerging Trace Contaminants**

#### **4.3.1 Endocrine Disrupting Compounds and Other Priority Contaminants**

##### **4.3.1.1 Background**

The foundations of the endocrine system are the hormones and glands. Hormones have an effect on the human body when they bind to specific receptors and trigger a response. Hormones regulate growth / development, mental development and mood, sex maturation and immune functions. Wide ranges of compounds have the capability to bind to hormone receptors and act in an irregular fashion altering the endocrine system of an organism. These compounds are called Endocrine Disrupting Compounds (EDCs).

Examples of EDCs include natural and synthetic hormones such as 17β-estradiol (E2) and its metabolites estrone (E1), estriol (E3) and 16α-hydroxyestrone (16α-OH-E1) and testosterone, the synthetic contraceptive hormone 17α-ethinylestradiol (EE2), some pesticides, dioxins and furans, polychlorinated biphenyls (PCBs), nonylphenol ethoxylate surfactants (NPEOs), and fluorinated telomers .

### **4.3.1.2 Point and Non-point Sources**

It has been demonstrated that many chemicals that are in everyday use (industrial and domestic) are released into the environment at concentrations high enough to disrupt the endocrine system of wildlife and humans, e.g., nonylphenol surfactants, EE2 (Parrott and Blunt 2005).

In urban environments, most compounds make their way in sewage from human use or disposal to WWTPs where the potential exists for their discharge in the liquid effluent or to be partitioned into the solids stream (biosolids) (Metcalf et al., 2003). In rural environments, drugs used by humans or administered to livestock or fish farms have the potential to enter the aquatic environment through runoff into surface water or through contamination of groundwater (Metcalf et al., 2003). In addition, through land applications of biosolids or manure, hormones and other compounds may enter the soil matrix. Dependent upon the characteristics of the individual substance, they may persist in the soil or leach into groundwater or surface water.

The major route for the release of hormones, PCBs, and nonylphenol surfactants to the Canadian environment is through discharge of municipal wastewater effluents and to a lesser extent, land application of biosolids. The concentration of these compounds is generally lower in treated effluents as they degrade and/or adsorb to sludge's.

### **4.3.1.3 Environmental Effects**

Adverse effects on birds, fish and other wildlife in the Great Lakes Basin that have been suggested to have been caused by EDCs include tumours, organ damage, physical deformities, eggshell thinning, behavioural changes, reproductive disorders and population decline (Environment Canada, 2001). The persistence of EDCs in the environment depends on the characteristics of each individual chemical. Many EDCs, such as PCBs, DDT, and dioxins are known to be persistent.

### **4.3.1.4 Fate and Removal in the Liquid and Solid Treatment Trains**

Further study is required to determine the optimum point of upgrading or optimizing treatment to reduce potential risk of discharging EDCs into the environment (Environment Canada, NWRI, 2001). Recent Canadian studies indicate secondary, tertiary as well as lagoon treatments are capable of reducing the hormones estradiol and estrone to below current analytical method detection limits. The dominant mechanism of reduction (i.e., biotransformation, mineralization or adsorption to sludge's) has not been clearly established (Servos et al., 2005).

## **4.3.2 Pharmaceuticals, Personal Care Products (PPCPs) and Antimicrobial Resistance**

### **4.3.2.1 Background**

Beginning in the 1970s, an escalation of research and monitoring revealed the presence of drugs and their metabolites in the environment. Human and veterinary Pharmaceuticals and active ingredients in Personal Care Products (PPCPs) are a diverse group of biologically active chemical compounds which include analgesics, lipid regulators, antibiotics, steroids, synthetic hormones, surfactants, musk fragrances, sunscreen agents and household cleaning and laundry products (Daughton and Ternes 1999).

The (over)use of antibiotics in humans and especially domestic animals may lead to the potential for accelerated development of resistance among naturally occurring pathogens. For example, triclosan,

triclocarban, and parabens are widely used antimicrobial preservatives used in foods and cosmetics (Danish EPA 2001) which can make their way WWTPs.

#### **4.3.2.2 Point and Non-point Sources**

Scientific studies indicate that PPCPs have been detected in drinking water, surface water, groundwater, and sewage influents and effluents in North America and Europe. The detected concentrations are generally low (ug/L – ng/L)

Most pharmaceuticals and their metabolites from human use, make their way into the environment by way of septic systems and municipal sewage treatment plants. Many unused pharmaceuticals in homes are flushed down the drain and this combined with the human excretion of un-metabolized pharmaceuticals result in their presence in sewage. Sewage treatment plants are unable to remove most PPCP's which are then discharged to rivers, lakes and streams in liquid effluent or to land surfaces through the spreading of the solids portion of the sewage (biosolids). In rural environments, drugs used by humans or administered to livestock or fish farms have the potential to enter the aquatic environment through runoff into surface water or through contamination of groundwater (Metcalf et al., 2003). Confined animal feeding operations (CAFOs) are a major source of antibiotics.

#### **4.3.2.3 Environmental Effects**

The risks posed to aquatic organisms (by continual life-long and multi-generational exposure) and to humans (by long-term consumption of minute quantities in drinking water) are essentially unknown. While the major concerns to date have been the promotion of pathogen resistance to antibiotics and disruption of endocrine systems by natural and synthetic sex steroids and hormones, many other PPCPs have unknown consequences. Aquatic pollution is particularly troublesome because the aquatic organisms are captive to continual, life-cycle, and multi-generational exposures of chemicals via MWWWE released to surface waters. The supply of chemical contaminants is also continually replenished. Subtle effects reported include impacts on development, spawning, and other behaviors in shellfish, ciliates, and other aquatic organisms (Purdom et al., 1993; Nichols et al., 1998).

Pharmaceuticals are designed to have specific biological effects on humans. Although PPCPs detected in the environment are found at levels well below any human “therapeutic” level, there are health concerns about individuals (especially those with specific drug allergies, the elderly and children) being chronically exposed to trace amounts of these substances through drinking water. The human health effects could include effects on the endocrine system, nervous system, and reproductive system, as well as contribute to antibiotic resistance.

#### **4.3.2.4 Fate and Removal in the Liquid and Solid Treatment Trains**

Removal efficiencies from treatment plants vary from chemical to chemical and between individual sewage treatment facilities generally because of different technologies and operating conditions. Municipal WWTPs are not specifically engineered for PPCP removal.

Within a WWTP, a compound may i) mineralize to carbon dioxide (CO<sub>2</sub>) and water ii) be retained in the solids portions of the treatment stream (biosolids) if the compound is lipophilic or iii) be released into the receiving water as the parent compound or a degradation product through the effluent. For example, musk fragrances are expected to sorb strongly to activated sludge, with some limited biodegradation (OSPAR 2004); volatilization is not anticipated to be an important removal mechanism. Although data are limited,

because of their hydrophobicity of the compounds, their presence in residual wastewater solids is expected.

Any improvement in technology for the removal of suspended solids, oxygen demand, or nutrients from wastewater will more than likely also remove the trace levels of PPCPs. Studies have shown ultraviolet irradiation or physical removal, such as membrane filtration, could remove these compounds (Ternes et al., 2002).

### **4.3.3 Brominated Flame Retardants**

#### **4.3.3.1 Background**

Bromine-based flame retardants (BFRs) are agents that are used in textiles, furniture, electronic components and building insulation sectors to slow the spread of fire. Tetrabromobisphenol-A (TBBPA), Hexabromocyclododecane (HBCDD) and Polybrominated Diphenyl Ethers (PBDEs) are particular types of BFRs (Alaee et al., 2003). BFRs have been demonstrated to have characteristics that would classify them as Persistent Organic Pollutants (POPs), they are bioaccumulative, persistent, undergo long-range transport, and are lipophilic (Alaee and Wenning, 2002).

The presence of BFR chemicals and in particularly PBDEs have become an increasing environmental concern. PBDEs are not used as individual compounds (congeners), but rather as mixtures of congeners. The three mixtures used commercially are Penta-BDE, Octa-BDE and Deca-BDE. PBDEs were first detected in fish from Sweden at levels higher than those of PCBs (Tommy et al., 2004) and were considered global contaminants in the mid 1980s (Alaee and Wenning, 2002).

#### **4.3.3.2 Point and Non-Point Sources**

PBDE production in North America is carried out by two facilities in the United States; Great Lakes Chemical Corp and Albermarle Corp (Hale et al., 2003). PBDEs may be released to the environment during the manufacturing process, throughout the life cycle of the products that contain these compounds, or when products are disposed of in the environment (Alaee et al., 2003). Inventories of the main BFRs (PBDEs, TBBPA, HBCDD) sources are not available in North America, thus making it very difficult to pin-point the exact sources of these compounds into the environment.

PBDEs have been increasing in North America since the 1970s which appears to be due to continued use of Penta-BDE (Watanabe and Sakai 2003). They are ubiquitous in the environment in that they can be found in all environmental compartments: water, air, aquatic system, birds and humans (Hites 2004) as well as in biosolids and soils. At present, it is not known how PBDEs are released into the environment, however, their presence in the environment indicates that they must be migrating from their original products. Predicting the environmental behavior of BFRs is difficult, moreover, it is not clear whether the concentrations found in the environment are due to current or past production.

#### **4.3.3.3 Environmental Effects**

PBDEs have been found in human blood, serum, adipose tissue, breast milk, placental tissue and in the brain. Levels in people worldwide seem to be increasing with a doubling time of four to five years (deWitt 2002). Around 86-99% of the total PBDE congeners found in human tissues are present in the Penta-BDE commercial formulation. Demonstrated toxicological endpoints of concern for environmental levels of PBDEs include thyroid and hormone disruption (Tomy et al., 2004; Legler, 2003), neurodevelopment deficits and cancer (Swedish EPA, 2003). Health Canada's draft screening assessment

(2004) of PBDEs found no evidence that the current levels of PBDEs in the Canadian environment are harmful to human health.

PBDEs have also been detected in surface waters from the Great Lakes. Generally, the highest concentrations were found in Lake Michigan and Lake Ontario. The half life of the major congeners that make up the Penta-BDE commercial formulation range from 150 -600 days in water. PBDEs have also been detected in wildlife. They have been found in Herring Gull eggs, Grey seals and Atlantic salmon (de Witt, 2002). Penta-BDE is highly toxic to invertebrates, whereas the Deca- and Octa-BDE may be of low risk to surface water organisms and top predators, but there is concern for soil organisms.

At this time knowledge about these chemicals, their sources, environmental behavior, and toxicity is limited, making risk assessment very difficult.

#### **4.3.3.4 Fate and Removal in the Liquid and Solid Treatment Streams**

It is expected that some PBDEs enter WWTPs due to their hydrophobicity, persistence, and widespread use in the market. Based on the chemical characteristics of PBDEs, they will tend to bind to the high organic carbon containing solids portion of the wastewater treatment stream i.e., the sludge or biosolids fraction. Concentrations of PBDEs in biosolids in the United States and Canada appear to be at least 10x greater than the European levels (Hale et al., 2003). The presence of congeners BDE 47, 99, 209 in biosolids indicate discharges to municipal wastewater treatment systems, either from households, traffic and/or diffuse releases to the environment.

Within the wastewater treatment process it is expected that due to the high degree of bromination of some of these compounds, they would degrade during secondary treatment. However, PBDEs have been detected in final effluents from wastewater treatment plants. It is important to consider the continual discharge that the effluent may be contributing to the receiving waters versus that which may be applied to agricultural land from biosolids.

## **5.0 Existing Potential Contaminants of Concern in Wastewater**

### **5.1 Review of Effluent Substances**

While it was beyond the scope of the initial terms of reference, the committee was asked to determine contaminants of potential concern in MWWE. As a starting point, a master list of 242 substances was compiled from a number of environmentally significant lists, including the Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes, the Canada-Ontario Agreement (COA) Respecting the Great Lakes Basin Ecosystem, the European Union list of priority substances from the Water Framework Directive, CCME Water Quality Guidelines, U.S. EPA Water Quality Guidelines, Health Canada Guidelines for Canadian Drinking Water Quality, Health Canada Drinking Water Substance Priority List, selected provincial Water Quality Guidelines, and a number of conventional wastewater parameters.

Preliminary concentrations of substances in MWWE were compiled from a number of sources, including a review of municipal effluent for CEPA Toxics completed by Environment Canada, analytical results from the effluents of 8 plants in Western and Central Canada, and the technical literature. Comparison of this data review with the master list showed the following:

- 69 substances were occasionally detected in MWWE at levels exceeding water quality and/or drinking water guidelines;

- 26 substances were detected in MWWE but lacked a benchmark or guideline value for comparison;
- 68 substances had a benchmark or guideline value but had either no concentration data or results were below unspecified analytical detection limits;
- 34 substances had neither benchmark/guideline values nor concentration data;
- 44 substances had benchmark/guideline values and all effluent results were below stated analytical detection limits.

The literature review identified a further 101 substances which have been detected in MWWE in North America and/or Europe, but which were not included in the original master list.

The complete report “Review of Effluent Substances”, PN 1356 can be viewed at [www.ccme.ca](http://www.ccme.ca). This review of existing data identified several information gaps:

- Small database of effluent concentration data;
- Comparison of effluent data with water quality objectives or drinking water guidelines, without factoring in dispersion in the mixing zone, is probably too stringent to apply to MWWE;
- Sampling and analytical methodology was probably not consistent and standardized between data sets.

Nevertheless, this preliminary review exercise served as a starting point for development of a characterization list of substances in MWWE,

## 5.2 Characterization List for MWWE

There are several challenges in identifying potential contaminants of concern for an individual MWWE. Each sewershed has different industrial, commercial and institutional inputs into the effluent, which must be considered in the determination of site-specific Effluent Discharge Objectives (EDOs). Additionally a number of substances enter wastewater from residential and non-point sources, influenced by regional use of consumer products and the extent of combined sewers in the urban area.

A database which aligns industries with potential contaminants is under development and will be on the CCME website. The database includes all of the information from the initial science report, CCME, EPA and Provincial water quality guidelines, drinking water guidelines, recreational and agricultural criteria, and substance categorization as persistent, bioaccumulative or toxic according to the USEPA Integrated Risk Information System and Toxic Release Inventory, and the Environment Canada National Pollutant Release Inventory (NPRI). In addition the database identifies the status of substances as toxics under the Canadian Environmental Protection Act (CEPA), Canada-US Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes (BTS), and the Canada-Ontario Agreement Respecting Great Lakes Basin Ecosystem (COA).

The Environmental Risk Management approach requires an initial characterization of potential contaminants in MWWE across Canada. The protocol for characterization of MWWE calls for a base list of “potential contaminants”, supplemented with additional substances added on a site-specific basis.

Determining an initial list of substances for characterization requires a balance between availability of standardized analytical methods and the likelihood of detecting a given substance in MWWE. For example it is unlikely that uranium would be present in MWWE although analytical methods are available for that metal. Measurement of fecal coliforms or total residual chlorine in each MWWE has little practical meaning due to the wide range of treatment levels and regional disinfection requirements in Canada. In contrast, banned chemicals such as DDT and PCBs should not be present in MWWE; however they would likely be detected due to their environmental persistence and the potential existence of unidentified residual sources. The knowledge gained from the Review of Effluent Substances (Section 5.1) and the professional judgement of many experts, including 2 CCME sub-committees, have been

utilized for the development of the “base” characterization list, taking into account the availability of standardized methods in commercial accredited laboratories, as represented by the Proficiency Tests offered by the Canadian Association of Environmental Analytical Laboratories (CAEAL). A series of test groups, as listed in Table 1, was identified which would provide an initial comprehensive, cost-effective data set to characterize MWW. The substances listed in Table 1 are generally expected to be detected in MWW and are of potential concern based on toxicology and adverse environmental impacts (persistence and bioaccumulation).

Table 1: CAEAL Test Groups for Wastewater Characterization, with estimated cross-Canada costs

Test Group	Parameters	Lab 1					Lab 2
		Atlantic	Quebec	Ontario	Alberta	BC	cross-Canada
C-01A Selected major ions	Fluoride	15.00	18.00	15.00	15.00	12.00	23.20
	Nitrate	30.00	18.00	12.00	15.00	12.00	
	Nitrate + Nitrite	15.00	24.00	24.00	30.00	24.00	
C-01B	Ammonia	15.00	22.00	13.00	15.00	13.00	10.40
C-02A	Dissolved Metals and Metal Hydrides, full range	58.00	50.00	50.00	50.00	50.00	52.00
C-03	Total Phosphorus	22.00	25.00	15.00	22.00	15.00	14.40
C-04A	Total Suspended Solids	12.00	16.00	12.00	14.00	12.00	9.60
C-04B	carbonaceous BOD (5-day)	30.00	20.00	20.00	35.00	25.00	27.20
C-04D	COD	26.00	20.00	20.00	25.00	25.00	17.00
C-06	Organochlorine Pesticides	135.00	135.00	125.00	135.00	135.00	130.00
C-06	PCBs	75.00	115.00	60.00	75.00	75.00	62.40
C-07	PAHs	117.00	80.00	80.00	100.00	100.00	115.60
C-14	Cyanide (total)	27.00	25.00	25.00	30.00	30.00	23.80
C-15	pH	9.00	5.00	5.00	5.00	5.00	5.00
C-16	Volatile Organic Compounds	110.00	100.00	100.00	100.00	100.00	135.00
C-19	Mercury	19.00	20.00	13.00	19.00	13.00	13.00
C-25	Phenolic compounds	140.00	100.00	140.00	140.00	140.00	160.00
	<b>Total</b>	<b>855.00</b>	<b>793.00</b>	<b>729.00</b>	<b>825.00</b>	<b>786.00</b>	<b>798.60</b>

### **5.3 Research Needs for Contaminants in MWWE**

The initial list of contaminants for characterization purposes does not include every substance identified in the review exercise, for example BFRs, PPCPs, or EDCs. Standardized analytical methods have not yet been established for these and many other substances, nor are there enough data on environmental and human health effects to warrant a widespread and costly monitoring program.

Understanding of the presence and implications of substances in MWWE will be an ongoing process as research on contaminants continues. Research needs regarding contaminants in MWWE include:

- Compilation of standardized characterization data from treatment plants across Canada to identify the contaminants present in MWWE regionally and nationally. A large database will direct the refinement of the base list for future monitoring purposes;
- Determination of the impacts of these contaminants on the receiving ecosystems;
- Development of effluent quality guidelines to protect receiving ecosystems from deleterious impacts; and
- Determination of the treatability of contaminants through treatment optimization, upgrades, and innovative technologies. The ability of wastewater treatment processes to reduce effluent concentrations of industrial chemicals, pesticides, emerging contaminants, and other substances is only partly understood. Several research groups in Canada are investigating substances in MWWE from a treatability perspective but this information is widely dispersed. In the Review exercise (Section 5.1) the ToxChem+ model was applied to those substances which exceeded guidelines, using various levels of treatment. The model results were not verified with actual effluent data. The modeling exercise illustrated the value of a compendium of treatability for substances in MWWE. Such a compendium would assist municipalities and agencies in determining which substances might be candidates for source control, and which level of treatment would be appropriate or necessary for the removal of specific substances where source control would not be feasible.

### **6.0 Analysis of Municipal Wastewater and Biosolids**

Measurement of a chemical in the environment requires the appropriate analytical technology and a pure standard of the chemical for comparison and quantification. Analytical technology is continuously improving, developing better methods for isolating and concentrating the compounds of interest, and more sensitive detectors to measure smaller concentrations in environmental samples. The chemical nature of the compound and the concentration present in the environment determines the amount of resources required to produce an analytical result with sufficient accuracy and precision.

Accurate and precise analysis of municipal wastewater and biosolids is necessary for process control, regulatory compliance, and assessment of conventional and innovative treatment technologies for removal of contaminants. Analysis of municipal wastewater and biosolids has developed and expanded over the last 100 years (APHA 2005). In order to become a “standard” method, an analytical method must undergo development, validation, and collaborative testing to meet specific requirements and be widely used in the North American wastewater industry. This section presents a brief overview of the current state of analytical methods and sampling considerations for wastewater and biosolids.

#### **6.1 Nutrients and Aggregate Organics**

Wastewater treatment systems are designed to remove organic matter, solids nitrogen and phosphorus in order to protect the receiving aquatic ecosystem from oxygen depletion and eutrophication. Analytical methods for wastewater have until recently focused on measurement of these parameters for process

control and regulatory compliance, and the methods are well established. Gravimetric methods for measurement of solids have been used since the 1950s. Nitrogen species (ammonia, ammonium, nitrate, nitrite, and organic nitrogen) and phosphorus have been measured with electrode or colourimetric techniques since the 1970s. Oxygen demand has been determined using the Biochemical Oxygen Demand (BOD) test since the 1930s and the Chemical Oxygen Demand (COD) test since the 1950s. These “conventional” parameters are measured in the ppm (parts per million) range. Due to their long history, analytical technology is well developed and affordable, and wastewater practitioners have a high degree of familiarity with the accuracy and precision (typically  $\pm 10\%$ ) of analytical results.

## 6.2 Metals

Metals can be associated with the liquid and/or the solids in municipal wastewater. Depending on the metal and its concentration, its effect on the receiving environment (water or agricultural land) can range from benign to extremely toxic. Analysis of metals involves digestion of the water or solids sample to release the metals into the liquid phase. Metal analysis used colourimetric techniques in the 1950s, and then moved to atomic absorption spectrophotometry (AA) in the 1970s, inductively coupled plasma (ICP) in the 1980s, and ICP with a mass spectrometer detector (ICP/MS) in the 1990s. Metals concentrations are measured in the ppm (parts per million) or ppb (parts per billion) range. Again the long history of these parameters has resulted in well developed, affordable analytical technology and a high degree of familiarity with their presence in wastewater.

## 6.3 Trace Contaminants – Legacy

The most commonly measured specific organic compounds in wastewaters are volatile organic compounds (VOCs) and extractables. Analysis of these “legacy” organics involves isolation and concentration of the compounds using solvent or gas, separation of the compound mixture using gas chromatography (since 1980s) or liquid chromatography (since 1990s), and identification and quantification with a detector chosen for the compound characteristics. These compounds are measured in the ppb range. These compounds are relatively recent additions to *Standard Methods* and require more specialized analytical equipment and operator training. The nature of these compounds also causes larger variability in results (typically  $\pm 30\%$ ) compared to conventional parameters and metals.

## 6.4 Trace Contaminants – Emerging

A review of the timeline from initial analytical attempts to the establishment and publication of an analytical method as a “standard method” indicates that this process can take 10 to 15 years. This process of standardization includes not only the refinement and comparison of analytical methods, but sufficient evidence that the compound is of concern in wastewater to merit the cost of its analysis.

EDCs, PPCPs, and BFRs are currently the most widely studied emerging contaminants of concern in municipal wastewater. A variety of analytical methods have been developed for their measurement and there has been enough evidence of effects in the receiving waters to maintain concern about their presence in wastewater. These compounds are measured in the ppb to ppt range with variability of up to  $\pm 100\%$ .

A recent review of effluent substances identified a need for a comprehensive survey of substances present in municipal effluents in Canada, preceded by a review of the availability and adequacy of analytical methods (CCME 2005). Current issues in the analysis of these compounds in wastewater include the limited availability of labeled standards to confirm accuracy of results, limited availability of analytical instrumentation, particularly LC/MS-MS, lack of consensus on adequacy of detection limits, and limited availability of methods for analysis of these compounds in biosolids (most trace contaminants that do not

get mineralized during wastewater treatment will partition to the solids phase). A recent Environment Canada workshop on PPCPs in the environment identified the top priorities for PPCP research in Canada as (1) information exchange on chemical methods and effects research, and (2) increased access to resources (labeled standards, equipment, operators) to move forward with analytical methodologies (NWRI 2006). Coordination of research activities and resources across Canada has the potential to shorten the timeline for standardization of analytical methods for these emerging contaminants in wastewater.

## 6.5 Sampling Considerations

The result of any test is no better than the sample on which it was performed. Samples must accurately represent the material being sampled, retain the relative proportions or concentrations of all pertinent compounds, and be handled such that no significant changes in composition occur before the tests are performed. Trace contaminants require particular attention during sampling as they can volatilize, adsorb to container walls, or be degraded by microbial activity or exposure to light. Sampling a wastewater treatment system requires an understanding of the physical and chemical processes that occur at each step in the process, the inherent variability in wastewater composition, the diurnal nature of the flows, the characteristics of the compounds under study, and the objective of the sampling program. A review of international literature on trace contaminants in municipal wastewater indicates a need for coordination of sampling criteria to better compare results from different treatment systems.

## 7.0 Summary of Issues and Data Gaps

The subcommittee convened a focus group including representatives from universities, municipalities, Canadian Water and Wastewater Association, Water Environment Association of Ontario, National Research Council, Canadian Water Network, CCME Water Quality Task Group, Ontario WERF representative, Ontario Centre for Excellence Earth & Engineering Technology, Environment Canada to review information, assess gaps and recommend action.

The key recommendation of the focus group was the need for a collaborative Canadian research partnership forum.

The preliminary list from the focus group, combined with reports and provincial and national staff expertise, the following research gaps were identified.

- 1) The following are key **research** gaps which need addressing:
  - Presence and frequency of contaminants in wastewater
  - Impact of effluent contaminants on aquatic and human environment
  - Cumulative impacts of multiple chemicals that are present in MWW- additive and synergistic toxic effects
  - Analytical methods for measuring contaminants in effluents and biosolids
  - Cost effective treatment technologies for treating established and emerging substances of concern.
  
- 2) The following gaps have been identified in **management** of research
  - Lack of co ordination between research projects
  - Co ordination of environment and health in risk assessment

- Research is not prioritized. Priorities should be determined through a broad risk evaluation process which would look at substances, define the risk, the cumulative impact, and control or treatment
- Decision to focus research on contaminant by contaminant research on impacts or focus research on removals
- Systematic method to link to international research efforts and incorporate into the risk assessment process.
- Understanding of how to influence industry and public behaviour for source control and increase understanding of costs for removal. Public education on both the contaminants in wastewater and the impacts and implications of removal is an important component of research priorities and future management of trace contaminants of concern.

Currently, research is undertaken in Environment Canada and Health Canada for risk assessment of substances. There is collaboration between the two departments but a need to strengthen the linkages and ensure a strong mechanism to focus on environmental impacts of contaminants to aquatic and human health. The focus group recommended having both Health Canada and Environment Canada as part of the research advisory board to assist in priority setting for municipal wastewater research.

Strategic decisions must be made to focus research on contaminant by contaminant research or focus research on removals. Thousands of chemicals are created and put on the market every year. The potential impact on aquatic and humans is examined labouriously one contaminant at a time after many years of development on analytical methods. Cumulative impacts as stated are not studied. A recent EU study in the Netherlands (Stowa 2005) has focused on removals. A key aspect of research priority determination is to collaborate internationally and use international (EU) recommendations to guide the prioritization of emerging trace contaminants (e.g. alkylphenols, surfactants, pharmaceuticals, personal care product, brominated flame retardants and fluorinated telomers).

Public education and discussion on contaminants of concern is a key component in making management decisions. Decisions on removals of contaminants in the past has focused on industries and the removal of harmful contaminants from industrial processes. Emerging trace contaminants are related to personal care products, (fragrances, shampoos) pharmaceuticals, and commercial products such as flame retardants. Public education is essential to ensure an intelligent societal debate on decisions to change our products and behaviours. An understanding of the costs of removal, banning products and societal change is required. Municipal, provincial and federal decision making relies on this type of public understanding and input.

It is clear from all sectors that coordinated research linking science with policy, health initiatives and with environmental risk assessment needs to be adequately and consistently funded to deal with environmental impacts.

The value of this research is to support sound decision making for future wastewater infrastructure.

## 7.1 Recommendations

There is a strong consensus on *what* needs to be done in terms of research with the following recommendations:

1. Compilation of standardized characterization data from treatment plants across Canada to identify the contaminants present in MWWWE regionally and nationally.
2. Analytical Research Needs – Standardization of methods is needed as well as an evaluation of the adequacy of detection limits relative to environmental effects for substances. As development of

analytical techniques often takes considerable time, a prioritization of potential substances of concern is required.

3. Environmental Effects Impacts – Determination of the impacts on aquatic ecosystems and human health, particularly highly sensitive individuals with specific drug allergies, the elderly and children, by long-term consumption of impacted drinking water is essentially unknown, making risk assessment difficult. Traditional risk assessment methods are not appropriate for emerging compounds. New methods are required. Cumulative impacts which examine synergistic and mixture effects need addressing.
4. Treatment Research Needs – Existing technologies should be further refined and evaluated for more efficient reduction of conventionals. Fortuitous removal of trace contaminants by existing treatments should also be investigated. New and innovative technologies should be developed and evaluated to target both conventionals and prioritized contaminants of concern in municipal wastewater effluents and sludge. Determination of the treatability of contaminants through treatment optimization, upgrades, and innovative technologies. The ability of wastewater treatment processes to reduce effluent concentrations of industrial chemicals, pesticides, emerging contaminants, and other substances is only partly understood. Several research groups in Canada are investigating substances in MWW from a treatability perspective but this information is widely dispersed. In the Review exercise (Section 5.1) the ToxChem+ model was applied to those substances which exceeded guidelines, using various levels of treatment. The model results were not verified with actual effluent data. The modeling exercise illustrated the value of a compendium of treatability for substances in MWW. Such a compendium would assist municipalities and agencies in determining which substances might be candidates for source control, and which level of treatment would be appropriate or necessary for the removal of specific substances where source control would not be feasible.
5. Combined Sewer Overflow Research Needs – Research is also needed on CSO variability and the monitoring frequency which is sufficient to characterize CSO quality and what treatments should be required for protection of the receiving environment.
6. Education Needs - Need to educate the public on the legacy and emerging trace contaminants, how they are prioritized for research and the societal implications of source control, treatment, or banning.
7. Co ordination Needs – There is a strong need to prioritize research through a broad risk evaluation process which would look at substances or classes of substances, their presence (concentration and frequency) in effluents, cumulative impacts, current controls and treatments. Co ordination is required between:
  - municipalities, universities and government research
  - science and engineering solutions and policy
  - Canadian and international research efforts
  - Human and environmental health considerations .

A Canadian Wastewater Research Agency is recommended to include and ensure effective linkages between: universities, municipalities, CWWA, Infrastructure Canada, Environment Canada (CEPA and National Water Research Institute), Health Canada, EU, NGOs, and provinces.

The body would undertake the following functions:

- ranking the legacy and emerging trace contaminants for municipal effluent for research

- ensure strategic link between research (science, engineering) and policy
- maintain an inventory of MWWWE research;
- assess emerging issues and determine the necessary actions to be taken to address these issues;
- disseminate information to municipalities, governments, universities, other agencies, and the public;
- educate the public on the implications of source control, treatment and product removals to control discharges of trace contaminants
- co-ordinate research and research funding;
- sponsor an annual workshop; and
- link to international research.

Activities could include:

- assessment of science and technology needs associated with the management of emerging contaminants of concern;
- investigation of the impacts of MWWWE on environmental and human health;
- development of analytical techniques;
- assessment of levels of contaminants entering and exiting treatment plants;
- examine concentrations (diurnally, seasonally) in receiving waters;
- investigate the impacts of MWWWE on environmental and human health;
- examine emerging contaminants of concern and the science and technology needs associated with their management;
- strengthening linkages to leading jurisdictions;
- examine specific science and research needs for northern conditions;
- carry out public education.

## 7.2 Implementation Options

Two options are identified:

1. Establish a federal-provincial-territorial wastewater task group associated with CCME:
  - a. a separate CCME wastewater task group could be established to co ordinate the research and other wastewater management activities an independent task group that networks with other CCME groups (i.e., the Water Quality Task Group and Committee on Health and Environment) and coordinates a number of subcommittees which would encompasses MWWWE sector groups to fulfill the identified functions and address the key areas of work; or
  - b. the scope of the existing Water Quality Task Group (WQTG) is expanded to address municipal wastewater research issues and link to water quality guidelines for MWWWE.
  - c. the Committee on Health and Environment could explore undertaking some of this work
2. Explore possibilities to establish a wastewater task group separate from CCME either under:
  - d. NWRI is directed to undertake this work under Environment Canada
  - e. Led by an NGO such as the Canadian Water Network or Canadian Water and /or Wastewater Association a self-funded independent partnership of MWWWE sector groups including those groups indicated in option 2c, among others.

**The preferred option** – A CCME wastewater task group.

Affiliation with CCME provides a neutral national forum for all participants. A national forum will be more effective in developing national partnerships between governments and NGO's. Research co-ordination and information exchange would be ensured through a national task group with strategic linkages to Health Canada, Environment Canada and the WQTG. While the scope of work that would be required by the wastewater task group is beyond the purview of the WQTG, linkages to the WQTG for guideline development and other effluent research work would be a logical extension of water quality guideline work. Additionally, as the biosolids work commences, the need for a clearing-house for

information and the linkages required with wastewater would be more easily managed if both groups were housed under CCME.

## **Appendix 1 - ANALYSIS OF OPTIONS**

### **Options 1 – A CCME Group**

A wastewater task group under CCME, with strategic linkages to the WQTG and/or a health and environment committee, would ensure that provinces and municipalities receive the up-to-date information needed to improve effluent quality. Health Canada and Environment Canada could provide strong input into the research priorities. CCME would provide some base funding; however its primary role would be as coordinator/administrator and to bring/encourage leveraged funding of partners.

#### **Advantages**

- Strategic links between research (science, engineering,) and policy would be ensured.
- Ensure research co ordination and information exchange with Provinces, Federal, Territorial governments and WQTG and future biosolids initiative.
- Provide an opportunity to develop partnerships with MWW sector groups interested in MWW research, science, engineering and infrastructure development.
- Indicates a clear commitment to address emerging contaminants of concern and incorporate these into appropriate technology.
- Municipalities and MWW sector groups would participate as members of subcommittees.

#### **Disadvantages**

- CCME may not want to expand its role to research co-ordination and its associated costs.

### **Option 2 – Independent of CCME**

Through the CCME review of this topic, initial discussions with possible partners were undertaken. Members of the sector recommend that wastewater issues are significant enough to merit a focused wastewater table. An independent municipal wastewater body self funded with contributions from participants. The tasks of co-ordination, prioritization of research needs, information dissemination and leveraged funding is beyond the purview of any one of the partners and strategic links to policy are required. This option would require possible partners discussing how they might co-operate and would require a strong champion to lead this initiative. In this option, municipalities and other partners would be equal at the table rather than providing input through subcommittees. Options to explore include expansion of existing water and wastewater groups.

#### **Advantages**

- The focus of many of these groups is already water and wastewater. It may be easier to start this process as it is an expansion of existing roles.
- Municipalities and other wastewater groups may prefer to be involved at the table rather than through subgroups.

#### **Disadvantages**

- There is no framework, mandate or method to ensure linkages and strategic direction for municipal effluent management.
- No group has volunteered to lead and/or administer a new partnership.
- Major negotiation and co-ordination is required to get potential funding partners to the table. This may be difficult without some commitment to an administrative mechanism.
- With the public growing concern for contaminants in wastewater, a clear commitment for the co-ordination of MWW research with linkages to Environment and Health Canada is required, which may not exist with this option.
- An initial risk analysis to prioritize research may be difficult to fund collectively without commitment of all the funding partners to carry out this work. MWW science and engineering

research may not receive the priority funding which is required to assist in key infrastructure and public health decisions.

## References

- Alaee, M, and Wenning RJ. The Significance of Brominated Flame Retardants in the Environment: Current understanding, issues and challenges, *Chemosphere* Vol.46, (2002) pp.579-582
- Alaee, M, Arias, P, Sjödin, A & Å. Bergman. An Overview of Commercially used Brominated Flame Retardants, their Applications, their use Patterns in different countries/regions and possible modes of release, *Environment International*, Vol. 29 (2003) pp. 693-689
- APHA 2005. Standard Methods for the Examination of Water and Wastewater, 21<sup>st</sup> edition. American Public Health Association, Washington DC, 2005.
- Braghetta, AA.H., Gillogly, T., Brownawell, B and Benotti, M 2002, Removal of Pharmaceuticals and Endocrine Disrupting Compounds through Advanced Wastewater Treatment Technologies. Proc Water quality Technology Conference, American Water Works Association ( CD- ROM) Denver, CO
- CCME 2005. Review of the State of Knowledge of Municipal Effluent Science and Research: Review of Effluent Substances. PN 1356, June 2005. [www.ccme.ca/publications/list\\_publications.html](http://www.ccme.ca/publications/list_publications.html)
- Danish EPA (2005)
- Daughton CG and Ternes TA. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environmental Health Perspectives* V107 Suppl 6 (1999).
- de Witt, C. An Overview of Brominated Flame Retardants in the Environment, *Chemosphere* Vol. 46 (2002) pp. 583-624
- Environment Canada 2001. The State of Municipal Wastewater Effluents in Canada. Cat. No. En1-11/96E. [www.ec.gc.ca/soer-ree/english/SOER/MWWE.cfm](http://www.ec.gc.ca/soer-ree/english/SOER/MWWE.cfm)
- Hale, R., Alaee, M., Manchester-Neevig, J.B., Stapleton, H.M., & M.G. Ikonou. Polybrominated diphenyl flame retardants in the North American Environment, *Environment International*, Vol. 29 (2003), pp. 771-779
- Hites, R.A. Polybrominated diphenyl ethers in the Environment and in People: A Meta-Analysis of Concentrations, *Environmental Science & Technology*, Vol. 38. No. 4 (2004) pp 945-956
- Lee et al ( 2005)
- Legler, J. & A. Brouwer. Are brominated flame retardants endocrine disruptors? *Environment International*, Vol. 29 (2003) pp. 879-885
- Lishman L, Smyth SA, Sarafin K, Kleywegt S, Toito J, Peart T, Lee B, Servos M, Beland M, Seto P. Occurrence and reduction of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada. *Sci Total Environ* Vol 367 (2006) pp 544-558..
- Metcalf and Eddy. Wastewater engineering: treatment and reuse. McGraw Hill Inc, Boston, 2003.

Metcalfe CD, Miao XS, Koenig BG and Struger J. Distribution of acidic and neutral drugs in surface waters near sewage treatment plants in the lower great lakes, Canada. *Environ Tox and Chem*. Vol 22, 12 (2003) pp. 2881-2889

MOE, MISA, Thirty Seven Municipal Water Pollution Control Plants, Pilot Monitoring Study Volume 1, Interim Report, (December 1988)

Muir et al 2001

Nichols KM, Miles-Richardson SR, Snyder EM, Giesy JP. Effects of exposure to municipal wastewater in situ on the reproductive physiology of the fathead minnow (*PIMEPHALES PROMELAS*). *Environ Tox and Chem* Vol 18 (1998) pp. 2001-2012

NWRI 2006. Environment Canada Workshop on Pharmaceuticals and Personal Care Products in the Environment. March 2006, Burlington, ON.

OSPAR commission (2004). Musk Xylene and Other Musks. Available from [www.ospar.org/eng/html/welcome.html](http://www.ospar.org/eng/html/welcome.html).

Parrott JL and Blunt BR. Life-cycle exposure of fathead minnows (*Pimephalas promelas*) to an ethinylestradiol concentration below 1 ng/L reduces egg fertilization success and demasculinizes males. *Environ Toxicol* 2005, 20: 131-141.

Peck AM and Hornbuckle KC. Synthetic musk Fragrances in Lake Michigan. *Environ Sci and Tech* Vol 38, 2 (2004) pp.367-372

Purdum CE, Hardiman PA, Bye VJ, Eno NC, Tyler CR and Sumpter JP. Estrogenic effects of effluents from sewage treatment works. *Chem and Ecology*. Vol 8 (1993) pp. 275-285

Servos MR, Bennie DT, Burnison BK, Jurkovic A, Mcinnis R, Neheli T, Schnell A, Seto, P, Smyth SA, Ternes TA. Distribution of estrogens, 17 $\beta$ -estradiol and Estrone, in Canadian municipal wastewater treatment plants. *Sci Total Environ* 2006, 335: 155-170.

STOWA Exploratory Study for Wastewater Treatment Techniques and the European Water Framework Directive, Rapport 34, 2005, , [stowa@stowa.nl](mailto:stowa@stowa.nl) ISBN 90.5773.316.1

Swedish Environmental Protection Agency. Organic Contaminants in Biosolids, Report 5217 (February 2003) ISBN 91-620-5217-9

Ternes TA, Meienheimer M, McDowell D. Removal of pharmaceuticals during drinking water treatment. *Environ Sci Technol* Vol 36 (2002) pp.385

Tomy, G.T., Palace, V.P., Halldorson, T., Braekevelt, E., Danell, R., Wautier, K., Evans, B., Brinkworth, L. & A. Fisk. Bioaccumulation, biotransformation and biochemical effects of brominated diphenyl ethers in juvenile lake trout (*Salvelinus namaycush*), *Environmental Science & Technology*, Vol. 38 (2004a) pp 1496-1504

Watanabe, I. & S. Sakai. Environmental release and behaviour of brominated flame retardants, *Environment International*, Vol. 29 (2003) pp. 665-682

Water Environment Association of Ontario (WEAO, 2001, R. V. Anderson Associates Limited, M. D. Webber Environmental Consultant, Senes Consulting Limited, Fate and Significance of Selected Contaminants in Sewage Biosolids Applied to Agricultural Land Through Literature Review and Consultation with Stakeholder Groups, Final Report