



## **D1.2 BAT REVIEW**

Evaluation of Best Available Technologies for Water Management

Water-M project

Teollisuustaito Oy

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Attachment 2	Summary table of techniques to be considered in the determination of BAT for industrial waste water treatment plants
Attachment 3	Reported monitoring practice of industrial waste water treatment plants

## **Summary**

This report contains a review of two BAT reference documents: 1 CWW BREF regarding emissions to water from industrial installations 2) ROM report regarding the measurement of these emissions. In addition, the report source material include Finnish BAT guides for urban waste water treatment and waste water sludge treatment and reuse processes. The conclusions and recommendations of these BAT documents are compared with current industry practice and the requirements of Finnish legislation concerning urban water treatment plants.

**Effluent:** Monitoring and measurement of effluent, influent and process operation parameters is an important part of CWW BAT conclusions. CWW BAT emission limits are slightly stricter than those set in Finnish legislation for urban waste water treatment plants. Emission limits or monitoring frequency are, however, not stricter than the current practice at industrial plants. CWW BAT requires online monitoring of industrial effluent for pH and flow whereas the Finnish legislation only defines periodic laboratory analysis of chemical and microbiological parameters.

There are several acceptable analytical methods for effluent quality analysis. CWW BREF recommends EN standards, whereas Finnish legislation does not define a standard, but describes the method verbally. Unit processes for the treatment of urban waste water in Finland are similar to the recommended process techniques in CWW BAT and Finnish BAT guides.

**Drinking water:** Monitoring frequency and accuracy of analytical method for the follow-up of drinking water quality are precisely defined in Finnish legislation. The analytical method is not strictly defined. Standardized analytical methods, which could be applied for drinking water quality measurements, can be found in ROM Report ANNEX 2 and in CWW BREF document background data.

Online monitoring of drinking water quality parameters is not required in Finnish legislation. However, according to preliminary results from a survey (Water-M project), it is quite common to monitor pH and temperature with online instruments at Finnish plants.

CWW BREF includes descriptions of water purification unit processes, which are commonly used at drinking water purification plants as well. Thus the recommendations for instrumentation of these processes are applicable at drinking water plants as well.

**Waste water treatment sludge:** Waste water sludge quality has to be monitored periodically according to Finnish legislation. In case the sludge is intended to be used as soil improvement agent, legislation defines more strict requirements for the quality and quality monitoring as well as analytical methods.

Unit processes for the treatment of urban waste water sludge are similarly described in CWW BAT and Finnish BAT guides. Finnish BAT guides include description of biogas production process, the most important parameters for optimal operation of the process. The document mentions a number of impurities which are inhibiting for the process.

New impurities (POP compounds) have been identified as harmful impurities both in the sludge and treated waste water.

## 1. Introduction

This report is a review of best available techniques and associated monitoring requirements for drinking water purification, waste water treatment, and waste water treatment sludge processing. This report consists of two main parts:

1) Review of urban drinking water, waste water treatment, and waste water sludge treatment processes in Finland and the requirements for monitoring of emissions or process parameters

The first part is based on generally available information on typical unit processes and on Finnish legislation regarding monitoring of these processes. A comparison to European directives is included.

2) Review of BAT reference documents (BREF's, according to Industrial Emission Directive) for industrial waste water treatment and monitoring, and Finnish BAT guides for sludge treatment

Although urban water treatment facilities are not under IED requirements, valuable information on purification processes and their monitoring can be found in BAT reference documents. This is due to the similarity of certain unit processes at industrial and urban water treatment facilities. As consequence, similar methods for analysis may be applied as well. Two BREF documents are reviewed in this part:

- Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector FINAL DRAFT 2014 (abbreviation CWW)
- JRC Reference Report on Monitoring emissions from IED-installations FORMAL DRAFT 2013 (abbreviation ROM)

The BAT review concentrates on conclusions, recommendations, and background data regarding monitoring, analysis methods, and analysis frequency. A comparison to part 1 and current industry practices is included in this part.

This report is a part of TEKES founded WATER-M project, Work Package 1. The report has been written in cooperation with Measurepolis Development Ltd and Teollisuustaito Oy.

## 2. Objectives of the review

The objective of this review is to find out the requirements for industrial water treatment processes and the associated monitoring requirements based on BAT reference documents.

These requirements are compared to the current requirements for urban waste water treatment processes, and to the current industry practice.

When applicable, comparisons to current requirements for drinking water plants are also included.

Treatment and monitoring of sludge originating from urban waste water treatment plants is discussed as well.

## 3. Urban waste water treatment and drinking water plants

This paragraph describes current industrial processes for the purification of drinking water, for the treatment of urban waste water, and for the treatment of waste water plant sludge in Finland.

In addition, this paragraph includes information on the requirements effluent/drinking water/sludge quality monitoring, analytical methods, and analysis frequency based on legislation:

- Certain requirements for drinking water quality are defined in Finnish legislation, which follows European Union Directives.
- Similarly, the quality of treated waste water/effluent or the performance of waste water treatment plants is defined in the legislation.
- Finnish legislation sets requirements for monitoring of the waste water sludge quality. Additional requirements are set for the sludge in case it is treated for further utilization.

## 3.1. Drinking water treatment processes

Treatment of drinking water (tap water) generally consists of solids removal, adjustment of chemical quality, and removal of microbiological contaminants. Source water quality defines the concept of the water treatment process. Surface water will require several purification steps than ground water.

#### 3.1.1. Treatment of surface water

Main impurities in Finnish surface water include solid material, organic compounds (humic acids, humines, biopolymers), microbiological contaminants, and traces of certain metal ions.

A block diagram including typical unit processes, waste streams, and process chemicals is described in Figure 1. (Source 1).

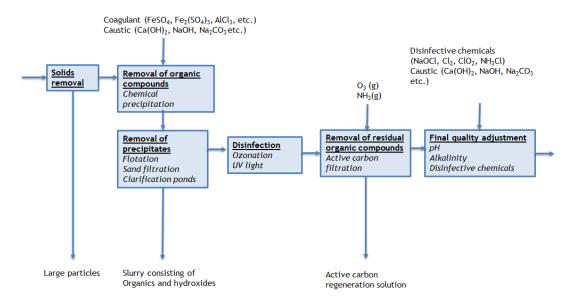


Figure 1 Block diagram of a typical surface water purification process.

One example of a drinking water purification process is the Helsinki Region Environmental Services HSY, which produces drinking water for the capital area in Finland. The main water source is Lake Päijänne. The purification process consists of the following stages (Source 2).

### 1. Removal of organic compounds

- addition of coagulant (ferric sulphate, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>): coagulants collect organic molecules to aggregates; ferric sulphate also lowers the pH of the water
- gentle mixing
- two stage solids removal: flotation / clarification ponds and sand filters

### 2. pH control

• addition of lime water (Ca(OH)<sub>2</sub> in water?), which raises the pH of the solution

#### 3. Disinfection

ozonation

#### 4. pH control

• with carbon dioxide (CO<sub>2</sub>)

### 5. Removal of organic compounds

• two stage active carbon filtration

#### 6. Disinfection

• UV light

### 7. Final quality adjustment

- addition of chlorine
- pH adjustment with lime water and carbon dioxide

### 3.1.2. Treatment of ground water

Unlike surface water, ground water does typically not contain any large solid particles, organic compounds, nor microbiological contaminants. pH control is typically required due to the low pH values. The chemical quality of the Finnish ground water varies depending on the location: ground water may contain traces of chlorides and fluorides, arsenic, iron, manganese, or radioactive compounds.

A block diagram including typical unit processes, waste streams and chemicals is described in Figure 2. In many cases, ground water is not treated at all, and it is also common not to include disinfection under normal operation of the plant. (Sources: 1 and 3)

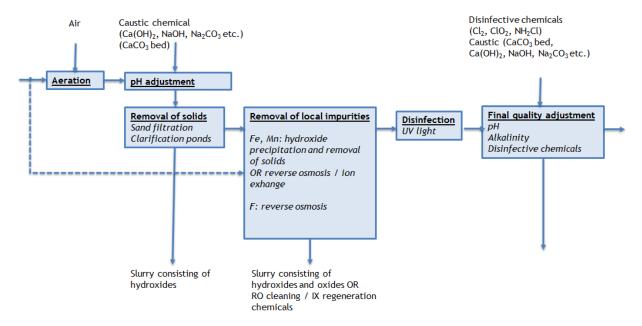


Figure 2 Block diagram of typical unit process at ground water treatment plant. The concept of the plant depends on local water quality; typically only one or some of these unit processes are needed.

One example of a ground water purification plant comes from Tuusula region in Finland. At this region, there are two main types of ground water purification plants (Source: 4).

#### Type 1 for water containing iron and manganese

- 1. Aeration to oxidize Fe and Mn
- 2. Removal of Fe and Mn precipitates with sand filters
- 3. Disinfection with UV light

#### Type 2 for water which requires adjustment of pH and alkalinity:

- 1. Adjustment of alkalinity and pH in a limestone bed
- 2. Disinfection with UV light

# 3.2. Requirements for drinking water quality and monitoring

Finnish legislation sets limits for both chemical composition and microbial quality of the water, which is supplied to the water network. The legislation gives recommendations of the technical quality (risk of corrosion / precipitation). In addition, certain requirements are set for analytical methods and monitoring of the water quality.

## 3.2.1. Water quality

The quality of the drinking water shall be according to the requirements set in Act 442/2014 by Ministry of Social Affairs and Health (Source 5).

The Act defines both microbiological and chemical quality of the water. Maximum concentrations for chemical contaminants are summarized in Table 1. Table 2 includes additional recommendations for drinking water quality.

For small drinking water plants the quality is defined in Act 401/2001 by Ministry of Social Affairs (Source 19). The requirements are similar to Act 442/2014.

Table 1 Maximum concentrations of chemical compounds in drinking water.

Compound	Maximum	Unit	Note
	concentration		
Acryl amide	0.10	μg/l	
Antimony	5.0	μg/l	
Arsenic	10	μg/l	
Benzene	1.0	μg/l	
	0.010	μg/l	
Boron	1.0	mg/l	
Bromate	10	μg/l	
Cadmium	5.0	μg/l	
Chromium	50	μg/l	
Copper	2.0	mg/l	Sampling at end user consumption point
Cyanides	50	μg/l	
1,2-dichloroethane	3.0	μg/l	
Epichlorohydrin	0.10	μg/l	
Fluoride	1.5	mg/l	
Lead	10	μg/l	
Mercury	1.0	μg/l	
Nickel	20	μg/l	
Nitrate	50	mg/l	Maximum nitrite concentration at water
			purification plant outlet 0,1 mg/l. (Nitrate
			concentration / 50 + nitrite concentration / 3)
			must be under value 1

Nitrate -N	11.0	mg/l	
Nitrite	0.50	mg/l	Maximum nitrite concentration at water
			purification plant outlet 0,1 mg/l. (Nitrate
			concentration / 50 + nitrite concentration / 3)
			must be under value 1
Nitrite - N	0.15	mg/l	
Pesticides	0.10	μg/l	
Pesticides, total	0.50	μg/l	
Polysyclic aromatic hydrocarbons	0.10	μg/l	
Selenium	10	μg/l	
Tetrachloroethene and	10	μg/l	
trichloroethene			
Trihalomethanes, total	100	μg/l	
Vinyl choride	0.50	μg/l	
Chlorofenyles, total	10	μg/l	
Uranium	30	μg/l	

For small drinking water plants the quality is defined in Act 401/2001 by Ministry of Social Affairs (Source 19). Recommendations are similar to Act 442/2014 with few exceptions:

- Ammonia-N max 0.4 mg/l
- Chloride max 100 mg/l
- KMnO4 number max 20 mg/l

Table 2 Recommendations for drinking water quality.

Compound	Maximum	Unit	Note
	concentration		
Aluminium	200	μg/l	
Ammonia	0.50	mg/l	
Ammonia-N	0.50	mg/l	
Oxidativiness (COD <sub>Mn</sub> -O <sub>2</sub> )	5.0	mg/l	
Chloride	250	mg/l	To reduce corrosion of water supply system
Manganese	50	μg/l	
Sodium	200	mg/l	
Iron	200	μg/l	
Sulphate	250	mg/l	To reduce corrosion of water supply system
Conductivity	2 500	μS/cm	To reduce corrosion of water supply system
рН	6.5–9.5		To reduce corrosion of water supply system
Tritium	100	Bq/l	
Radioactivity	0.10	mSv/year	

## 3.2.2. Analytical methods

Drinking water quality monitoring is a requirement for every water supply facility. The analytical method has not been limited to a certain technology, but the selected method must fulfil requirements of ISO standard 5725 for the trueness, precision, and limit of detection. In addition, the selected method must fulfil the requirements of Table 3.

Table 3 Requirements for analytical methods.

	Trueness, % of the limit	Precision, % of the limit	Limit of detection, % of the
			limit
Antimony	25	25	25
Arsenic	10	10	10
Benzene	25	25	25
	25	25	25
Boron	10	10	10
Bromate	25	25	25
Cadmium	10	10	10
Chromium	10	10	10
Copper	10	10	10
Cyanides	10	10	10
1,2-dichloroethane	25	25	10
Fluoride	10	10	10
Lead	10	10	10
Mercury	20	10	10
Nickel	10	10	10
Nitrate	10	10	10
Nitrite	10	10	10
Pesticides	25	25	25
Polysyclic aromatic	25	25	25
hydrocarbons			
Selenium	10	10	10
Tetrachloroethene	25	25	10
Trichloroethene	25	25	10

## 3.2.3. Frequency

Sampling frequency requirements depend on the capacity of the water supply facility. According to Finnish legislation and European directives, the facilities shall have sufficient instrumentation and sampling system to minimize the identified contamination risks.

Drinking water quality is monitored by authorities, and the monitoring requirements are divided into continuous and periodic monitoring (see Table 4). Continuous monitoring includes analysis of the following compounds:

- Microbiological quality
- Appearance
- pH
- Conductivity
- Iron
- Manganese
- Nitrite
- Aluminium
- Ammonia

Periodic monitoring includes analysis of the microbiological impurities as well as chemical quality as defined in paragraph 3.2.1.

Table 4 Number of samples in continuous and periodic monitoring by authorities.

Quantity of the supplied or treated	Number of sample per year	
water (m³/day)	Continuous monitoring	Periodic monitoring
10–50	1	1 every 2 years
51–100	4	1
101–1 000	5	1
1001–2000	7	2
2001–3 000	10	2
3001–4 000	13	2
4001–5 000	16	3
5001–6 000	19	3
6001–7 000	22	3
7001–8 000	25	4
8001–9 000	28	4
9001–10 000	31	4
over 10 000–100 000	31 + 3 additional samples for	4 + 1 additional samples for
	evevery additional 1 000 m³/day	evevery additional 10 000
		m <sup>3</sup> /day
over 100 000	304 + additional samples for	10 + 1 additional samples for
	evevery additional 1 000 m³/day	evevery additional 25 000
		m³/day

## 3.3. Waste water treatment processes

Treatment of urban waste water generally consists of three stages: solids removal, biological and chemical purification, and final treatment. A summary of unit processes for each stage is presented in Figure 3.

Ministry of Environmental Affairs has published a guide concerning the best available techniques of waste water and sludge treatment in Finland (Source 6). This publication includes information of the current and recommended waste water treatment processes:

Basically all Finnish waste water treatment facilities use a biological process for the removal of suspended organic material and nitrogen. Nitrogen removal is based on two type of microbes, first of which oxidize ammonium and nitrite (reaction equations 1 and 2), and second of which reduce nitrate to nitrogen gas (reaction equation 3). Process conditions have to be carefully controlled to obtain good purification results – e.g. oxidation and pH control as well as temperature control in phase 1 are very important parameters.

$$NH_4^+ + 1.5O_2$$
  $\Leftrightarrow NO_2^- + 2H^+ + H_2O$  (AOB, ammonium oxidizing bacteria)[1]  
 $NO_2^- + 0.5O_2$   $\Leftrightarrow NO_3^- (NOB, nitrite-oxidizing bacteria)$  [2]  
 $2NO_3^- + 2H^+$   $\Leftrightarrow O_2 + N_2 + 2H_2O$  [3]

Phosphorous is removed by chemical precipitation by addition of e.g. ferric sulphate. There is an alternative method for phosphorous removal, which is based on microbiology. This alternative could allow utilization of phosphorous from the solid waste.

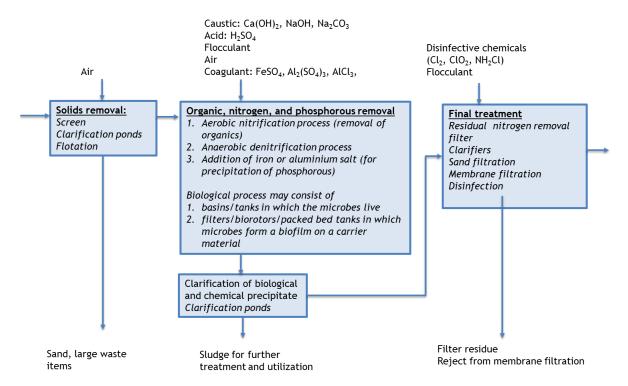


Figure 3 Unit processes, chemicals and waste streams of an urban water treatment plant.

The Act 888/2006 concerning treatment of urban waste waters in Finland defines general requirements of the waste water treatment plant structure (Source 7):

- Waste waters shall be treated in a biological process or in a process, which results in the same purification
- Phosphorous shall be removed according to the Act (see paragraph 3.4)
- Need of nitrogen removal shall be defined in the environmental permit. Nitrogen shall be removed in case this improves the condition of the receiving water.
- Nitrogen removal shall fulfil the requirements of the Act (see paragraph 3.4)
- Sludge which is accumulated or formed in the water treatment plant shall not be released to receiving waters.

## 3.4. Requirements for waste water quality and monitoring

Urban waste water treatment plants are required to apply for an environmental permit. The environmental permit will define the required water quality, monitoring, and analytical methods. Both national legislation and European Council directive set certain requirements for the purification result and related monitoring and analysis.

## 3.4.1. Water quality and performance of water treatment plants

Tables 5 and 6 summarize the requirements for of the biological treatment and nutrient removal efficiency set by Act 888/2006 and corresponding Urban Waste Water Directive 91/271/ETY by European Council (Sources 7 and 8). Concentration and efficiency may be alternative, meaning that either the concentration or the efficiency should be achieved.

Many urban water treatment plants receive industrial waste waters. These waters contain other contaminants such as heavy metals. Heavy metal removal processes or limits are not yet defined in the legislation – instead, the environmental permit will set the requirements.

Table 5 Comparison of the requirements for biological treatment in Finnish legislation and in the corresponding EY Directive. PE= population equivalent

Finnish legislation Act 888/2006		Directive 91/271/ETY		
Parameter	Maximum concentration	Minimum removal efficiency	Maximum concentration	Minimum removal efficiency
Biological oxygen demand (BHK <sub>7</sub> )	30 mg/l O <sub>2</sub>	70 %	25 mg/l O <sub>2</sub>	70-90 % (40 % for PE > 10 000)
Chemical oxygen demand	125 mg/l O₂	75 %	125 mg/l O <sub>2</sub>	75 %
Solid concentration	35 mg/l	90 %	35 mg/l O <sub>2</sub> for PE > 10 000 60 mg/l O <sub>2</sub> for 2000 < PE < 10 000	90 % for PE > 10 000 70 % for 2000 < PE < 10 000

Table 6 Comparison of the requirements for removal of nutrients in Finnish legislation and in the corresponding EY Directive. PE= population equivalent

		Finnish legislation	n Act 888/2006	Directive 91/271/ETY	
Parameter	PE	Maximum concentration	Minimum removal efficiency	Maximum concentration	Minimum removal efficiency
Phosphorous	<2000	3 mg/l	80 %		80 %
	2 000-100 000	2 mg/l		2 mg/l (PE	
				10 000 -	
				100 000)	
	>100 000	1 mg/l		1 mg/l	
Nitrogen	10 000-100 000	15 mg/l	70 %	15 mg/l	70-80 %
	>100 000	10 mg/l		10 mg/l	

In Finland, nitrogen removal is mostly not required for temperatures below 12 °C.

## 3.4.2. Analytical methods and sampling

Table 7 summarizes the requirements of analytical methods. Act 888/2006 and corresponding Urban Waste Water Directive 91/271/ETY by European Council have similar requirements.

Table 7 Analytical method according to Finnish legislation.

Compound	Analytical method, Finnish legislation	Additional information
Biological oxygen demand (BHK <sub>7</sub> )	Homogenized, unfiltered, unclarified sample.  Dissolved oxygen analysis before and after 7 days incubation at 20°C ± 1° C in a dark room.	Can be replaced by TOC or TOD, if the relation between the
	Denitrification chemical.	methods can be defined
Chemical oxygen	Homogenized, unfiltered, unclarified sample.	Can be replaced by other method,
demand	Kalium dichromate as oxidant.	if the relation between the
Solids	Filtration of a representative sample with 0,45 micrometer membrane. Drying at 105°C and weighing.	methods can be defined
Phosphorus	Molecular absorption spectrophotometry	
Nitrogen	Molecular absorption spectrophotometry	

The Act 888/2006 requires the structure of the water treatment plant to be constructed in a manner which allows representative sampling of incoming water, of the water in the process, and of discharged water.

## 3.4.3. Frequency

Monitoring frequency is dependent on the population equivalent. The required number of samples is defined in Table 8.

Table 8 Number of samples according to Finnish legislation and European Directive.

PE	Number of samples, Finnish legislation	Number of samples, European Directive
<499	2	
500-1999	4	
2 000 - 9 999	12 first year, 4 the following years if no deviation from the limits during first year	12 first year, 4 the following years if no deviation from the limits during first year
10 000 - 49 999	12	12
> 50 000	24	24

## 3.5. Treatment and recycling processes waste water sludge

## 3.5.1. Treatment processes for waste water treatment sludge

The Finnish BAT regarding best available techniques of waste water and sludge treatment in Finland (Source 6) describes current sludge treatment practices and gives BAT recommendations for the treatment of the sludge. BAT recommendations are discussed further in paragraph 4.3.

Typical sludge treatment process contains a dewatering stage, which can be based on gravity separation (thickening), mechanical separation (filters, centrifuges) or heat (evaporation of water). The last alternative is naturally very energy intensive, and it is always preceded by mechanical or gravity separation stage.

It is common to enhance thickening and mechanical separation process by addition of flocculants. In conditioning, oxidizing chemicals, such as hydrogen peroxide or sulphuric acid, may be added to hydrolyze microbes and to further reduce the moisture of the sludge. Thermal hydrolysis is one alternative technique for condition, but may become expensive due to high energy consumption.

Stabilization of the sludge means removal of microbiological contaminants, i.e. disinfection to a certain level, which is necessary for further utilization of the sludge. Stabilization methods include anaerobic digestion, aerobic digestion, or pH adjustment to a high level with lime milk.

These unit processes are illustrated in Figure 4 (Source 6).

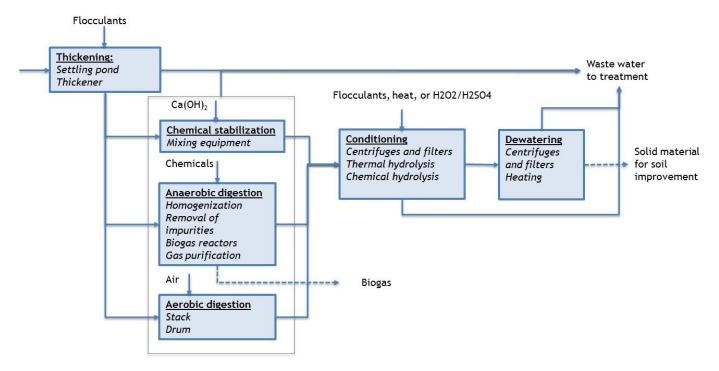


Figure 4 Unit processes, waste streams and products, and chemicals for the treatment of waste water sludge.

## 3.5.2. Further treatment and utilization processes for waste water treatment sludge

According to the Finnish national strategy of waste management, the target is to reuse 100 % of the sludge which is formed in urban waste water treatment facilities by 2016 (Source 12). There are two main uses for the waste:

#### 1) Utilization as soil improvement agents

Quality of the soil improvement agent / fertilizer product is quite strictly defined, and will in all cases require removal of microbiological contaminants. Disinfection processes as well as dewatering processes are commonly required as pretreatment process (see previous paragraph).

Requirements for quality, monitoring, analytical methods, and frequency of the analysis are defined in paragraph 3.7.

2) Production of biogas and use of the gas as energy source

A typical biogas production process consists of (Source 13, Finnish BAT guide regarding biogas production):

- Pretreatment of the raw material: particle size reduction, removal of harmful compounds, dewatering
- Dry or wet anaerobic digestion process for the production of biogas: typically agitated tank containing a number of microbes
- Purification of the produced biogas: removal of e.g. hydrogen sulphide, siloxans, and moisture
- Treatment and reuse of the solid residue: dewatering and or drying of the residue, aerobioc digestion, and disinfection of the residue, if required
- Treatment of gases from different steps of the process
- Treatment of the formed process waters according to composition

# 3.6. Requirements for waste water treatment sludge quality and monitoring

## 3.6.1. Monitoring of the sludge quality

Urban waste water treatment plants are required to monitor the quality of solid waste independent of the final use or storage of the solids. The Council of Sate Act concerning wastes 179/2012 requires analysis of the following parameters (Source 14):

- Heavy metals and other harmful compounds (at least cadmium, chromium, copper, nickel, lead, zinc, mercury)
- Total nitrogen
- Total phosphorous

## 3.6.2. Analytical methods

The analytical method must be an EN or ISO standardized method. (Source 14)

## 3.6.3. Frequency

The frequency of the analysis depends on the population equivalent. The minimum frequency has been defined in Table 9. (Source 14)

Table 9 Minimum frequency for the analysis of solid waste from urban waste water treatment plants.

	Minimum frequency of the analysis, times per year		
Population equivalent	Year 1 Following years		
>100 000	12	4	
40 000 – 100 000	6	3	
5000 – 40 000	4	2	
200 – 5000	1	1	
<200	1	every other year	

# 3.7. Requirements for fertilizer product quality and monitoring

## 3.7.1. Monitoring of the product quality

There are several types of impurities, which may limit the reuse of solid wastes as fertilizers, for example:

- 1) microbiological contaminants
- 2) heavy metals
- 3) POP compounds

The <u>microbiological quality</u> of the fertilized soil must be according to the Act by Ministry of Agriculture and Forestry regarding fertilizer products 24/11 (Source 15).

The maximum values for <u>heavy metal concentrations</u> in the soil, which has been fertilized with products originating from urban waste water treatment plant sludge, are defined in the Act by Ministry of Agriculture and Forestry regarding fertilizer products 12/12 (Source 16):

- Mercury 0.2 mg/kg solids
- Cadmium 0.5 mg/kg solids
- Chromium 200 mg/kg solids
- Copper 100 mg/kg solids
- Lead 60 mg/kg solids
- Nickel 60 mg/kg solids
- Zinc 150 mg/kg solids
- pH of the soil must be above 5.8.

Fertilizer product is allowed to contain max 50 mg cadmium per kilogram of phosphorous, in case the phosphorous content of the product is above 2.2 % (Source 16). The allowable amount of arsenic depends on the end use of the nutrient, being 25-40 mg per kilogram of dry fertilizer product (Source 15).

Additionally, there are limits for the amount of above listed compounds per hectare of soil. (Source 16). There are also certain requirements for the nutrient concentrations are set in Act 24/11 (Source 15).

In addition, the so-called <u>POP compounds</u> (persistent organic pollutants) may limit use of urban waste water treatment plant sludge. According to a report by Finnish Environment Institute, these compounds may be toxic or carcinogenic, and they may cause disturbance to hormonal systems. The report found out that both the untreated sludge at urban waste water treatment plant and the treated waste water contains a range of POP compounds. (Source 17)

## 3.7.2. Analytical methods

The analytical methods for the analysis of <u>heavy metal concentrations and pH</u> of the soil, which has been fertilized with products originating from urban waste water treatment plant sludge, are defined in the Act by Ministry of Agriculture and Forestry regarding fertilizer products 12/12 (Source 16):

- cadmium, chromium, copper, nickel, lead, zinc according to SFS-EN 13346
- mercury according to prCEN/TS 16175-1 and prCEN/TS 16175
- pH according to SFS 3021

## 3.7.3. Frequency and sampling plan

The Act 12/12 gives instructions on the sampling plan and frequency of soil quality analysis:

- The samples should be taken prior to first fertilizing time in case the soil is suspected to contain heavy metals
- If over-the-limit values can be expected, the analysis should be repeated every five years
- One sample shall consists of at least seven sub-samples
- In case the section has a size of over 0.5 hectares, one sample per every 5 hectares shall be taken
- In case the section has a size of max 0.5 hectares, one sample per every 2 hectares shall be taken

## 3.8. Requirements for biogas raw material quality and monitoring

Recommendations for biogas raw material quality and process monitoring are described in Paragraph 4.3.4.

# 4. BREF documentation review - from the perspective of urban waste water and drinking water industry

BAT reference document (BREF) conclusions apply for facilities under the Industrial Emission Directive (IED, 2010/75/EU). According to the IED, BAT conclusions should be the guideline for national legislation concerning industrial facilities and their environmental effects. This means, for example, that the BAT emission limits should be considered as guidelines for environmental permits.

There are several BREF documents, which specify the requirements for different industries. Each document generally gives information on a specific industrial/agricultural sector in the EU, on the techniques and processes used in this sector, current emission and consumption levels, techniques to consider in the determination of the best available techniques (BAT) and emerging techniques. (Source 9)

Urban water treatment or water supply facilities are not under the IED. Nevertheless, emissions from urban water treatment facilities represent a significant part of emissions to water in total – and this is similar for both nutrients and heavy metals. This can be noticed from Figures 5 (nitrogen) and 6 (cadmium).

There are several common impurities and water treatment processes for industrial and urban water treatment facilities – thus similar technologies for measurement, analysis and monitoring could be utilized at both type of facilities.

This paragraph discusses two BREF documents from the perspective of urban waste water treatment, drinking water treatment, and waste water sludge treatment:

- Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (abbreviation CWW) (Source 10)
- 2. JRC Reference Report on Monitoring emissions from IED-installations (abbreviation ROM) (Source 11)

Both BREF documents are at Final Draft status meaning that the contents of the documents may still change slightly before final adaptation.

This part of the report also includes comparisons between the practices and requirements for urban and for industrial water treatment plants.

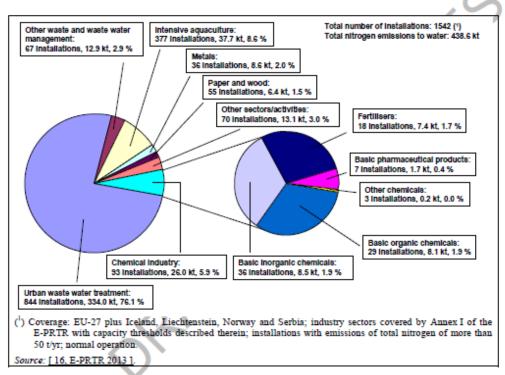


Figure 1.5: Emissions of total nitrogen to water by industry sector/activity in Europe in 2010

Figure 5 Share of nitrogen emissions to water, classified by industry sectors. Share of Urban waste water treatment plants is 76.1 %.

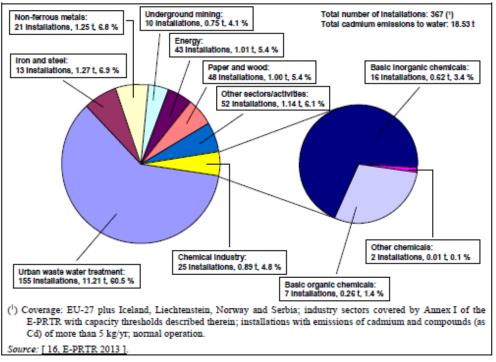


Figure 1.7: Emissions of cadmium to water by industry sector/activity in Europe in 2010

Figure 6 Share of cadmium emissions to water, classified by industry sectors. Share of Urban waste water treatment plants is 60.1 %.

## 4.1. CWW BREF and ROM report: Waste water treatment

### 4.1.1. BAT AEL's - Emission levels

The CWW BREF conclusions regarding discharge water quality are summarized in Table 10, which includes the so called BAT – AEL's (BAT associated emission levels).

BAT AEL's are somewhat stricter when compared to the requirements of urban waste water plants (more details in Tables 5-6):

- COD < 125 mg/l
- TSS < 35-60 mg/l
- TP < 1-3 mg/l
- TN < 10-15 mg/l

Both urban water treatment plant effluent limits and industrial water treatment plant effluent limits are dependent on the quantity of the emission, however, the defining unit is different (population equivalent versus emission compound mass per year). BAT AEL's cover a larger number of contaminants, including heavy metals and AOX.

Table 10 Summary of emission limits for waste water quality.

		BAT - AEL	
Parameter	Abbreviation	(yearly average)	Conditions
Total organic carbon	TOC	<10-33 mg/l	Emission exceeds 3.3 t/a
Chemical oxygen demand	COD	<30-100 mg/l	Emission exceeds 10 t/a
Total suspended solids	TSS	5.0-35 mg/l	Emission exceeds 3.5 t/a
Total nitrogen	TN	5.0-25 mg/l	Emission exceeds 2.5 t/a
Total inorganic nitrogen	Ninorg	5.0-20 mg/l	Emission exceeds 2.0 t/a
Total phosphorous	TP	0.50-3 mg/l	Emission exceeds 300 kg/a
Absorbable organically bound halogens	AOX	0.20-1.0 mg/l	Emission exceeds 100 kg/a
Chromium	Cr	5.0-25 μg/l	Emission exceeds 2.5 kg/a
Copper	Cu	5.0-50 μg/l	Emission exceeds 5 kg/a
Nickel	Ni	5.0-50 μg/l	Emission exceeds 5 kg/a
Zinc	Zn	20-300 μg/l	Emission exceeds 30 kg/a

## 4.1.2. BAT conclusions concerning monitoring frequency and analytical methods

<u>CWW BREF conclusion 3</u> states that 'BAT is to monitor key process parameters relevant for emissions to water (e.g. influent to pretreatment and final treatment) as identified by the inventory of waste water streams (see BAT 2), including continuous monitoring of waste water flow, pH and temperature'.

This, in combination with BAT 1 and BAT 2 gives a very strong recommendation for arranging reliable instrumentation and monitoring for the plant.

#### **BAT 1:**

V. checking performance and taking corrective action, paying particular attention to:

- a) monitoring and measurement (see also the Reference Report on Monitoring of emissions to Air and Water from IED-installations ROM);
- b) corrective and preventive action;
- c) maintenance of records;
- d) independent (where practicable) internal or external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;

#### **BAT 2:**

II. information, as comprehensive as is reasonably possible, about the characteristics of the waste water streams, such as:

- a) average values and variability of flow, pH, temperature, and conductivity;
- b) average concentration and load values of relevant pollutants/parameters and their variability (e.g. COD/TOC, nitrogen species, phosphorous, metals, salts, specific organic compounds);
- c) data on bioeliminability (e.g. BOD, BOD/COD ratio, Zahn-Wellens test, biological inhibition potential (e.g. nitrification));

When compared to Attachment 3, which includes a summary table of the reported, currently used analyses, it can be seen that most industrial plants monitor continuously both the influent and the effluent quality.

<u>CWW BAT conclusion 4</u> includes detailed instructions for the analytical method and for the frequency for the analysis. This conclusion is summarized in Table 11 on the next page.

BAT conclusion 4 does not specify one single standardized method for analysis of heavy metals (chromium, copper, nickel, zinc, lead), nitrogen, phosphorous, or COD. If EN standards are not available, BAT conclusion 4 recommends to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

Two standardized methods are mentioned in ROM report ANNEX 2 for analysis of heavy metals (chromium, copper, nickel, zinc, lead):

- EN ISO 11885:2009 (ICP-OES)
- EN ISO 17294-2:2004 (ICP-MS)

For the analysis of phosphorous, ROM report mentions three standardized methods:

- EN ISO 10695:2000 (GC)
- EN ISO 15681-1:2004 (FIA)
- EN ISO 15681-2:2004 (CFA)

For the analysis of nitrogen, ROM report mentions five standardized methods:

- EN 25663:1993 (Kjeldahl-L)
- EN ISO 11905-1:1998 (Digestion with oxidative digestion with peroxodisulphate)
- EN ISO 13395:1996 (FIA and CFA)
- EN ISO 14402:1999 (FIA and CFA)
- EN ISO 6878:2004 (Ammonium molybdate spectrometric method)

For the analysis of COD, ROM report mentions two standardized methods:

- ISO 15705:2002 (1. Photometric detection at 600 nm, 2. titrimetric)
- ISO 6060:1989 (Reduction of oxidisable substances with potassium dichromate in strong sulphuric acid; titration)

The limits of detection of above mentioned techniques as well as description of the other standardized analytical methods can be found in ANNEX 2 of ROM report.

When compared to Attachment 3, which includes a summary table of the reported, currently used analyses, it can be concluded that the current monitoring frequency is mostly according to BAT, and in some cases even more frequent than the required level.

When compared to Table 7 concerning the recommended analytical methods for urban waste water plants, some differences can be noticed.

Table 11 CWW BREF conclusions regarding the frequency and method of analysis.

Substance/parameter		Standard(s)	Minimum monitoring frequency $\binom{1}{2}\binom{2}{2}$
Total organic	carbon (TOC) ( <sup>3</sup> )	EN 1484	Daily
Chemical oxyg	gen demand (COD) (³)	No EN standard available	Daily
Total suspende	ed solids (TSS)	EN 872	Daily
Total nitrogen	(TN) ( <sup>†</sup> )	EN 12260	Daily
Total inorganic	c nitrogen (N <sub>inorg</sub> ) ( <sup>4</sup> )	Various EN standards available	Daily
Total phospho	rous (TP)	Various EN standards available	Daily
Adsorbable or	ganically bound halogens (AOX)	EN ISO 9562	Monthly
Metals	Cr Cu Ni Zn	Various EN standards available	Monthly Monthly Monthly Monthly Monthly Monthly
	Other metals, if relevant		Monthly
	Fish eggs (Danio rerio)	EN ISO 15088	
	Daphnia (Daphnia magna Straus)	EN ISO 6341	
		EN ISO 11348-1,	To be decided
	Luminescence bacteria (Vibrio fischeri)	EN ISO 11348-2 or	based on a risk
Toxicity (5)		EN ISO 11348-3	assessment, after
	Duckweed (Lemna minor)	EN ISO 20079	an initial
		EN ISO 8692,	characterisation
	Algae	EN ISO 10253 or	
		EN ISO 10710	

- (1) Monitoring frequencies may be adapted if the data series clearly demonstrate a sufficient stability.
- (\*) The sampling point is located where the emission leaves the installation.
- Either TOC or COD is monitored. TOC monitoring is the preferred option, because it does not rely on the use of very toxic compounds.
- (4) Either TN or N<sub>inorg</sub> is monitored.
- (5) An appropriate combination of these methods can be used.

[These BAT conclusions are based on information given in Sections 3.2.2.1 and 3.2.2.2.]

The Finnish BAT guide (Source 6) regarding best available techniques of waste water and sludge treatment in Finland gives several recommendations related to measurements, instrumentation and monitoring:

### 1. Operational performance of the water treatment plant

- Incoming water quality and its variations are monitored
- Process control instruments are maintained and calibrated regularly
- The automation level of the plant should allow operation without manpower
- The automation system should be duplicated at least for most critical parts and at the largest plants
- Process automation must be equipped with UPS equipment
- There must be spare ICT equipment for process control system
- By pass of any operation should result in alarm

#### 2. Monitoring of the plant

- Incoming water sampling point should be selected so that it includes all incoming water streams but excludes internal circulation waters
- · Sampling points must allow representative sampling
- Observations must be written in the operation diary
- By pass of any operation at the plant or at the water network must be measured or estimated from e.g. pump operation data

When compared to previously described CWW BAT conclusions, similar requirements are mentioned in both documents. Many of the Finnish BAT guide recommendations are similar to those of ROM report (see paragraph 4.4).

## 4.1.3. Limits of detection of frequently used analytical methods

CWW document (Paragraph 4.2 Analysis of key parameters) describes commonly used analytical methods and their limits of detection / quantification for certain parameters. These parameters include all associated BAT AEL's but also other parameters. The limits of detection have been described in Table 12.

When comparing the reported LOD, LOQ, and the limits of application of the standardized methods to the BAT AEL's and to the requirements of urban waste water treatment plants, it can be concluded that the standardized methods are sufficiently accurate for the purpose. Solution matrix may cause the limit of detection to be higher than what is stated in the standard. Also the reported LOD and LOQ values are mostly accurate enough.

Additional information on standardized analytical methods can be found in ROM report ANNEX 2.

Table 12 Limits of detection for a number of parameters in waste water.

Parameter	Abbreviation	Reported LOD, mg/l	Reported LOQ, mg/l	Additional data (Green font = CWW BAT Conclusion)
Chemical oxygen demand	COD	Belgium 7	Germany 15	ISO 6060 ISO 15705 COD measurements are affected by high CI content
Total organic carbon	TOC	Belgium 10		EN 1484 (LIMIT OF APPLICATION 0.3) ISO 8245
Biochemical oxygen demand	BOD5	Belgium 3 Spain 8		EN 1899-2 (LIMIT OF APPLICATION 3) ISO 5815-2 Analysis result depends on

				the local laboratory conditions Solids removal affect the result
Total suspended solids	TSS	Belgium 2 Spain 2		EN 872 (LIMIT OF APPLICATION 2) ISO 11923 (LIMIT OF APPLICATION 2)
Adsorbable organically bound halogens	AOX	Belgium 20 μg/l	Germany 15 μg/l	EN ISO 9562
Metals	Abbreviation	Reported LOD, μg/l	Reported LOQ, μg/I	Limits of detection are affected by solution matrix
Cadmium	Cd		Belgium 0.01	EN ISO 17294–1 EN ISO 11885 (LIMIT OF APPLICATION 0.2) EN ISO 17294–1 (LIMIT OF APPLICATION 0.1)
Chromium	Cr		Belgium 10 Germany 0.1	EN ISO 17294–1 EN ISO 11885 (LIMIT OF APPLICATION 2) EN ISO 17294–1 (LIMIT OF APPLICATION 1)
Chromium	Cr VI		Belgium 10	ISO 11083 EN ISO 23913
Copper	Cu		Belgium 25 France 5 Germany 0.1	EN ISO 17294–1 EN ISO 11885 (LOQ 2) EN ISO 17294–1 (LOD 1)
Mercury	Hg		Belgium 0.25 France 0.5 Germany 0.01 Germany 0.1	EN ISO 17852 EN 1483 EN ISO 17852 EN 1483
Nickel	Ni		Belgium and France 10 Germany 1	EN ISO 17294–1 EN ISO 11885 (LIMIT OF APPLICATION 2) EN ISO 17294–1 (LIMIT OF APPLICATION 1)
Lead	Pb		Belgium 25 France 5	

			Germany 0.1	EN ISO 17294–1 (EN ISO 11885 (LIMIT OF APPLICATION 5) EN ISO 17294–1 (LIMIT OF APPLICATION 1)
Zinc	Zn		Belgium 25 France 10 Germany 1	EN ISO 11885 EN ISO 17294–1 (LIMIT OF APPLICATION 1)
Nutrients	Abbreviation	Reported LOD, mg/l	Reported LOQ, mg/l	
Total nitrogen	TN		Belgium 2 Spain 10 Germany 1	EN 12260 (LIMIT OF APPLICATION 0.5) EN ISO 11905–1 (LIMIT OF APPLICATION 0.02) ISO 29441 (LIMIT OF APPLICATION 0.2-2)
Inorganic nitrogen	Ninorg		Belgium 2 Germany 1	
Nitrites and nitrates	NO2-N:		Belgium 0.1 Belgium 0.5	EN ISO 10304–1 (LIMIT OF APPLICATION 0.05) EN ISO 10304–1 (LIMIT OF APPLICATION 0.1)
Ammonia	NH3	0.05 mg/l based on.	Belgium 0.2 Germany 0.05	EN ISO 11732 (LIMIT OF APPLICATION 0.1)
Phosphorous	P	standards for the determination of TP exist: specifies methods for the determination of different types of		EN ISO 6878 (2004) EN ISO 15681–1 and –2 (LIMIT OF APPLICATION 0.1) EN ISO 11885 (LIMIT OF APPLICATION 0.009)
Phenols			Belgium 0.2 μg/l	There are phenol specific standards for several compounds.
Anions	Abbreviation	Reported LOD, mg/l	Reported LIMIT OF APPLICATION, mg/I	Additional data
Chloride	Cl		Belgium 25	ISO 9297 (LIMIT OF APPLICATION 5) EN ISO 10304–1 (LIMIT OF

			APPLICATION 0.1)
Sulphate	SO <sub>4</sub> <sup>2-</sup>	Belgium 25	
			EN ISO 10304–1 (LIMIT OF
			APPLICATION 0.1)
			ISO 22743 (LIMIT OF
			APPLICATION 30)
Cyanides		Belgium 0.01	Total cyanide
			concentration is typically
			monitored
			Several standards
Toxicity*			

 $<sup>\</sup>ensuremath{^{*}}\textsc{Toxicity}$  analysis are not discussed in this document.

## 4.1.4. Recommended purification technologies and their performance

CWW BAT does not strictly define one certain purification technique for the contaminants. Instead, <u>BAT</u> <u>conclusions 10 and 12</u> require the use of 'an appropriate combination of final waste water treatment techniques'. The recommendation is to include primary treatment (solids removal), secondary treatment (removal of soluble impurities) and final treatment (removal of residual impurities and solids).

The corresponding, recommended process technologies are summarized in Table 13. These techniques are so-called end-of-pipe solutions. For industrial plants, it is recommended to use process integrated techniques, which reduce the formation of waste water and increase the recycling rate of waste water.

Table 13 Summary of the recommended techniques for certain impurities.

Parameter	Recommended process
Total organic carbon	Biological treatment: activated sludge process or membrane bioreactor
Chemical oxygen demand	Biological treatment: activated sludge process or membrane bioreactor
Total suspended solids	Primary treatment:
	Physical separation, e.g. screens, sieves, grit separators, grease separators or primary settlement tanks
	Final treatment:
	Coagulation and flocculation, sedimentation, filtration, flotation
Total nitrogen	Biological nitrification – denitrification process
Total phosphorous	Chemical precipitation
Adsorbable organically bound halogens	
Chromium	Neutralisation and solid separation
Copper	Neutralisation and solid separation
Nickel	Neutralisation and solid separation
Zinc	Neutralisation and solid separation

A short description of each waste water process technology is provided in Attachment 1. CWW BREF also describes the achieved purification results of a number of purification processes – these descriptions are included in Table 16, Paragraph 4.2.2.

The recommended techniques given in Finnish BAT guide (Source 6) for urban waste water treatment are summarized in Table 14. When compared to Table 13, it can be concluded that the techniques are in line with CWW BAT conclusions.

Table 14 Main recommendations of the Finnish BAT document concerning urban waste water treatment plants.

Unit process	BAT recommendations
Solids removal	<ul> <li>Every plant should have a mechanical screen or similar equipment</li> <li>Large plants should have parallel solid removal equipment</li> <li>Middle size and large plants should include sand separation and possibility to remove sludge from the water surface in the pre-treatment process</li> </ul>
Organic, nitrogen and phosphorous removal	<ul> <li>The process should include a biological part</li> <li>The process should have appropriate sections</li> <li>Oxygen concentration should be adjusted automatically</li> <li>There should be at least 1 spare air compressor</li> <li>Middle size and large plants should have at least two parallel biological treatment processes</li> <li>Addition of phosphorous precipitation chemical must optimized and the location has to be chosen correctly</li> </ul>
Final treatment	<ul> <li>The plant may include final treatment section with the following parts:</li> <li>Phosphorous and solid residue removal with sand filtration, flotation and clarification</li> <li>Nitrogen residue removal with denitrifying filter or anoxic biorotors</li> <li>Disinfection with e.g. UV treatment, membrane treatment, or harmless chemicals</li> </ul>

The performance of FInnish urban water treatment processes described process concepts is described in the Finnish BAT guide.

- **Organic material** is efficiently removed at Finnish water treatment plants, BHK7 (ATU) levels commonly reach values of 5-10 mg/l.
- **Solid removal** mostly reach values under 10 mg/l. Solid removal is enhanced by sufficient settling time and correct flocculant dosage. Final treatment, i.e. filters, lower the concentration as well.
- Typical **phosphorous** levels are 0.3-0.5 mg/l. Phosphorous removal is enhanced by larger dosage of chemicals and efficient solids removal process as phosphorous is in solid form after the treatment.
- Total nitrogen concentration after the treatment process has been 35-65 mg/l. Nitrogen removal process is temperature dependent, and at temperatures under 12 °C operation of the process is sometimes not required. In some cases, addition of carbon source may improve the microbiological treatment process. Use of filters in the final treatment part of the process further increases nitrogen removal efficiency.

<u>CWW BAT conclusion 8</u> includes a guideline to 'segregate uncontaminated waste water streams from other waste water streams that require treatment'. If applied at urban waste water treatment plants, this conclusion would lead e.g. to the separation of rain and storm waters from household waste water. This guideline also requires monitoring of the incoming water quality, which is also required for urban waste water plants.

## 4.1.5. Recommended measurements for treatment processes

The BREF document includes information regarding each process technology and its monitoring – which analysis / instrumentation are important for the operation of each type of process. These instructions have been listed to Table 15. Solid-liquid separation techniques are similarly described in Paragraph 4.3.

Table 15 Recommended monitoring and analysis for the above described processes.

Process/Equipment	Instrumentation	Analysis
Chemical precipitation	pH measurement and control	
	Careful dosage and measurement of all	
	chemicals (flowrate)	
Crystallization	Water flow to keep the fluidised bed	The concentration of the metal
	working	in influent and in the effluent
	Careful dosage and measurement of all	
	chemicals (flowrate)	
	pH measurement and control	
Chemical oxidation	pH measurement and control	Oxidant concentration in the
	redox monitoring	effluent
	Ozone concentration monitoring	AOX content in the effluent if
	Oxygen content in the gas phase	chlorine chemicals are used
Wet oxidation with H2O2	Influent and reactor pH measurement	COD and H2O2 concentration in
	Catalyst feed control	the effluent
	Influent flow rate	
	Reaction temperature and pressure	
	Oxygen content in the gas phase	
Wet air oxidation	Pressure, temperature, oxygen content	
	at all stages of the process	
Reduction (e.g. sodium	Caustic / acid addition control based on	
sulphide precipitation)	pH measurement	
	Reducing agent control based on redox	
	measurement	
Chemical hydrolysis	pH measurement and control	Hydrolysis chemical in the
Shermout Hydrorysis	Pressure, temperature	effluent
	Residence time control and	
	measurement (flow meters)	
Nanofiltration and RO	Pressure difference and flow across the	
	membrane should be	
	monitored continuously	

Adsorption	TOC / conductivity measurement in effluent	The input and output monitored according to the compounds in question
Ion exchange	pH measurement and control Pressure measurement and control Conductivity measurement and control	Influent and effluent quality
Biological removal of heavy metals and sulphate	Influent waste water stream for pH and COD content Influent be free of substances that can destroy the sulphur-active bacteria or inhibit their growth	Heavy metals, sulphate, COD
Biological nutrient and organic removal	See attachment 3	

# 4.2. CWW BREF and ROM report: Drinking water purification and supply

The CWW BAT conclusions concerning water quality can naturally not be compared with those set for drinking water quality. However, information of the analytical methods can be exploited, as well as background information, which has been given for certain unit processes and their monitoring. In addition, some general process design guidelines are given in the CWW BREF, and these guidelines apply for basically all kind of water treatment plants.

## 4.2.1. Water quality, monitoring, and analytical methods compared to current industry practice

CWW BREF as well as ROM report recommend to use EN standardized methods for the analysis of water quality. ISO is acceptable, if EN standards are not available. The Finnish legislation refers to ISO standard 5725 (Accuracy of Measurement Methods and Results Package) but does not specify one certain analytical method for the measurements.

According to preliminary results of Water-M survey for Finnish water supply plants (Source 18), the practice at drinking water plants is to continuously monitor certain parameters. Most common continuously monitored parameters include:

- Source water pH, temperature, conductivity, turbidity, oxygen (questions 6 and 8)
- Process conditions at water purification plant: pH, turbidity, temperature (question 15)
- Water quality in the network: pH, conductivity, turbidity (question 29)

Online monitoring of incoming water flow and quality is not as common as for waste water treatment plants. One reason for this is most likely the small capacity of some of the drinking water plants, and also the good quality of ground water.

In addition, drinking water supply plants control water quality by periodic sampling and analysis. Examples of the periodically analysed parameters include microbiological quality, heavy metals, pesticides, chlorides and sulphates (questions 5, 6, 7).

Similar parameters are mentioned for waste water purification processes Table 12 (Paragraph 4.1.5).

Table 12 also includes analytical methods and their limits of detection – and when comparing these LOD's to the requirements of drinking water quality (Tables 1 and 3), it can be concluded that these standardized methods are sufficiently accurate for the application. Additional data on different analytical methods for water quality parameters can be found in ROM Report ANNEX 2.

# 4.2.2. Potential purification techniques for urban drinking water plants

The CWW BREF describes a large number of unit processes, which could be used as an alternative for the recommended waste water purification processes. Some of these unit processes can be applied, and are similar to those used at drinking water purification plants.

The applicability of the unit processes for removal of certain impurity compounds, which are harmful in drinking water, are presented in Table 16. When comparing the contents of this table to Figures 1 (surface water treatment) and 2 (ground water treatment), similar unit processes can be found.

Attachment 2 includes a more comprehensive summary a table of techniques, which could be considered for both waste water treatment and for drinking water purification.

Table 16 The maximum concentrations of certain impurities in drinking water, and potentially suitable techniques for the removal of these metals according to CWW BREF.

Compound	Maximum concentration in drinking water	Unit	Purification techniques in CWW BREF	Removal efficiency in CWW BREF
Acryl amide	0,10	μg/l		
Antimony	5,0	μg/l	Heavy metals in general: Precipitation (neutralization + coagulation), Nanofiltration and Reverse Osmosis, Ion exchange	
Arsenic	10	μg/l	Sodium sulphide precipitation Heavy metals in general: Precipitation (neutralization + coagulation), Nanofiltration and Reverse Osmosis	
Benzene	1,0	μg/l	Adsorption Oxidation techniques	70-93 %
	0,010	μg/l		
Boron	1,0	mg/l		
Bromate	10	μg/l		
Cadmium	5,0	μg/l	Sodium sulphide precipitation Precipitation (neutralization + coagulation) Nanofiltration	<15 μg/l
Chromium	50	μg/l	Precipitation (neutralization + coagulation) Heavy metals in general: Nanofiltration and Reverse Osmosis	<50 μg/l
Copper	2,0	mg/l	Precipitation (neutralization + coagulation) Heavy metals in general: Nanofiltration and Reverse Osmosis, Ion exhange	<50 μg/l
Cyanides	50	μg/l	Chlorine oxidation and other chemical oxidation techniques Chemical hydrolysis	
1,2-dichloroethane	3,0	μg/l	Organics in general: different oxidation	

			techniques, adsorption	
Epichlorohydrin	0,10	μg/l	Organics in general: different oxidation	
			techniques, adsorption	
Fluoride	1,5	mg/l	Adsorption	
			Crystallization	
			Precipitation	
Lead	10	μg/l	Precipitation (neutralization + coagulation)	<25 μg/l
			Heavy metals in general: Nanofiltration and	
			Reverse Osmosis, Ion exhange	
Mercury	1,0	μg/l	Precipitation (neutralization + coagulation)	<5 μg/l
			Nanofiltration	>90%
			Adsorbtion	80 %
Nickel	20	μg/l	Precipitation (neutralization + coagulation)	<50 μg/l
			Crystallisation	1 mg/l
			Heavy metals in general: Nanofiltration and	
			Reverse Osmosis, Ion exhange	
Nitrate	50	mg/l	Activated sludge process	
			Membrane bioreactor	6.9 mg/l
Nitrate -N	11,0	mg/l	Activated sludge process	
			Membrane bioreactor	
Nitrite	0,50	mg/l	Activated sludge process	
			Membrane bioreactor	0 mg/l
Nitrite - N	0,15	mg/l	Activated sludge process	
			Membrane bioreactor	
Pesticides	0,10	μg/l	H2O2 oxidation	>99 %
			Adsorption	97-99.9 %
			Chemical hydrolysis (e.g. H2SO4)	
Pesticides, total	0,50	μg/l	H2O2 oxidation	>99 %
			Chemical hydrolysis (e.g. H2SO4)	
Polysyclic aromatic	0,10	μg/l	Organics in general: different oxidation	
hydrocarbons			techniques, adsorption	
Selenium	10	μg/l		
Tetrachloroethene	10	μg/l	Organics in general: different oxidation	
and			techniques, adsorption	
trichloroethene				
Trihalomethanes,	100	μg/l	Organics in general: different oxidation	
total			techniques, adsorption	
Vinyl choride	0,50	μg/l	Organics in general: different oxidation	
			techniques, adsorption	
Chlorofenyles, total	10	μg/l	Organics in general: different oxidation	
			techniques, adsorption	
Uranium	30	μg/l	Heavy metals in general: Precipitation	
			(neutralization + coagulation), Nanofiltration	
			and Reverse Osmosis	

Aluminum	200	μg/l	Crystallisation	20 mg/l
Ammonia	0,50	mg/l	Activated sludge process	
			Membrane bioreactor	0 mg/l
Ammonia-N	0,50	mg/l	Activated sludge process	
			Membrane bioreactor	
Oxidativines	5,0	mg/l		
Chloride	250	mg/l	Reverse osmosis	
Manganese	50	μg/l		
Sodium	200	mg/l		
Iron	200	μg/l	Heavy metals in general: Precipitation	
			(neutralization + coagulation), Nanofiltration	
			and Reverse Osmosis, Ion exchange	
Sulphate	250	mg/l	Reverse osmosis, nanofiltration	
			Biological reduction	
Conductivity	2 500	μS/cm		
рН	6,5–9,5		Neutralization	
Tritium	100	Bq/l		
Radioactivity	0,10	mSv/		
		year		

#### 4.2.3. Process design and instrumentation guidelines

The CWW BREF describes good practices related to the <u>design</u> of a water treatment plant. These recommendations ca be applied for both drinking water purification and supply plants as well as for waste water plants. Recommendations concerning analysis and instrumentation include:

- Water quality and expected emission limits (or water quality requirements) should be basis for the selection of correct purification process
- Water quality combined with capacity is the basis for mass balance calculations mass balance calculations are basis for consumption figures, equipment sizes, and costs of the plant

The CWW BREF recommends to design a reliable <u>process control and automation</u> system. Design of a process control system requires comprehensive online instrumentation and understanding of the process. The process system can further be developed by using statistical methods for analyses of disturbance situations.

According to the CWW BREF, instrumentation should be utilized to prevent and to reduce **exceptional releases** to the environment. Examples of such instrumentation:

- Level instrumentation for tanks and tank cars to reduce risk of overflow
- Quality (conductivity, pH) monitoring of e.g. cooling water, abnormal values indicate leakage

Processes should be equipped with sufficient instrumentation for ensuring all <u>operating requirements</u>. Typical instrument and analysis needs for unit processes have been described in Table 15 and in Attachment 3.

# 4.3. CWW BREF and Finnish BAT documents: Sludge treatment and reuse

This paragraph discusses the monitoring of sludge treatment and reuse processes according to CWW BREF and Finnish BAT documentation.

It should be noted that a separate BREF document regarding waste industries exists. The review of the waste industry BREF is not in the scope of this report.

#### 4.3.1. Recommended solid / liquid separation technologies

CWW <u>BAT conclusion 13</u> regarding sludge management is to ensure that 'waste is prevented, prepared for reuse, recycled or otherwise recovered'. This is in line with the Finnish national waste strategy.

In order to reduce the volume of waste water sludge requiring further treatment or disposal, and to reduce its potential environmental impact, <u>CWW BREF conclusion 14</u> states that 'BAT is to use one or a combination of the techniques given below' (Table 17).

Table 17 is almost identical with the recommendations given in the Finnish BAT document regarding urban waste water treatment plants (Source 6). These techniques are commonly used at current waste water plants as well.

If designed according to CWW BREF, the utilization of nutrients in the sludge should be increased as much as possible.

Table 17 Techniques to be considered for sludge management according to CWW BREF.

	Technique	Description	Applicability
a	Conditioning	Chemical conditioning (i.e. adding coagulants and/or flocculants) or thermal conditioning (i.e. heating) to improve the conditions during sludge thickening/dewatering.	Not applicable to inorganic sludges. The necessity for conditioning depends on the sludge properties and on the thickening/dewatering equipment used.
ь	Thickening/dewatering	Thickening can be carried out by sedimentation, centrifugation, flotation, gravity belts, or rotary drums. Dewatering can be carried out by belt filter presses or plate filter presses.	Generally applicable.
o	Stabilisation	Sludge stabilisation includes chemical treatment, thermal treatment, aerobic digestion, or anaerobic digestion.	Not applicable to inorganic sludges. Not applicable for short- term handling before final treatment.
d	Drying	Sludge is dried by direct or indirect contact with a heat source.	Not applicable to cases where waste heat is not available or cannot be used.

[This BAT conclusion is based on information given in Sections 3.4.2.2 and 3.4.2.3.]

The Finnish BAT guide for the treatment of sludge from urban waste water plants includes the following recommendations:

- Every facility shall include a thickening process or similar equipment
- Middle size and large plants shall have at least two parallel thickening lines
- Middle size and large plants shall have at least two parallel mechanical drying lines
- There must be sufficient storage capacity for the slurry for exceptional situations
- The dewatering capacity should be based on equipment capacity, not large storage volumes
- Sludge ca be alternatively transported to another location for treatment
- Sludge treatment equipment should be installed indoors or covered to reduce odour emissions

# 4.3.2. Recommended measurements for solid-liquid separation processes

CWW BREF recommends a number of online or laboratory analysis for the optimal operation of solid-liquid separation processes. These recommendations are described in Table 18 (Source 10).

In addition, efficient operation of aerobic and anaerobic digestion requires good control of residence time (flow or mass flow meters) and temperature (Source 20).

Table 18 Instrumentation and analysis associated with sludge treatment techniques.

Process/Equipment	Instrumentation	Analysis
Coagulation	Automated dosage of the coagulant: flow	
	meters	
	pH measurement and control	
Flocculation	Automated dosage of the flocculant: flow	
	meters	
	pH measurement and control	
Thickening / Sedimentation		Sludge input turbidity / visual
		monitoring
		Effluent / overflow quality:
		suspended solids, settleable
		solids, or turbidity
Thickening / Flotation		Effluent quality: turbidity,
		COD/TOD and TSS
		Analysis of the foam
		compounds
Thickening / Filters	Pressure drop over the filter	Sludge input quality / visual
		monitoring to prevent large
		particles from entering the
		equipment
		Filtrate quality: turbidity
Stabilization / Chemical	Lime chemical dosage equipment	
	pH measurement and control	
	Automated dosage of the	
	flocculant/coagulant: flow meters	
Stabilization / Aerobic	Ensurance of oxygen feed by e.g. flow /	
digestion	pressure meters	
	Automated dosage of the	
	flocculant/coagulant: flow meters	
Stabilization / Anaerobic	Automated dosage of the	
digestion	flocculant/coagulant: flow meters	
Drying		

#### 4.3.3. Recommended biogas production technologies

The best available technique for biogas production process has been described in the Finnish BAT guide regarding biogas production (Source 13). The requirements are relatively flexible, including e.g. the following conclusions:

- BAT is to choose a suitable process for the intended raw material
- BAT is to know the quality of the raw material and waste streams
- BAT is to treat odorous gases as soon as possible and to minimize emissions to water and air
- BAT is to be prepared to treat both wet and dry raw materials
- BAT is to reuse the solid residue

#### 4.3.4. Recommended measurements for biogas processes

The Finnish BAT guide regarding biogas production (Source 13) recognises a number of important parameters, which should be monitored in order to enhance process performance:

- pH of the process solution
- Temperature of the process solution
- Organic load in the feed material: increase of VFA (Volatile Fatty Acids) may indicated too high load
- Moisture of the feed material

Some parameters may enhance or inhibit the process depending on the concentration (Table 19). Inhibiting compounds may also include disinfection and cleaning agents, antibiotics and heavy metals.

Table 19 Influence of certain parameters for the biogas production process

Parameter	Concentration, mg/I	Influence
Na, K, Ca, Mg ions	75 -400	Stimulating
	1000 – 5 500	Slightly inhibiting
	3 000-12 000	Strongly inhibiting
Ammonia	150	Inhibiting

Best available technique is to be prepared to measure certain parameters (organic load, pH, alkalinity, volatile fatty acids), if process disturbances occur.

# 4.4. Review of ROM - Definitions and guidelines of water measurements

ROM document summarizes the commonly available information on the monitoring of emissions to water (and air). The document has been written before the publication of CWW draft, which can be noticed in the definitions of water pollutants.

As the ROM document is not a BAT Reference document, it does not give BAT conclusions. The document focuses on monitoring of emissions, and does not cover process monitoring. These aspects are covered in industry specific BREF documents, when considered relevant, in this case meaning the CWW BREF.

This paragraph summarizes the general measurement related part and water emission related part of ROM document, and compares the contents to the previously discussed applications.

The report also includes information of the standardized analytical method and its range of application for a large number of parameters. These standards can be found in ROM report ANNEX 2, and have been partly discussed in previous parts of this review (paragraphs 4.1-4.2).

#### 4.4.1. **Quality**

According to ROM document, data quality is the most critical aspect on monitoring. Reliability of the measurement is required in numerous applications, which include:

- prevention of accidents
- process optimization, e.g. chemical dosage
- performance of a certain technique / comparison of techniques
- basis for deciding the allowable limits for emissions

One approach to the quality of the measurement is standardization of analytical methods and procedures related to the analysis. Standards also address the qualification of laboratory personnel, sampling personnel, and maintenance personnel.

#### 4.4.2. Uncertainty

Uncertainty of the measurement is affected by several factors:

- qualification of personnel and human factors;
- laboratory facilities and environmental conditions;
- test and calibration methods and method validation;
- equipment and software used;
- measurement traceability;
- sampling plan, procedures and process;
- transportation and handling of test and calibration items

There are different methods and standardized calculation procedures, which can be used for defining the uncertainty for different types of emissions.

According to the Industrial Emission Directive, continuous measurements should always be reported with the associated uncertainty value.

#### 4.4.3. Limit of detection

The ROM document sites the European Commission Directive regarding technical specifications for chemical analysis and monitoring of water status (2009/90/EC) for the definition of limit of detection:

'the output signal or concentration value above which it can be affirmed, with a stated level of confidence that a sample is different from a blank sample containing no determinant of interest.'

According to ROM document, the limit of detection should in general be less than 10 % of the emission limit value. The Finnish legislation requirements for drinking water quality analysis vary between 10-25 % (See Table 3). The Directive 2009/09/EC sets the limit to 30 %.

According to the same directive, 'limit of quantification' means a stated multiple of the limit of detection at a concentration of the determinant that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, exc.

#### 4.4.4. Analysis regime

The BAT AEL values apply for normal operating conditions. When selecting and calibrating the analysis method, also other than normal operating conditions should be considered. Other than normal operating conditions include scheduled plant shutdowns, maintenance breaks, exceptional rain seasons, accidents etc. In addition, the range of values which can be considered as normal, is highly process dependent: e.g. batch process parameter values will naturally vary significantly even when working properly.

For continuous measurements, the calibration range should cover both normal and other than normal conditions.

Per periodic measurements, the variations in operating conditions should be taken into account in the sampling plan.

### 4.4.5. Direct and indirect water analysis

Analysis methods can be divided to direct and indirect analysis.

The direct analysis means definition of a certain compound and its specific concentration. For water emissions, e.g. metal ion concentrations, specific organic compound, and e.g. ammonia concentration are direct analysis.

Indirect analysis means definition of either a qualitative or a quantitative parameter, which itself does not indicate the concentration of a specific compound. For water emissions, e.g. TOC, COD and total N analysis are so called quantitative surrogate parameters. Qualitative surrogate analysis for water emissions could include e.g. conductivity, when the parameter to be followed is actually the total metal and counter ion concentration.

Toxicity tests are always indirect analysis. There are several standards which include guidelines for different toxicity tests, and toxicity tests have also been defined as BAT AEL's for industrial waste water treatment plants (see Table 13). For urban waste water treatment plants such parameters have not been defined in the legislation.

Whole effluent assessment considers, in addition to toxicity, also the persistency (or biodegradability) and bioaccumulation potential of the effluent.

## 4.4.6. Continuous and discontinuous measurements of water quality and flow

For **continuous (on-line) measurements,** the measurement devices are directly positioned in the effluent flow. Measurement value is continuous. It is common to use a 1-hour average value.

**Online, continuous sampling** mean that the sample is taken at a set frequency and analysed automatically. Continuous sampling can be based on manual, regular samples and analysis in the laboratory. Measurement value is discontinuous.

**Periodic sampling** means sampling with different intervals. The interval can be based on e.g. variations in water flow, variations in the continuously analysed parameters. Measurement value is discontinuous.

#### **Online water measurements**

The most common online measurements include pH, conductivity, temperature, and flow. The following quality parameters can be analysed with fairly standard online instruments:

- direct electrochemical measurement of e.g. pH, dissolved oxygen, conductivity;
- specific ion electrodes for the measurement of e.g. nitrate and ammonia;
- anodic stripping voltametry for the measurement of e.g. metals;
- colorimetric (spectrometry) for the measurement of e.g. ammonia, phosphate, total phosphorus, iron;
- measurement of TOC;
- measurement of turbidity;

As the monitoring of total emissions requires reliable data on the flows, online flowmeters are basically always place at least to effluent pipelines. There are many types of water flowmeters, e.g.

- open channel flowmeters,
- pipe flow meters, for partly filled pipes

- pipe flow meters, for pipes which are completely filled (most common type, electromagnetic measurement)

Online instruments require regular maintenance and calibration, which is many times based on parallel laboratory analysis.

According to ROM document, the following factors should be considered when selecting the type of sampling:

- the need to control highly variable and/or excessive waste water emissions;
- the instability of the parameter during sampling, transportation and storage (e.g. volatile compounds);
- the expected impact of the waste water emission on the environment, taking local conditions into account;
- the need to monitor and control the performance of the waste water treatment plant and,
- possibly, to promptly react according to the generated data (e.g. analyse chemical parameters);
- the availability and reliability of measurement equipment, depending on the industrial
- sector and on the waste water emission;
- the specific requirements of the industrial sector, and/or the specific circumstances of the
- installation;
- the costs of continuous measurements (economic feasibility).

Online instruments of quality parameters have not been set an on obligatory requirement for water treatment plants. CWW BREF does very strongly recommend continuous and online monitoring. In addition, some parameters such as pH, temperature and conductivity are likely to be monitored with online instruments in as an industry practice.

Continuous measurement of at least effluent flow is most likely a standard for all plants, as it is needed for calculating the load of each impurity parameter. Continuous measurement of influent and chemical flows are strongly recommended in the CWW BREF document. (Conclusion 2)

#### Continuous sampling and periodic sampling

For continuous manual sampling and for periodic sampling, a detailed sampling plan is necessary. The contents of a sampling plan is described in Paragraph 4.4.7

Periodic sampling is further divided into

- composite sampling, where the samples are taken periodically, during a specific time period (one day), and combined into one composite sample before analysis; and
- spot (or grab) sampling, where discrete samples are taken and analysed separately.

According to CWW BREF as well as the urban water treatment plant legislation, practically all quality parameters should be analysed according to a continuous sampling plan (See BAT Table 13 and tables 4 and 9 concerning the frequency of samples for urban drinking water plants and water treatment plants).

### 4.4.7. Sampling plan

The sampling plan describes the measurement objectives, parameters, handling of the samples, analytical methods as well as documentation. The plan should include description of

- measurement objective including specification of the water pollutants and sum parameters;
- collection of data to clearly describe normal and other than normal operating conditions
- collection of data related to the waste water flow and other parameters, if relevant, such as temperature, pH;
- volume of waste water that the sampling intends to represent;
- sampling method, including sampling equipment;
- necessary pretreatment and preservation of samples;
- sampling location, and sampling point;
- handling and storage of samples;
- sampling frequency;
- analytical parameters that have to be analysed in the samples at the laboratory;
- data treatment;
- quality assurance measures;
- documentation and reporting

Sampling plan should include also exceptional situations, as described in paragraph 4.4.4.

### 4.4.8. Sampling point, handling and storage of the sample

The location of the sampling point(s) should ensure that the sample is representative of the effluent discharge. It is recommended to accurately describe and mark the sampling point on the process flowsheet, if possible supplemented with photographs to facilitate identification of the exact location.

The ROM document gives very detailed instructions of the location of sampling point, which are not included here (Paragraph 4.3.2.5.4).

Handling and storage should be well instructed to preserve the pollutants until the sample has been analysed.

## 5. Key findings and ideas for future work

#### Findings of this review:

- Monitoring and measurement of effluent, influent and process operation parameters is an important part of CWW BAT conclusions
- CWW BAT emission limits are slightly stricter than those set in Finnish legislation for urban waste water treatment plants
- CWW BAT requires online monitoring of industrial effluent for pH and flow whereas the Finnish legislation only defines periodic laboratory analysis of chemical and microbiological parameters
- There are several acceptable analytical methods for effluent quality analysis. CWW BREF recommends EN standards, whereas Finnish legislation does not define a standard, but describes the method verbally.
- Unit processes for the treatment of urban waste water in Finland are similar to the recommended process techniques in CWW BAT and Finnish BAT guides
- Monitoring frequency and accuracy of analytical method of drinking water quality are precisely defined in Finnish legislation
- The analytical method is not strictly defined. Additional information of standardized analytical methods, which are suitable for drinking water quality parameters can be found in ROM Report ANNEX 2.
- Online monitoring of water quality parameters is not required. According to a preliminary results from a survey, it is quite common to monitor pH and temperature with online instruments.
- CWW BREF includes descriptions of water purification unit processes, which are commonly used at drinking water purification plants as well. Thus the recommendations for instrumentation of these processes are applicable at drinking water plants as well.
- Waste water sludge quality has to be monitored periodically according to Finnish legislation
- The legislation defines more strict requirements for the quality and quality monitoring as well as analytical methods, in case the sludge is intended to be used as soil improvement agent
- New impurities (POP compounds) have been identified as harmful impurities both in the sludge and treated waste water
- Unit processes for the treatment of urban waste water sludge are similarly described in CWW BAT and Finnish BAT guides. In addition, Finnish BAT guides include information of recycling processes of the waste sludge and compounds which may cause problems in recycling processes.

#### Ideas for future work:

- Follow-up of BAT reference document preparation and the application of BAT conclusions in environmental permits
- Review of standardized analytical online monitoring techniques for water pollutants
- Review of BAT reference document for waste industries
- More detailed analysis of sludge treatment processes and their instrumentation needs
- More detailed review of analytical methods for POP compounds

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### 7. List of abbreviations

AEL Associated emission limit

BAT Best available technique

BREF BAT reference document

CFA Continuous flow analysis

CWW Common Waste Water and Waste Gas Treatment/Management Systems in

the Chemical Sector

FIA Flow injection analyzer

GC Gas chromatography

ICP Inductively coupled plasma

IED Industrial Emissions Directive

LOD Limit of detection

LOQ Limit of quantification

(ICP-)MS Mass spectrometry

(ICP-)OES Optical emission spectrometry

ROM JRC Reference Report on Monitoring emissions from IED-installations

Technique	Description
Activated sludge process	The biological oxidation of dissolved organic substances with oxygen using the metabolism of microorganisms. In the presence of dissolved oxygen – injected as air or pure oxygen – the organic components are mineralised into carbon dioxide, water or other metabolites and biomass (i.e. the activated sludge). The microorganisms are maintained in suspension in the waste water and the whole mixture is mechanically aerated. The activated sludge mixture is sent to a separation facility from which the sludge is recycled to the aeration tank.
Biological nitrification/denitrification	A two-step process that is typically incorporated into biological waste water treatment plants. The first step is the aerobic nitrification where microorganisms oxidise ammonium (NH <sub>4</sub> ) to the intermediate nitrite (NO <sub>2</sub> ), which is then further oxidised to nitrate (NO <sub>3</sub> ). The second step is the anoxic denitrification where microorganisms chemically reduce nitrate to nitrogen gas.
Chemical precipitation	The conversion of dissolved pollutants into an insoluble compound by adding chemical precipitants. The solid precipitates formed are subsequently separated by sedimentation, air flotation, or filtration. If necessary, this may be followed by microfiltration or ultrafiltration. Typical chemicals used for metal precipitation are lime, dolomite, sodium hydroxide, sodium carbonate, sodium sulphide and poly-organosulphides. Calcium salts (other than lime) are used to precipitate sulphate or fluoride. Multivalent metal ions (e.g. calcium, aluminium, iron) are used for phosphorous precipitation.
Coagulation and flocculation	Coagulation and flocculation are used to separate suspended solids from waste water and are often carried out in successive steps. Coagulation is carried out by adding coagulants with charges opposite to those of the suspended solids. Flocculation is carried out by adding polymers, so that collisions of microfloc particles cause them to bond to produce larger flocs.
Equalisation	Balancing of flows and pollutant loads at the inlet of the final waste water treatment by using central tanks. Equalisation may be decentralised or carried out using other management techniques.
Filtration	The separation of solids from a waste water carrier by passing them through a porous medium. It includes different types of techniques, e.g. sand filtration, microfiltration and ultrafiltration.
Flotation	A process where solid or liquid particles are separated from the waste water phase by attaching to fine gas bubbles, usually air. The buoyant particles accumulate at the water surface and are collected with skimmers.
Membrane bioreactor	A combination of activated sludge treatment and membrane separation.  Two variants are used:  - an external recirculation loop between the activated sludge tank and the membrane module;  - immersion of the membrane module into the aerated activated sludge tank, where the effluent is filtered through the hollow fibre membrane, the biomass remaining in the tank; this variant is less energy-consuming
Neutralisation	and results in more compact plants.  The process by which the pH of the incoming waste water is adjusted to the neutral pH level (approximately 7) by the addition of chemicals. For neutralising waste waters, in general, sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH) <sub>2</sub> ) is used to increase the pH; whereas, sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ), hydrochloric acid (HCl) or carbon dioxide (CO <sub>2</sub> ) is used to decrease the pH. The precipitation of some substances may occur during neutralisation.
Sedimentation	Separation of suspended particles and suspended material by gravitational settling.

Chapter 1

Table 1.1: Major waste water contaminants and their respective treatment techniques

Technique	TSS	BOD COD TOC	Refractory COD/TOC	AOX EOX	N total	NH <sub>4</sub> -N (NH <sub>3</sub> )	PO <sub>c</sub> -P	Heavy metals	Sulphides	Sulphate	Phenols	Oil	Acids, alkalis	Section in this document
Neutralisation	(X)							(X)					X	3.3.2.3.1
Grit separation	X													3.3.2.3.2.1
Coagulation/flocculation	X	$X^{(b,q)}$						X	X			X (°)		3.3.2.3.2.2
Sedimentation	X	(X) (*)						(X) ( <sup>0</sup> )	X (*)					3.3.2.3.2.3
Flotation	X	X (°)						(X) ( <sup>0</sup> )		)		X		3.3.2.3.2.4
Filtration	X	(X) (°)						(X) (¹) ∢						3.3.2.3.2.5
Microfiltration (MF)/ Ultrafiltration (UF)	(X) (°)	(X) (* 9)						N.	1			X		3.3.2.3.2.6
Oil-water separation	X	X										X		3.3.2.3.2.7
Hydrocyclone	X													3.3.2.3.2.8
Electrocoagulation	X	X					4	X						3.3.2.3.2.9
Chemical precipitation			X				X	X		X				3.3.2.3.3.1
Crystallisation							<ul><li>X</li></ul>	w X						3.3.2.3.3.2
Chemical oxidation (pre)		X	X	X					X		X			3.3.2.3.3.3
Wet oxidation with hydrogen peroxide (pre) (1)		x	x	X	x						x			3.3.2.3.3.3.2
Wet air oxidation (pre) (1)		X	X	X					_		X			3.3.2.3.3.3.3
Chemical reduction			^		4	-		XΦ						3.3.2.3.3.4
Chemical hydrolysis		X		X				A()						33.2.3.3.5
Nanofiltration (NF)/Reverse						1								
Osmosis (RO)		X	X	X	X	X	X	X			X			3.3.2.3.3.6
Electrodialysis			X											3.3.2.3.3.7
Electrolysis														3.3.2.3.3.8
Adsorption		X (*)	X	X	▼ X	X		X			X	X		3.3.2.3.3.9
Ion exchange		(X) (°)	(					X		X				3.3.2.3.3.10
Extraction		X	X	7							X			3.3.2.3.3.11
Pertraction		X	X	X							X			3.3.2.3.3.12
Distillation/rectification		X	X	X										3.3.2.3.3.13
Evaporation (1)		(X) (°)		X	X	X	X	X						3.3.2.3.3.14
Pervaporation		X (')	X()	$X^{(t)}$										3.3.2.3.3.15
Stripping		(X) (Y)		X	X	X		X	X (*)		X			3.3.2.3.3.16
Waste water incineration (FT)		X	X	(X) (*)	X	X		(X) (*)			X	X		3.3.2.3.3.17
Anaerobic treatment	. (	X		(X) (*)	(X) (*)			X (1, m)		X				3.3.2.3.4.1

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#### Chapter 1

Technique	TSS	COD TOC	Refractory COD/TOC	AOX EOX	N total	NH <sub>4</sub> -N (NH <sub>3</sub> )	PO <sub>4</sub> -P	Heavy metals	Sulphides	Sulphate	Phenols	Oil	Acids, alkalis	Section in this document
Biological removal of sulphur compounds/heavy metals								X	X	х	1			3.3.2.3.4.2
Aerobic treatment		X		(X) (b)	X	X	X	(X)	X		X			3.3.2.3.4.3
Biological nitrification/denitrification					X	X								3.3.2.3.4.4
Enhanced biological phosphorous removal							X	4	7					3.3.2.3.4.5
Phosphorous removal by chemical precipitation							X							3.3.2.3.4.6
Retention ponds	X	X												3.3.2.3.5.1
Sand filters	X													3.3.2.3.5.2

NR:		
NIR.		

- X: primary application.
- (X): secondary application.
  (pre): used in particular as a pretreatment, for example before final biological treatment.
- (FT): used as a final treatment technique.
- (\*) Only solid.
- (\*) Finely dispersed and low concentration.
  (\*) Non-volatile organic content.
- (\*) Special incinerator equipment required.
  (\*) Undissolved heavy metal compounds.
- () In combination with sulphate precipitated as sulphides.
- (\*) Colloids.
- (P) Hydrogen sulphide.
- () Side effect of ammonia or nitrate removal.

- (\*) Including colour agents, surfactants, nitrocompounds, chlorocompounds, phenols.

  (1) Techniques applicable on concentrated effinents [ 148, SUEZ 2007 ].
- Source: [ 227, TWG comments 2009 ]

Undissolved organic content.
Clonic organic species.
Volatile organic content.

- Only biodegradable part.

  Transferred to ash or waste water originating from incinerator.
- (") Transferred to sludge.
- (\*) Ammonia.
- (5) Some macromolecules.
- (\*) Side solubilisation.
- (\*) Includes nitrification/denitrification and one-step nitrogen removal process of Annamox type.

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Table 3.3: Monitoring regimes reported for the WWTPs

	Parameter	Frequency
	Routinely	monitored
	Waste water flow	Continuous
	pH	Continuous
	Temperature	Continuous
		Continuous
	COD	Daily/weekly/monthly
	Non-routine	
		Continuous
	TOC	Daily/weekly/monthly
	BOD,	Daily/weekly/monthly
<u>e</u>	Total suspended solids (TSS)	Daily or other
influent to the WWTP	• .	Continuous
*	Total Nitrogen (TN) (1)	Daily/weekly/monthly
2	Total inorganic nitrogen (N <sub>inorg</sub> ) ( <sup>1</sup> )	Daily/weekly or other
7	Ammonia (NH <sub>4</sub> -N)	Daily/weekly or other
<b>£</b>	Nitrite (NO <sub>2</sub> -N)	Daily/weekly or other
2	Nitrate (NO <sub>2</sub> -N)	Daily/weekly or other
- E		Continuous
-	Total Phosphorous (TP)	Daily/weekly/monthly or other
	Orthophosphate (PO <sub>4</sub> -P) (*)	Daily/weekly
	AOX	Daily/weekly/monthly
	Heavy metals (*)	
	- 1	Daily/weekly/monthly or other Daily/monthly
	Bacteria toxicity (*)	
	Phenols (*)	Daily/weekly or other
	Chloride (*)	Daily/weekly or other
	Sulphate (*)	Daily weekly monthly
	Cyanide(free) (*)	No information provided
	Other (*)	Site-specific
		monitored
	Waste water flow	Continuous
	Hq.	Continuous
		Daily or other
	Temperature	Continuous
	COD	Daily/weekly/monthly or other
	BOD <sub>5</sub>	Daily/weekly/monthly or other
	Total suspended solids (TSS)	Continuous
		Daily/weekly/monthly or other
F	Total Nitrogen (TN) (1)	Daily/weekly or other
₹	Total inorganic nitrogen (N <sub>inorg</sub> ) (1)	Daily/weekly or other
=	Ammonia (NH <sub>4</sub> -N)	Daily/weekly or other
ě	Nitrite (NO <sub>2</sub> -N)	Daily/weekly or other
Ę.	Nitrate (NO <sub>3</sub> -N)	Daily/weekly or other
9	Total Phosphorous (TP)	Daily/weekly/monthly or other
4		
ě	Orthophosphate (PO <sub>4</sub> -P) (*)	Daily/weekly
lucat fr	Orthophosphate (PO <sub>4</sub> -P) (*)  Heavy metals (*)	Daily/weekly Daily/weekly/monthly or other
Effluent from the WWTP		
E.Buent fr	Heavy metals (')	Daily/weekly/monthly or other Daily/weekly/monthly or other
E.Buent fr	Heavy metals (*) Chloride (*) Non-routinel	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored
Efficent	Heavy metals (*) Chloride (*) Non-routinel TOC	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored Daily or other
Effication	Heavy metals (*) Chloride (*) Non-routinel TOC AOX (*) Toxicity (a.g. fish or fish and daybnia algae	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored Daily or other Daily/weekly/monthly or other
Efficient	Heavy metals (*) Chloride (*) Non-routinel TOC AOX (*) Toxicity (a.g. fish or fish and daybnia algae	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored Daily or other
Efficients	Heavy metals (*)  Chloride (*)  Non-routinel  TOC  AOX (*)  Toxicity (e.g. fish or fish egg, daphnia, algae, luminiscence) (*)	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored Daily or other Daily/weekly/monthly or other Monthly or other
Efficient	Heavy metals (*)  Chloride (*)  Non-routinel  TOC  AOX (*)  Toxicity (e.g. fish or fish egg, daphnia, algae, luminiscence) (*)  Sulphate (*)	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored Daily or other Daily/weekly/monthly or other Monthly or other Daily/weekly/monthly or other
Efficiently	Heavy metals (*)  Chloride (*)  Non-routinel  TOC  AOX (*)  Toxicity (e.g. fish or fish egg, daphnia, algae, luminiscence) (*)	Daily/weekly/monthly or other Daily/weekly/monthly or other y monitored Daily or other Daily/weekly/monthly or other Monthly or other

Source: [ 222, EIPPCB 2013 ].

Other (hydrocarbons, truonide, etc.) () | sine-specific

() Refers only to biological WWTPs.
() Corresponding data were only collected during the first survey.
() The following heavy metals were asked for in both surveys: Cd, Cr, Cu, Hg, Ni, Pb, Zn. The heavy metals monitored are site-specific based on the characteristics of the waste water to be treated and the final effluent discharge medium.
(\*) Other parameters (e.g. hydrocarbons, fluoride) can be included in the monitoring regime depending on the characteristics of the waste water to be treated, the type of treatment techniques used and the final effluent discharge medium.



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