OÜ Eesti Keskkonnauuringute Keskus

Study on the wastewater in the Põltsamaa wastewater collection area

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1 Introduction

Based on the inventory of sources of substances hazardous to the aquatic environment [EKUK, 2018], the following substances were found in all investigated wastewater treatment plants: volatile organic compounds (toluene, xylene), phthalates (DEHP), metals and pesticides (glyphosate, LC-pesticides).

Some of the industries operating in the collection area of the Põltsamaa wastewater treatment plant are carrying out such activities, where these substances and groups of substances can be found and can end up in the treatment plant.

At present, Põltsamaa Varahaldus Ltd does not have information on the content of hazardous substances in wastewater from customers, and as a result, the company commissioned a corresponding study from the Estonian Environmental Research Center Ltd.

2 Current situation

2.1 Põltsamaa waste water collection area

Põltsamaa is a town in Jõgeva county with a population of about 4,000 people. The size of the catchment area of Põltsamaa is 436.7 hectares and according to the Estonian Environmental Register, the pollution load is 22,330 personal equivalents (PE).

There are 15 companies in the Põltsamaa wastewater collection area whose wastewater, based on the field of activity, may potentially contain hazardous substances or substances that inhibit the treatment process. Five companies operate on an industrial scale (2 food industries, 2 metal industries and a wood industry).

The wastewater of the Põltsamaa catchment area is treated in the Põltsamaa municipal wastewater treatment plant (WWTP), whereas and the receiving water body is the Põltsamaa River (Põltsamaa_3, chemical status not assessed).

2.2 Substances analysed

The following hazardous and priority hazardous substances were under inspection in this study: polyaromatic hydrocarbons (PAHs), phthalates, etroleum products, nonylphenols, perfluorinated compounds, volatile organic compounds (VOC,), BOD_7, COD, suspended solids, total nitrogen, total phosphorus, pH, heavy metals (As, Ba, Hg, Cd, Cr, Ni, Pb, Zn, Cu), BTEX (benzene, toluene, ethylbenzene, xylenes) and various groups of pesticides (including organochlorine pesticides).

2.2.1 Pesticides

Pesticides are intended to protect plants or plant products against all harmful organisms and to affect the life process of plants other than as a nutrient in the form of growth regulators. Plant protection products can also be used to preserve plant products, destroy undesirable plants or plant parts, and control or prevent undesirable plant growth [EKUK, 2015].

2.2.2 Volatile organic compounds (VOC)

Volatile organic compounds (VOCs) are chemical compounds that normally evaporate significantly to the atmosphere. The most common VOCs are methane, aldehydes, ketones and others.

2.2.3 Perfluorinated compounds

Perfluorinated compounds, including PFOS, have a very significant environmental impact. Since 2009, PFOS has been included in Annex B of the Stockholm Convention on Persistent Organic Pollutants. Perfluorinated compounds can be used in various industries, but in most cases, the exact use in Estonia is not known because the relevant information is not collected.

The use of perfluorinated compounds is not reflected in environmental permits. Concentrations in the products used remain within the established limit values [EKUK, 2018].

2.2.4 Octylphenols

The molecular formula of octylphenol is $C_{14}H_{22}O$ and the molar mass is 206.33 g/mol. 4-tert-octylphenol is a white solid substance having a boiling point of 158°C and a melting point of 84-84°C. There are no specific restrictions on the use of octylphenols (REACH Regulation 1907/2006/EC), but general requirements for the handling of chemicals, such as the CLP Regulation on packaging and labelling (1272/2008/EC), shall be followed.

For outdoor use, octylphenols are applied in chemicals used for coating materials for treating metal, wood and plastic surfaces, such as building structures and building materials. Indoor use has been confirmed for floor coverings, toys, furniture, curtains, footwear, leather goods, paper products and electronics (ECHA 2018). There are many uses, which also makes environmental emissions very likely. The amount of octylphenols used in Estonia cannot be quantified because the contents of hazardous substances in products are not measured or recorded [EKUK, 2018].

2.2.5 Nonylphenols

The group of nonylphenols is large, for example, 261 different nonylphenols are registered in ECHA (European Chemicals Agency). Nonylphenols are widely used in products that are imported to Estonia from third countries and thus circulate in Estonia. The use of these substances is limited, but the content in products can still be up to 0.1% by weight (1907/2006/EC). Nonylphenols continue to enter the waste cycle for a long time due to their high use in products and long-term use of products [EKUK, 2018].

Under Regulation 1907/2006/EU (REACH Regulation), nonylphenols and nonylphenol ethoxylates:

(a) nonylphenol $C_6H_4(OH)C_9H_{19}$ CAS No 25154-52-3 EC No 246-672-0 and

(b) nonylphenol ethoxylate $(C_2H_4O)nC_{15}H_{24}O)$

shall not be placed on the market, or used, as substances or in mixtures in concentrations equal to or greater than 0.1 % by weight for the following purposes:

(1) industrial and institutional cleaning except:

— controlled closed dry cleaning systems where the washing liquid is recycled or incinerated,

— cleaning systems with special treatment where the washing liquid is recycled or incinerated.

(2) domestic cleaning;

(3) textiles and leather processing except:

— processing with no release into waste water,

— systems with special treatment where the process water is pre-treated to remove the organic fraction completely prior to biological waste water treatment (degreasing of sheepskin);

(4) emulsifier in agricultural teat dips;

(5) metal working except:

uses in controlled closed systems where the washing liquid is recycled or incinerated;

(6) manufacturing of pulp and paper;

(7) cosmetic products;

(8) other personal care products except spermicides;

(9) co-formulants in pesticides and biocides. However national authorisations for pesticides or biocidal products containing nonylphenol ethoxylates as co-formulant, granted before 17 July 2003, shall not be affected by this restriction until their date of expiry.

2.2.6 Petroleum products

C_{10} - C_{40} hydrocarbons, or in the legal terms "petroleum products", is a group of substances consisting of thousands of individual hydrocarbons (mostly alkanes, cycloalkanes, aromatics) with boiling points ranging from 174 to 525°C. They are used as a general indicator for the assessment of fuel and chemical pollution in the aquatic environment. Mixtures and products containing C_{10}-C_{40} hydrocarbons can be hazardous and therefore their use is controlled and regulated at the legislative level. The main applications are liquid fuels (including light and heavy fuel oil, lubricating oil, solvents and other chemicals [EKUK, 2018].

2.2.7 Phthalates or phthalic acid esthers

Phthalates are one of the most common synthetic substances in our everyday environment. Phthalates are mainly used as plasticizers in plastics, but also in the production of a variety of lubricants and solvents, such as in cosmetics, toys, paints, adhesives, packaging, pesticides and floor coverings. In the pharmaceutical industry, phthalates are used in capsule casings, but also as lubricants, stabilizers, dispersants and emulsifiers. Phthalates are used in plastics (mainly PVC) to provide flexibility [EKUK, 2015].

Table 1: Fields of applications for phthalates [EKUK, 2015]

Phthalic acid ester	Field of application
Diethylphthalate - DEP	Body care products, cosmetics, fertilizers and plant protection products.
Butylbenzylphthalate - BBP	Vinyl records, conveyor belts in the food industry, imitation leather, car interior materials, cones (in traffic), fertilizers and plant protection products.
Di-n- butylphthalate - DnBP	PVC plastic, latex adhesive, cosmetics, body care products, cellulose plastic, paint thinner, fertilizers and plant protection products.
Di(2-ethylhexyl)phthalate – DEHP	Building materials (wallpaper, insulation of wires and cables), car products (upholstery, seats), clothing (shoes, raincoats), food packaging, children's goods (dolls, toys), medical equipment, plant protection products and fertilizers.
Di-n-hexylphthalate - DnHP	Tool handles, dishwasher parts, flooring, vinyl gloves, flea collar for pets and conveyor belts in the food industry.
Di-n-octylphthalate - DnOP	In mixtures with C_6-C_{10} phthalates, garden hoses, pool covers, floor tiles, fertilizers and plant protection products.
Diisononylphthalate - DINP	Garden hoses, pool covers, floor tiles and toys.
Diisodecylphthalate - DIDP	PVC plastic, wire and cable insulation, imitation leather, toys, carpets, pool covers

Under REACH (1907/2006/EU), the **use of DEHP, BBP and DBP has been banned since 21 February 2015.**

However, REACH stipulates that the **use is not prohibited** in the following uses:

a) use in plant protection products falling under the scope of Directive 91/414/EEC;

b) use in biocidal products falling under the scope of Directive 98/8/EC;

c) use as motor fuels in accordance with Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels;

d) use as a fuel in mobile or stationary combustion plants for mineral oil products and as a fuel in closed systems.

Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs in the **food industry** - DEHP, BBP and DBP may only be used: (a) as a plasticiser in reusable materials and articles in contact with non-fatty foods; (b) as a technical adjuvant in concentrations up to 0.1% in the finished product. SML = 1.5 mg/kg in the food simulant.

According to Directive 2005/84/EC of the European Parliament and of the Council of 14 December 2005 amending for the 22nd time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (phthalates in toys and childcare articles) phthalates as substance or preparations shall not make up more than 1% of the mass of the be used plasticized material (DEHP, DBP, BBP, DINP, DIDP and DNOP).

Directive 76/768/EC on the approximation of the laws of the Member States relating to cosmetic products and prohibiting the use of phthalates in cosmetic products bans the use of phthalates in **cosmetic products**.

2.2.8 Polyaromatic hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) consist of fused benzene rings, which do not contain any heteroatoms or substituents. PAHs include more than 300 compounds that differ in the number and location of benzene nuclei in the molecule [EKUK, 2015].

PAHs arise as a by-product of combustion of fuels and other organic material, as well as in incomplete combustion of organic matter.

The main sources of PAHs in the environment are industrial processes, traffic and domestic fuel combustion. PAHs are also formed as a result of natural processes such as forest fires, volcanic eruptions and bacterial decomposition of organic matter [EKUK, 2015].

PAHs are used in the manufacture of paints, plastics, organic semiconductors, as insecticides and fungicides, and the manufacture of explosives.

PAHs include several compounds identified as priority hazardous to the aquatic environment, such as benzo(a)pyrene, anthracene, naphthalene. Compounds with significant effects in the aquatic environment are considered to be: compounds with a common environmental quality standard (EQS) for benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene.

A separate a compound basis norm has been established for anthracene, florantene and naphthalene.

In the future, PAHs (benzo(a)pyrene and fluoranthene) will have to be determined as indicators in biota to have a correct assessment of the status of water bodies and the impact of PAHs on biota (Directive 2013/39/EC.) PAHs can be found in almost all types of water. They adsorb to solid particles, but are also present in the liquid phase. Some of them have highly carcinogenic and/or mutagenic properties in humans [EKUK, 2015].

2.2.9 Aromatic hydrocarbons – BTEXs

- Benzene CAS 71-43-2
- Ethylbenzene CAS 100-41-4
- Toluene CAS 108-88-3
- m,p-xylene CAS 108-38-3; 106-42-3
- o-xylene CAS 95-47-6

BTEXs refer to six light aromatic compounds: benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene, which are commonly found together in petroleum products. These are volatile monocyclic aromatic hydrocarbons used as solvents and for the production of other chemicals. Due to their volatile properties, BTEX compounds do not persist in the environment for a long time and help to identify the use of recent substances [EKUK, 2015].

2.2.10 Heavy metals

Arsenic is a chemical element with the sequence number 33. As a simple substance, arsenic is rare. All water-soluble arsenic compounds are toxic to the human body. The best known of these is As4O6, or arsenic. The main sources of anthropogenic arsenic pollution are the metal industry and the production of energy from fossil fuels, as well as the production and use of arsenic-containing pesticides and wood preservatives.

The toxicity of **mercury** depends largely on the form in which the substance enters the body, either as metallic, liquid mercury or as mercury vapour. Metallic liquid mercury is not as dangerous to the body as mercury vapour. Mercury compounds are also toxic to the body, causing major damage to the lungs and brain. In water, the body absorbs mercury in the form of methyl mercury, which damages the nervous system. Mercury is also a substance that is concentrated in the food chain, so there may be fish in some seas with a pretty high concentration of mercury compounds. Thus, eating such fish is very harmful to health.

Cadmium is toxic at very low levels of exposure, causing acute and chronic effects on human health and the environment. Cadmium is released into the atmosphere mainly during the processing or incineration of products containing cadmium (plastics, dyes, rubber, batteries). Mineral fertilizers and fungicides are also sources of cadmium pollution. In the marine environment, cadmium is mainly present as dissolved ions or chloride complexes.

Chromium: Chromium compounds are toxic and can cause various health effects: skin and mucous membrane corrosion, allergies. Chromium and chromium compounds (especially dichromates) are used in galvanic chromium plating of metal objects in the leather and textile industries, photography, paper, varnish, paint and dairy industries. cement, anti-corrosion materials, coolants and polishing pastes also contain chromium. 3- and 6-valent chromium is more commonly used in the industry. The largest user of chromium is the steel industry. Chromium metal and its 6-valent compounds have carcinogenic effects. Leather products containing chromium VI (gloves, footwear, workwear, etc.) have been repeatedly removed during market surveillance .

Nickel: Nickel is found in nature only as compounds. Nickel is extremely toxic. Nickel-containing dust causes lung cancer. Nickel compounds enter the human body mostly through drinking water and food. Nickel can also enter the human body when using Ni-containing tableware (stainless steel). When nickel levels are high in seawater or on the ground, higher erythrocyte counts are observed in animals.

Lead is a chemical element whose biological use is unknown. The substance is toxic to human and animal organisms in small amounts. A significant part of the lead load is transmitted through the atmosphere, indirectly from car traffic and other anthropogenic sources (plant protection industry, ceramics industry, battery production). The transfer of the substance to water bodies is limited by the low solubility of lead compounds.

Zinc: Metallic zinc is not toxic, but the free zinc ions in solution are toxic. Zinc is the fourth most used metal. In terms of usability, it is surpassed only by iron, aluminium and copper. Zinc is used to galvanize steel to prevent corrosion, in alloys, tinning, as an anode in batteries. Zinc chloride is used as a deodorant and even as a wood preservative, zinc sulphide is used as a luminescent dye.

Copper: In nature, copper occurs mainly as compounds. In compounds, copper may have two metal cations: less stable Cu^{+} and more stable Cu^{2+}. All copper compounds are toxic. In its pure form, copper is widely used in electrical engineering, in the manufacture of cable, bare and contact wire rods, electric generators, telephone and telegraph equipment and radio equipment. Copper alloys are used in the machinery, automotive and tractor industries and the manufacture of chemical equipment. Copper is also used in the manufacture of batteries.

3 Methodology

A summary of the sampling and analysis results is provided in the following subsections.

3.1 Sampling from waste water treatment plants

The work was performed in two stages. The **first stage** aimed at finding out the peculiarities of the formation of pollution loads in the Põltsamaa wastewater collection area (from which region which substances originate) and to evaluate the efficiency of the wastewater treatment plant in removing these substances. The wastewater collection area was conditionally divided into three parts – two of which described different areas of the town and most of the wastewater was expected to be of domestic origin and one part industrial wastewater.

The two largest industries, whose pollution load accounted for about 60% of the total load in the wastewater collection area, were taken under special examination. To determine the efficiency of the wastewater treatment plant, samples were taken from the influent and effluent of the wastewater treatment plant.

The following parameters were analysed at all study points: Pb, Ni, Cd, As, Ba, Cr, Sn, Zn, Cu, Hg, phthalates, PAH, VOC, BTEX, LC pesticides, glyphosate, AMPA, petroleum products, nonylphenols, perfluoro compounds, BHT_7, COD , suspended solids, total nitrogen, total phosphorus and pH.

Based on the results of the first stage, in the **second stage** of the study, some more companies were examined, from which potentially certain hazardous substances could end up in the public sewer. Although the terms of reference also indicated the possibility of performing inhibition experiments, this did not prove necessary.

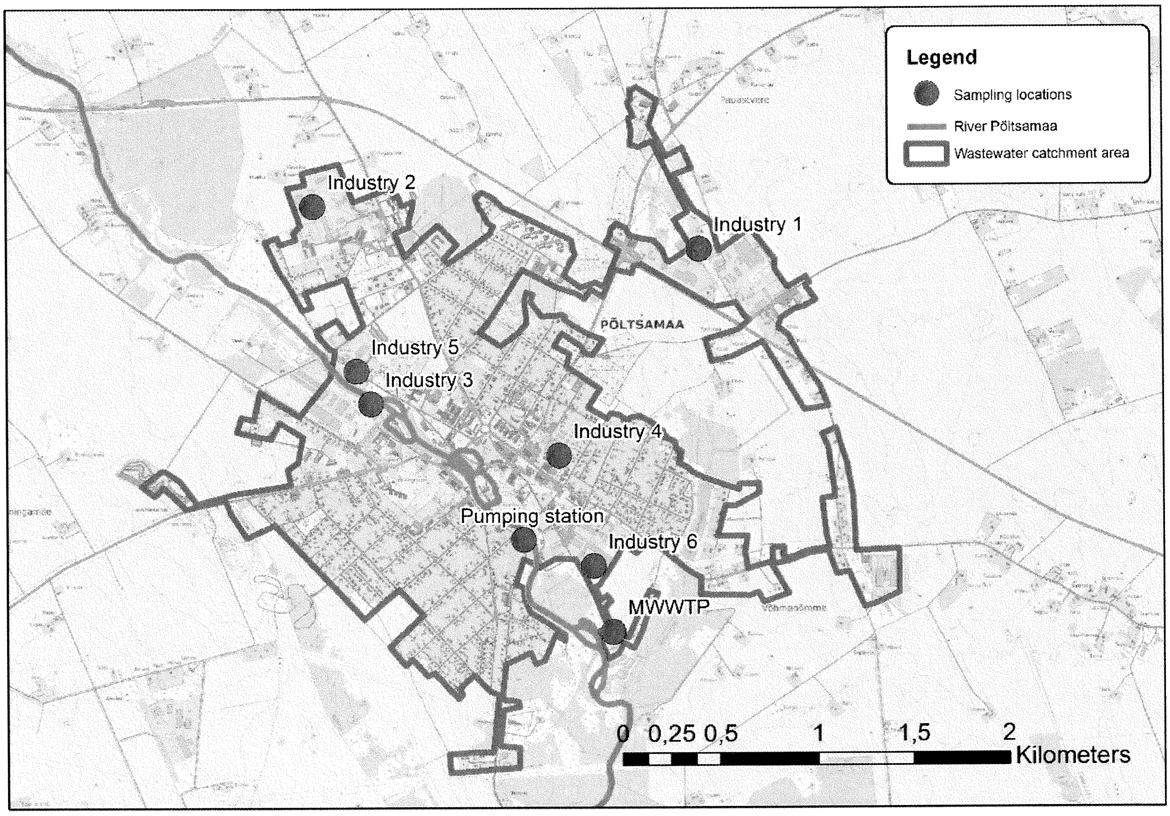

Figure 1. Põltsamaa waste water collection area and sampling sites.

Samples of hazardous substances were taken in accordance with the customer, both from the influent and effluent of the wastewater treatment plant and from the connection points of industrial enterprises. Sampling took place between 13.01.-18.03.2020. All wastewater and effluent samples were taken according to ISO standard 5667-10. The selection of the sampling method for hazardous substances was based in particular on the requirements for sample storage set out in standard ISO 5667-3, as a result of which grab sampling was the only possible way of sampling for most of the substances investigated.

In order to reduce the error due to randomness, both heavy metals and nutrients were sampled as averaged samples. The averaged samples were collected on a time proportion basis. An automatic sampling device was used to collect the samples, which flushed the sampling hoses with the with the test water before each subsample was collected.

3.2 Methods of analysis and detection limit

The methods of analysis were selected following EVS EN ISO/IEC standard 17025.

As there is no established reference method for several of the tested substances, methods validated, documented and accredited in accordance with EVS EN ISO/IEC-17025 were used. When choosing the appropriate method, the minimum criteria for analytical methods, with a maximum uncertainty of less than 50% (k = 2) and a maximum limit of 30% of the relevant standards were taken into account as far as possible.

All samples were analysed in the laboratories of the Estonian Environmental Research Centre (EAK accredited testing laboratory with registration number L008).

4 Results

4.1 Wastewater characteristics

The Põltsamaa River divides the town into right and left bank parts. There are predominantly smaller households on the right bank, while on the left bank most of the businesses and enterprises are located, as well as larger apartment buildings. Although the town's two largest food industries are located on one side and the other on the other side of the river, both companies have their own sewerage pipelines built practically until to the wastewater treatment plant. The town's wastewater can in principle be divided into three: right bank, left bank and industry (see Table 2).

Table 2. Distribution of flow rates in the town

	Unit	WWTP	Right bank	Left bank	Industry
Median	m^3/d	1 408	160	359	890
Average	m^3/d	1 365	161	322	882
Min	m^3/d	1 133	138	206	789
Max	m^3/d	1 511	188	366	957
Standard deviation	m^3/d	177	21	84	72

Table 2 indicates that the food industry (industries 3 and 4 in Figure 1) produces on average 65% of the wastewater that reaches the treatment plant. The remaining 35% is of domestic origin (includes both domestic wastewater from domestic consumption and wastewater from other urban enterprises).

In this study, a total of six industrial enterprises operating in the areas listed in Table 3 were taken under separate examination.

Table 3. Examined industries

	Field of activity	Average wastewater volume (m^3/d)
Industry 1	Manufacturer of milled beams for garden houses and glulam, deep impregnated garden products, and heating pellets	1.8
Industry 2	Manufacturer of electric motors (including manual and robotic welding, CNC machining, surface treatment and final assembly)	2.8
Industry 3	Food industry	321.3
Industry 4	Dairy industry	469.9
Industry 5	Manufacturer of stainless steel and metal products	1.9
Industry 6	Manufacturer of glued window blanks for windows and doors	5.7

4.2 Results of analyses of hazardous substances

The results of the analysis of hazardous substances are presented in Tables 4-7.

None of the tested 72 hazardous substances were found in the wastewater samples above the detection limit. Since according to the legislation currently in force in Estonia (Regulation No. 75 of the Minister of the Environment "Establishing Requirements for Hazardous Substances Discharged into Public Sewerage"), limit values have been established only for 23 organic and 14 inorganic compounds, which do not predominantly overlap with the list of priority hazardous substances, it can be only concluded based on Table 4 that the limit values laid down in the Regulation have not been exceeded for any of the substances analysed.

Table 4. Concentrations of hazardous substances (excluding heavy metals) in wastewater

Parameter analysed	Unit	Right bank pumping station	Industry 1	Industry 2	Industry 3	Industry 4	Industry 5	Industry 6
		28.01.20	18.03.20	18.03.20	20.01.20	20.01.20	14.01.20	14.01.20
1,1,1-trichloroethane	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,2-Dichloroethane	µg/l	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06
2,4-D	µg/l	**0.34**	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
4- Nonylphenol (branched)	µg/l	**2.6**	< 0.05	**0.074**	**0.098**	**0.076**	**4.3**	**0.4**
4-n- Nonylphenol	µg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	**0.084**	< 0.05
4-tert-Octylphenol	µg/l	**0.025**	< 0.003	**0.005**	**0,038**	**0.032**	**0.066**	**0.072**
AMPA	µg/l	**0.65**	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	**0.2**
Amethrin	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Amidosulfuron	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Anthracene	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acetamiprid	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthene	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthylene	µg/l	< 0.01	< 0.01	< 0.01	**0.026**	< 0.01	< 0.01	< 0.01
Benzene	µg/l	< 0,06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06
Benzo(a)anthracene	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(a)pyrene	µg/l	< 0.005	< 0.005	< 0.005	**0.037**	< 0.005	< 0.005	< 0.005
Benzo(b)fluoranthene	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Benzo (g,h,i) perylene	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Benzo(k)fluoranthene	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Benzyl butyl phthalate (BBP)	µg/l	< 0.3	< 0.3	**1.3**	< 0.3	< 0.3	< 0.3	< 0.3
Bromodichloromethane	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Di-2-ethylhexyl phthalate (DEHP)	µg/l	**11**	< 0.3	**4.3**	**0.99**	< 0.3	**1.8**	**11**
Di-n-octyl phthalate (DNOP)	µg/l	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Di-n-propyl phthalate (DPP)	µg/l	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Dibenzo (a,h) anthracene	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Dibromochloromethane	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 01
Dibutyl phthalate (DBP)	µg/l	**0.79**	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	**0.49**

Parameter analysed	Unit	Right bank pumping station	Industry 1	Industry 2	Industry 3	Industry 4	Industry 5	Industry 6
		28.01.20	18.03.20	18.03.20	20.01.20	20.01.20	14.01.20	14.01.20
Diethyl phthalate (DET)	µg/l	**2.3**	< 0.3	< 0.3	< 0.3	< 0.3	**0.93**	< 0.3
Diflufenican	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0,005	< 0.005
Diisobutyl phthalate (DIBP)	µg/l	**2.1**	< 0.3	**2.2**	**0.33**	< 0.3	**1.1**	**0.63**
Diclofenac	µg/l	**10**	**0.1**	**0.4**	< 0.1	< 0.1	**22**	**11**
Dichlorophos	µg/l	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Dichloromethane	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	**0.54**	< 0.1
Dichloroprop-P	µg/l	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Dimethenamid-P	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dimethoate	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dimethyl phthalate (DMP)	µg/l	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Dicyclohexyl phthalate (DCP)	µg/l	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Diundecyl phthalate (DUP)	µg/l	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Diuroon	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ethopropos	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 002	< 002	< 0.02
Ethylbenzene	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Phenanthrene	µg/l	**0.042**	< 0.01	< 0.01	**0.015**	< 0.01	**0.021**	**0.04**
Fenpropidine	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Fluoranthene	µg/l	**0.013**	< 0.01	< 0.01	**0.01**	< 0.01	< 0.01	**0.015**
Fluorene	µg/l	**0.018**	< 0.01	< 0.01	< 0.01	< 0.01	**0.012**	**0.021**
Fluroxypyr	µg/l	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Glyphosate	µg/l	< 0.1	< 0.1	**0.9**	< 0.1	< 0.1	< 0.1	< 0.1
Indeno(1,2,3-cd)pyrene	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Isoprocarb	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Isoproturon	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Quinoxyfen	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Chlormequat chloride	µg/l	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Clopyralid	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Chloroxuron	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Chlorotoluron	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Clothianidin	µg/l	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 02
Chrysene	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Linuron	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MCPA	µg/l	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Malathion	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Methabenzthiazuron	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Metasachlor	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Methiocarb	µg/l	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Metobromuro	µg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Methoxuron	µg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Parameter analysed	Unit	Right bank pumping station	Industry 1	Industry 2	Industry 3	Industry 4	Industry 5	Industry 6
		28.01.20	18.03.20	18.03.20	20.01.20	20.01.20	14.01.20	14.01.20
Monolinuron	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Naphthalene	µg/l	**0.026**	< 0.01	< 0.01	**0.011**	< 0.01	**0.027**	**0.033**
Petrolium products (hydrocarbons C_{10} - C_{40})	µg/l	**200**	< 20	**110**	**310**	< 20	**80**	**260**
Napropamide	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Nicosulfuron	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Nonylphenol (total)	µg/l	**2.6**	< 0.05	**0.074**	**0.098**	**0.076**	**4.3**	**0.4**
PAH total	µg/l	**0.11**	< 0.005	< 0.005	**0.11**	n.t.	**0.06**	**0.13**
Perfluoro-n-hexanoic acid (PFHxA)	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorobutanoic acid (PFBA)	µg/l	< 0.02	< 0.02	**0.04**	< 0.02	< 0.02	< 0.02	< 0.02
Perfluorodecanoic acid (PFDA)	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorododecanoic acid (PFDoA)	µg/l	< 001	< 001	< 0.01	< 0.01	< 0.01	< 0.01	< 001
Perfluorononanoic acid (PFNA)	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorooctanoic acid (PFOA)	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	**0.02**	< 0.01	< 0.01
Perfluorooctane sulfonic acid (PFOS)	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluoroundecanoic acid (PFUA)	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Pinoxaden	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Propaquizafop	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Propiconazole	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Pyrene	µg/l	**0.012**	< 0.01	< 0.01	**0.013**	< 0.01	< 0.01	**0.014**
Spiroxamine	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Styrene	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tebuconazole	µg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Terbutryn	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Tetrachloroethylene (perchlorethylene -PER)	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tetrachloromethane	µg/l	< 0.1	< 0.1	< 0.1	**0.28**	**0.91**	< 0.1	< 0.1
Thiacloprid	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Toluene	µg/l	**0.64**	< 0.1	**0.7**	**0.71**	**8.8**	**1.2**	**0.18**
Triadimenol	µg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Tribromomethane (Bromoform)	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Trichlorethylene	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Trichloromethane (chloroform)	µg/l	< 0.03	< 0.03	< 0.03	**0.97**	**3.5**	< 0.03	< 0.03
Tritosulfuron	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Cybutrin	µg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
m/p-xylene	µg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	**0.34**	**0.12**
o-xylene	µg/l	< 0.1	< 0.1	**0.4**	< 0.1	< 0.1	**0.22**	**0.12**

Table 5 summarizes the analysis results of hazardous substances in the inflow and outflow of the wastewater treatment plant (excluding heavy metals, see Table 7).

Although during the study period the results of the effluent analysis did not exceed the limit values of parameters listed in Annex 1 of Minister of Environment Regulation No. 61 (MoE 61) of 8.11.2019 "Requirements for Wastewater Treatment and Discharge of Sewage, Precipitation, Mining, Quarrying and Cooling Water, Measures for Conformity Assessment and Limit Values for Contaminants", attention should be drawn to the content of nonylphenols in the sample of the effluent of the device on 28.01.2020.

Although this sample was taken before sewage lagoons, it is important to bear in mind that nonylphenols do not degrade in the sewage lagoons and are likely to reach the receiving water body (the Põltsamaa River).

This finding suggests that higher levels of nonylphenols occasionally enter the wastewater treatment plant from the wastewater collection area. Based on the results of wastewater analysis (Table 4), it can be assumed that the main source of these substances is located on the right bank of the town.

There is one metal industry in the area that could use nonylphenols due to the nature of its activities.

Unfortunately, it was not possible to sample its wastewater during the fieldwork. Although the highest content of nonylphenols was found in the wastewater of Industry 5, the amount of the wastewater discharged by this company into the public sewerage system represents only 0.1% of the daily hydraulic load of the wastewater treatment plant.

Table 5. Concentrations of hazardous substances (except heavy metals) in the inflow and outflow of the wastewater treatment plant

Parameter analysed	Unit	MoE 61	Inflow to the treatment plant		Outflow from the treatment plant	Outflow to the receiving water body	
			28.01.20	18.03.20	28.01.2020	28.01.20	18.03.20
1,1,1-trichloroethane	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,2-Dichloroethane	µg/l	10	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06
2,4-D	µg/l	1*	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
4-Nonylphenol (branched)	µg/l	Shall not be found	**0.13**	< 0.05	**2.3**	< 0.05	< 0.05
4-n-Nonylphenol	µg/l	Shall not be found	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
4-tert- Octylphenol	µg/l	0,1	**0.021**	< 0.003	**0.018**	**0.003**	< 0.003
AMPA	µg/l		**0.3**	**0.8**	**0.3**	**0.2**	**0.3**
Amethrin	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Amidosulfuron	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Anthracene	µg/l	0,1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acetamiprid	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthene	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthylene	µg/l		**0.01**	**0.011**	< 0.01	< 0.01	< 0.01
Benzene	µg/l	50	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06
Benzo (a) anthracene	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(a)pyrene	µg/l	0.27	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Benzo(b)fluoranthene	µg/l	0.017	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005

Parameter analysed	Unit	MoE 61	Inflow to the treatment plant		Outflow from the treatment plant	Outflow to the receiving water body	
			28.01.20	18.03.20	28.01.2020	28.01.20	18.03.20
Benzo(g,h,i)perylene	µg/l	0.0082	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Benzo(k)fluoranthene	µg/l	0.017	< 0.005	< 0.005	< 0.005	< 0,005	< 0.005
Benzyl butyl phthalate (BBP)	µg/l		< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Bromodichloromethane	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Di-2-ethylhexyl phthalate (DEHP)	µg/l	Shall not be found	**3.4**	**2.3**	< 0.3	< 0.3	< 0.3
Di-n-octyl phthalate (DNOP)	µg/l		< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Di-n-propyl phthalate (DPP)	µg/l		< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Dibenzo(a,h)anthracene	µg/l		**0.005**	< 0.005	< 0.005	< 0.005	< 0.005
Dibromochloromethane	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dibutyl phthalate (DBP)	µg/l		**0.58**	< 0.3	< 0.3	< 0.3	< 0.3
Diethyl phthalate (DET)	µg/l		**0.73**	**0.3**	< 0.3	< 0.3	< 0.3
Diflufenican	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Diisobutyl phthalate (DIBP)	µg/l		**0.94**	**0.35**	< 0.3	< 0.3	< 0.3
Diclofenac	µg/l		**1.1**	**1.4**	**3.5**	**2.6**	**1.3**
Dichlorophos	µg/l		< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Dichloromethane	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dichloroprop-P	µg/l		< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Dimethenamid-P	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dimethoate	µg/l	1*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dimethyl phthalate (DMP)	µg/l		< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Dicyclohexyl phthalate (DCP)	µg/l		< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Diundecyl phthalate (DUP)	µg/l		< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Diuron	µg/l	1,8	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ethopropos	µg/l		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ethylbenzene	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Phenanthrene	µg/l		**0.022**	**0.011**	< 0.01	< 0.01	< 0.01
Fenpropidine	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Fluoranthene	µg/l	0,12	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Fluorene	µg/l		**0.011**	< 0.01	< 0.01	< 0.01	< 0.01
Fluroxypyr	µg/l		< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Glyphosate	µg/l	1*	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Indeno (1,2,3-cd) pyrene	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Isoprocarb	µg/l		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Isoproturon	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Quinoxyfen	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Chlormequat chloride	µg/l	1*	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Clopyralid	µg/l	1*	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Chloroxuron	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Chlorotoluron	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Parameter analysed	Unit	MoE 61	Inflow to the treatment plant		Outflow from the treatment plant	Outflow to the receiving water body	
			28.01.20	18.03.20	28.01.2020	28.01.20	18.03.20
Clothianidine	µg/l		< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Chrysene	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Linuron	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MCPA	µg/l	1*	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Malathion	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Methabenzthiazuron	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Metasachlor	µg/l	1*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Methiocarb	µg/l		< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Metobromuro	µg/l		< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Methoxuron	µg/l		< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Monolinuron	µg/l		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Naphthalene	µg/l	130	**0.019**	**0.058**	**0.016**	< 0.01	< 0.01
Petroleum products (hydrocarbons C_{10} - C_{40})	µg/l		190	< 20	< 20	< 20	< 20
Napropamide	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Nicosulfuron	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Nonylphenol (total)	µg/l	Shall not be found	**0.13**	< 0.05	**2.3**	< 0.05	< 0.05
PAH total	µg/l		**0.078**	**0.08**	**0.016**	-	< 0.005
Perfluoro-n-hexanoic acid (PFHxA)	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorobutanoic acid (PFBA)	µg/l		< 0.02	**0.04**	< 0.02	< 0.02	**0.06**
Perfluorodecanoic acid (PFDA)	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorododecanoic acid (PFDoA)	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorononanoic acid (PFNA)	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorooctanoic acid (PFOA)	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluorooctane sulfonic acid (PFOS)	µg/l	Shall not be found	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perfluoroundecanoic acid (PFUA)	µg/l		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Pinoxaden	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Propaquizafop	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Propiconazole	µg/l		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Pyrene	µg/l		**0.011**	< 0.01	< 0.01	< 0.01	< 0.01
Spiroxamine	µg/l	1*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Styrene	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tebuconazole	µg/l	1*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Terbutryn	µg/l	0,34	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Tetrachloroethylene (perchlorethylene e PER)	µg/l	10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tetrachloromethane	µg/l		< 0.1	**0.13**	< 0,1	< 0.1	< 0.1
Thiacloprid	µg/l		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Toluene	µg/l		**11**	**18**	< 0.1	< 0.1	< 0.1

Parameter analysed	Unit	MoE 61	Inflow to the treatment plant		Outflow from the treatment plant	Outflow to the receiving water body	
			28.01.20	18.03.20	28.01.2020	28.01.20	18.03.20
Triadimenol	µg/l		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Tribromomethane (Bromoform)	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Trichlorethylene	µg/l		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Trichloromethane (chloroform)	µg/l	2,5	**1.2**	**0.78**	< 0.03	< 0.03	< 0.03
Tritosulfuron	µg/l		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Cybutrin	µg/l	0,016	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
m/p-xylene	µg/l	5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
o-xylene	µg/l	5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

* The total concentration of pesticides in the effluent shall not exceed 1 µg/l.

The concentrations of heavy metals in the wastewater of all industries were below the limit values established in the Minister of the Environment Regulation No. 75 of 16.10.2003 "Establishment of Requirements for Hazardous Substances Discharged into Public Sewerage" (Table 6).

Table 6. Concentrations of heavy metals in the waste water of the industrial and right-bank pumping station

Source	Date	As	Ba	Hg	Cd	Cr	Ni	Pb	Tn	Zn	Cu
		µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Industry 1	18.03.2020	0.57	200	0.018	0.02	< 0.5	1.2	< 0.1	< 0.5	9.8	1.6
Industry 2	18.03.2020	0.79	310	0.018	0.047	6.7	3	1.2	< 0.5	570	33
Industry 3	20.01.2020	0.35	410	< 0.015	0.15	2.9	2.6	0.95	14	48	12
Industry 3	21.01.2020	0.37	480	< 0.015	0.079	2.3	2.6	0.66	2.4	46	4.9
Industry 3	22.01.2020	0.33	570	< 0.015	0.11	3.6	3	0.75	1.6	48	4.6
Industry 3	23.01.2020	0.29	470	< 0.015	0.053	1.1	2.4	0.33	3.1	27	1.4
Industry 4	20.01.2020	0.071	44	< 0.015	< 0.02	0.84	18	0.5	< 0.5	130	13
Industry 4	21.01.2020	0.082	26	0.021	< 0.02	1.1	14	0.35	< 0.5	100	16
Industry 4	22.01.2020	0.069	36	< 0.015	< 0.02	1	17	0.27	< 0.5	130	16
Industry 4	23.01.2020	0.064	28	0.022	< 0.02	0.81	14	0.26	< 0.5	100	13
Industry 5	13.01.2020	0.4	190	0.022	0.031	6.3	8.5	0.84	0.7	57	14
Industry 5	14.01.2020	0.38	140	0.025	0.021	3.9	7	0.72	1.3	63	8.9
Industry 6	13.01.2020	0.53	160	0.026	0.06	2	4.4	1.3	< 0.5	140	39
Industry 6	15.01.2020	0.52	990	< 0.015	0.055	58	6.9	1.2	< 0.5	100	39
Right bank pumping station	27.01.2020	0.58	250	< 0.015	0.078	2.5	6.3	1.2	1.3	130	22
Right bank pumping station	26.01.2020	0.67	250	< 0.015	0.11	1.8	5.5	1.8	1.3	120	32
Right bank pumping station	25.01.2020	0.48	250	< 0.015	0.099	1.5	4.8	1.4	1.2	130	28
Right bank pumping station	24.01.2020	0.51	260	0.019	0.05	0.85	4.2	0.87	0.72	73	23

Limit value when charging to the public sewage system	200		50	200	500	1000	500		2000	2000

No limit values for heavy metals have been established for the outflow of the Põltsamaa wastewater treatment plant by environmental permit No. L.VV/ 331040.

Consequently, the effluent results were compared with the limit values established in Minister of the Environment Regulation No. 61 of 08.11.2019 "Requirements for wastewater treatment and discharge of sewage, precipitation, mining, quarrying and cooling water, conformity assessment measures and pollutant content limit values" (Table 7). The contents of all heavy metals in the effluent of the wastewater treatment plant were below the limits established in the regulation of the Minister of the Environment.

Table 7. Concentrations of heavy metals in the inflow and outflow of the wastewater treatment plant.

Date	Clarification	As	Ba	Hg	Cd	Cr	Ni	Pb	Sn	Zn	Cu
		μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
18.03.2020	Inflow	0.86	340	0.025	0.092	1.1	8.3	1.6	< 0.5	170	27
27.01.2020	Inflow	0.39	320	< 0.015	0.074	1.6	9.5	1.1	1.1	250	15
26.01.2020	Inflow	0.53	320	< 0015	0.12	3.8	10	2.2	0.99	200	32
25.01.2020	Inflow	0.39	190	0.015	0.071	1.2	9.7	1.5	< 0.5	130	23
24.01.2020	Inflow	0.31	230	0.02	0.071	1.9	8.7	1.2	0.74	120	4
27.01.2020	Outflow from treatment plant	0.13	50	< 0.015	< 0.02	< 0.5	4.5	0.13	< 0.5	27	3.4
26.01.2020	Outflow from treatment plant	0.12	50	< 0.015	< 0.02	< 0.5	4.5	< 0.1	< 0.5	24	1.3
25.01.2020	Outflow from treatment plant	0.13	51	< 0.015	< 0.02	< 0.5	4.6	< 0.1	< 0.5	23	1.1
24.01.2020	Outflow from treatment plant	0.14	55	< 0.015	< 0.02	< 0.5	4.5	< 0.1	< 0.5	24	2
18.03.2020	Outflow to the receiving water body	0.2	30	< 0.015	< 0.02	< 0.5	2.9	< 0.1	< 0.5	13	< 1
28.01.2020	Outflow to the receiving water body	0.13	41	< 0.015	< 0.02	< 0.5	5	< 0.1	< 0.5	15	< 1
Limit value when entering the receiving water body		10	100	1	5	50	34	14	3	50	15

4.3 Treatment efficiencies of the wastewater treatment plant

It can be seen from Tables 4-7 that many analytical results stay below the limit of quantification (LOQ). To calculate the treatment efficiency of the wastewater treatment plant, these results were replaced by the value LOQ/√2.

In tables 8 and 9 the efficiencies of both the biological treatment process and the entire wastewater treatment plant (including treatment in the sewage lagoon) have been calculated separately.

Table 8. Nutrient removal efficiency of the wastewater treatment plant

	Efficiency of biological treatment	Efficiency of the treatment plant

Biological oxygen (BOD_7)	(99.0 ± 0.2) %	99.3%
Chemical oxygen demand (COD)	(96.6 ± 1.1) %	98.2%
Suspended solids	(97.4 ± 0.7) %	99.4%
Total phosphorus	(97.8 ± 0.9) %	97.5%
Total nitrogen	(93.8 ± 0.9) %	98.1%

It can be seen from Table 8 that the wastewater treatment plant is very good at removing nutrients. During the study period, all outflow analysis results met the requirements of the water permit.

Due to their properties, hazardous substances behave differently in a wastewater treatment plant. The substances may be biodegradable (half-life less than 10 days) or inert (half-life more than 150 days), hydrophobic (log Kow> 4.5) or hydrophilic (log Kow <3.5).

Hydrophobic substances are captured by activated sludge in the wastewater treatment process and can be recovered from the water in the wastewater treatment process. However, hydrophilic substances are difficult to remove in the wastewater treatment process and often go through the treatment process without significantly reducing their concentrations [Gasperi et al. 2010; Donner et al., 2008].

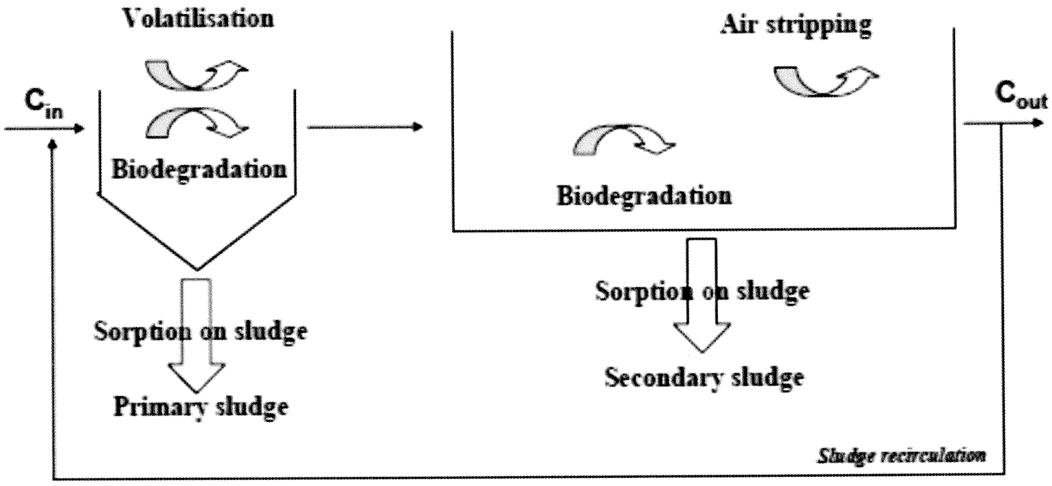

Figure 2. Methods of removing hazardous substances in wastewater treatment plants [Gasperi et al. 2010].

The removal efficiency of hazardous substances from the aqueous phase was found using formula 1:

$$\alpha\ (\%) = \frac{C_{0influent} - C_{0effluent}}{C_{influent}} \times 100\ \% \qquad (1),$$

In Formula 1, $C_{infuent}$ and $C_{effluent}$ denote the concentration of the chemical in the influent and in the effluent of the wastewater treatment plant respectively, and α denotes the removal efficiency (%) of the hazardous substance in the wastewater treatment plant.

On the hazardous substance side (Table 9) it can, however, be seen that barium, cadmium, lead zinc, copper, di-2-ethylhexyl phthalate, petroleum products, toluene and chloroform are most successfully removed in the cleaning process. The removal efficiency of some hazardous substances is relatively low (e.g. dibenzo(a,h)anthracene and fluorene).

The negative efficiencies in Table 9 mean that substances were only found in the effluent of the wastewater treatment plant. This may be due to the random nature of the sampling (the substance was not introduced to the treatment plant at the time of sampling but was done previously) or to the nature of the analytical method (e.g. effluent samples may contain other substances that interfere with successful extraction in sample preparation).

Table 9. Efficiency of removal of hazardous substances in the wastewater treatment plant(s)

Substance	Efficiency of biological treatment	Efficiency of the treatment plant
Arsenic (As)	(66.4 ± 9.2) %	76.7%
Barium (Ba)	(79.5 ± 5.8) %	91.2%
Mercury (Hg)	(38.1 ± 12.5) %	57.6%
Cadmium (Cd)	(82.3 ± 4.0) %	84.6%
Chrome (Cr)	(80.1 ± 8.4) %	67.9%
Nickel (Ni)	(52.1 ± 2.8) %	65.1%
Lead (Pb)	(93.6 ± 3.8) %	95.6%
Tin (Sn)	(61.5 ± 8.2) %	-
Zinc (Zn)	(84.9 ± 4.4) %	92.4%
Copper (Cu)	(79.6 ± 21.5) %	97.4%
4-Nonylphenol (branched)	-1669.2%	72.8%
4-tert-Octylphenol	14.3%	85.7%
AMPA	0.0%	(47.9 ± 20.6) %
Acenaphthylene	29.3%	(32.5 ± 45) %
Di-2-ethylhexylphthalate (DEHP)	93.8%	(92.3 ± 2.1) %
Dibenzo (a,h)anthracene	29.3%	29.3%
Dibutyl phthalate (DBP)	63.4%	63.4%
Diethyl phthalate (DET)	70.9%	(50.1 ± 29.5) %
Diisobutyl phthalate (DIBP)	77.4%	(58.4 ± 26.9) %
Diclofenac	-218.2%	(-64.6 ± 101.5) %
Phenanthrene	67.9%	(51.8 ± 22.7) %
Fluorene	35.7%	(35.7 ± 25.3) %
Naphthalene	15.8%	(75.3 ± 17.7) %
Petroleum products (hydrocarbons C_{10} - C_{40})	92.6%	(92.6 ± 65.4) %
Nonylphenol (total)	-1669.2%	72.8%
PAH total	79.5%	(95.5 ± 0.1) %
Perfluorobutaanhape (PFBA)	-	-50.0%
Pyrene	35.7%	35.7%
Tetrachloromethane	-	45.6%
Toluene	99.4%	(99.5 ± 0.2) %
Trichloromethane (chloroform)	99.8%	(99.8 ± 0.1) %

5 Summary

- The study examined the peculiarities of wastewater formation in the Põltsamaa wastewater collection area. The two largest industrial customers of the wastewater treatment plant provide on average 65% of the wastewater that reaches the treatment plant. The remaining 35% is rather domestic in properties (includes both domestic wastewater from domestic consumption and wastewater from other companies in the town). These food companies account for almost 90% of the carbon load and 32% of the nitrogen load and 21% of the phosphorus load. Most of the nitrogen and phosphorus load originates from other sources in the town.
- The wastewater treatment plant is very good at removing nutrients. During the study period, all effluent analysis results met the requirements of the water permit.
- Concerning hazardous substances, the limit values for effluents established in Regulation No. 61 of the Minister of the Environment were not exceeded during the study period. However, the levels of nonylphenols in effluents need to be considered with some caution. Although no violations of the limit values were detected during the study period, 2.3 µg/l of 4-nonylphenol was detected in the sample taken from the inflow to the polishing pond on 28.01.2020. Similar content was found in the wastewater of the right bank pumping station on the same day. There is one metal industry in the area which, due to the nature of its activities, could use nonylphenols, but during the fieldwork, it was not possible to sample the company's wastewater. Although the highest content of nonylphenols was found in the wastewater of Industry 5, the amount of wastewater discharged by this company into the public sewerage system represents only 0.1% of the daily hydraulic load of the wastewater treatment plant. At present, the Guidelines for the Use of Põltsamaa's Public Water Supply and Sewerage System contain all mechanisms for implementing sanctions, however, it is recommended to consult these companies first to make sure that Põltsamaa's two largest metal industry companies have brought their activities in line with REACH principles.
- Barium, cadmium, lead, zinc, copper, di-2-ethylhexyl phthalate, petroleum products, toluene and chloroform are most successfully removed in the cleaning process.
- The removal efficiency of some hazardous substances is relatively low (e.g. dibenzo(a,h)anthracene, fluorine), but still sufficient to ensure wastewater compliance.

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