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Harmful Substances in Wastewater, Possible Technical Solutions for Their Removal

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Declaration:

Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology, has not been previously submitted for doctoral or equivalent academic degree.

/Erki Lember/

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Ohtlikud ained reovees, võimalikud tehnilised lahendused nende eemaldamiseks

ERKI LEMBER

TTÜ KIRJASTUS

Contents

List of publications

The list of author’s publications, on the basis of which the thesis has been prepared. The academic publications are referred in the text as Paper I, Paper II, Paper III, Paper IV, Paper V:

I **Erki Lember**; Karin Pachel; Enn Loigu. (2016). Modelling diclofenac and ibuprofen residues in major Estonian seaside cities. Journal of Water Security, 2 (2), 1−7. ETIS classification 1.2.

II **Erki Lember**; Karin Pachel; Enn Loigu. (2017). Adsorption of diclofenac, sulfamethoxazole and levofloxacin with powdered activated carbon. In: 10th International Conference Environmental Engineering (1−7). Vilnius, Lithuania: Vilnius Gediminas Technical University Press "Technika". ETIS classification 3.1.

III **Erki Lember**; Karin Pachel; Enn Loigu. (2018). Heavy metals removal in biological wastewater treatment, dependent on process parameters. Desalination and Water Treatment [in press]. ETIS classification 1.1.

IV **Erki Lember**; Vitali Retšnoi; Karin Pachel; Enn Loigu. (2018). The combined interaction of heavy metals on the activated sludge process. Proceedings of the Estonian Academy of Sciences, 305-314. ETIS classification 1.1.

V **Erki Lember**; Karin Pachel; Enn Loigu. (2019). Removal of heavy metals and total organic carbon from wastewater using powdered activated carbon. Proceedings of the Estonian Academy of Sciences [in press]. ETIS classification 1.1.

Author’s contribution to the publications

Contribution to the papers included in this thesis is following:

Paper	Original idea	Study design and methods	Data collection and handling	Contribution to result interpretation and manuscript preparation	Responsible for result interpretation and manuscript preparation
I	EL	EL	EL, KP	EL, KP, EO	EL
II	EL	EL	EL	EL, KP, EO	EL
III	EL	EL	EL	EL, KP, EO	EL
IV	EL	EL, VR	EL, VR	EL, VR, KP, EO	EL, VR
V	EL	EL	EL	EL, KP, EO	EL

EL - Erki Lember
KP - Karin Pachel
EO - Enn Loigu
VR - Vitali Retšnoi

Introduction

Hazardous compounds such as heavy metals and pharmaceutical residues have become a serious environmental problem that is being tackled in many different fields of research. While the route of heavy metals into the environment is well known to us, the pharmaceutical residues is a relatively new problem faced by the pharmaceutical industry as well as the environmental technologists. The knowledge about these compounds contained in our environment and water cycle is a result of the rapid developments in analytical chemistry, which have brought the detection limits for examined parameters very low (ng/l in case of many compounds). Today, many of the scientists around the world are looking for a solution to this problem, but do it mainly by focusing on a specific substance of concern.

The main sources of heavy metals include products that contain heavy metals which we widely use, such as cosmetics, fuels, anti-corrosion chemicals, etc. Carried in wastewater and often also in stormwater, these compounds reach the wastewater treatment plants, which in Estonia still lack adequate technology for their removal. Most of the heavy metals accumulate in sewage sludge and a significant amount is carried to the environment with the effluent. It is hard to say what is the impact of heavy metals on the wildlife, after being discharged from the wastewater treatment plant into the environment, because the studies made have rather focused on individual compounds and their ecotoxicological characteristics. The results show that the quantities of heavy metals contained in the effluent of the municipal wastewater treatment plant, usually remaining in the range that can be measured in µg/l, do not present outright hazard, because for this, the concentrations should be 1000 times higher. But given their bioaccumulation and resistance in the environment, these compounds become hazardous. And, it is difficult to assess the combined interaction between all the hazardous compounds found in the environment and the wildlife.

The pharmaceuticals are designed to be biologically active and resistant, in order to have a guaranteed effect in the body. The activity of molecules in pharmaceuticals is what makes these compounds potentially hazardous to the environment. Pharmaceuticals are consumed both by humans and animals, but just a small part of pharmaceuticals is degraded in their metabolic system, while most of it is excreted with faeces and reach the wastewater treatment plants after running through the sewer system. In the wastewater treatment plant, some of the pharmaceutical residues accumulate in sewage sludge similarly to heavy metals, some degrade during biological treatment process, but also a large part is discharged to the environment with the effluent. In the case of pharmaceutical residues, a major threat is seen in their combined effect where different active ingredients, as a result of reaction with each other, can become potentially hazardous. Another complicated area is the pharmaceutical metabolites that are formed in partial degradation of pharmaceuticals, whether in the body, in the course of the biological treatment, or in the environment. As these compounds are mostly unknown, their long-term effect is almost impossible to assess.

Since the studies made have focused on the impact of individual hazardous compounds and their removal from wastewater, the present study aims to assess the problem of pharmaceutical residues and heavy metals as a whole. Furthermore, the study analyses the impact of various hazardous compounds on the environment, on the wastewater treatment process, and suggests the best possible technological solution for removing pharmaceutical residues and heavy metals from wastewater.

Abbreviations

AMO	amoxicillin
AOBs	ammonium oxidizing bacteria
APAC	powdered activated carbon dosed to aeration tank
As	arsenic
BOD_7	biochemical oxygen demand (7 days)
C_0	initial concentration of adsorbate
Cd	cadmium
C_e	equilibrium concentration of adsorbate
C_{HeM}	concentration of heavy metal in influent or effluent (mg/m^3)
C_n	final concentration of adsorbate
COD	chemical oxygen demand
Cr	chromium
Cu	copper
DCF	diclofenac
DOX	doxycycline
E1	estrone
E2	17-beta-estradiol
EE2	17-alpha-ethinylestradiol
F/M	food to microorganism ratio
GAC	granular activated carbon
H_2O_2	hydrogen peroxide
HeM	heavy metals
HRT	hydraulic retention time (h)
IBF	ibuprofen
K	Freundlich adsorption constant (mg/g)
$K_{average\text{-}c}$	concentration of pharmaceuticals in effluent
LFX	levofloxacin
M	mass of heavy metal (mg)
$M_{influent\ or\ effluent}$	total mass of heavy metal in influent or effluent (mg)
MLSS	mixed liquor suspended solids
MLSS(a)	influent flowrate of aeration tank (m^3/d)
MLSS(a)	mixed liquor suspended solids in aeration tank (kg/m^3)
MLSS(w)	mixed liquor suspended solids in waste activated sludge (kg/m^3)
$M_{removal}$	metabolism removal rate in human body
m_s	weight of adsorbed adsorbate (mg)

n	heterogeneity factor
NH_4	ammonium
Ni	nickel
NO_2	nitrite
NO_3	nitrate
NOBs	nitrite oxidizing bacteria
NSAID	non-steroidal anti-inflammatory drugs
N_{tot}	total nitrogen
O_2	maximum air consumption
O_3	ozone
PAC	powdered activated carbon
Pb	lead
$P_{population}$	number of population in the city analysed in year under review
P_{tot}	total phosphorus
q_e	adsorbate equilibrium concentration
Qe	removal of heavy metals per 1 g of PAC (PAC and APAC tests)
qe_{max}	maximum adsorption capacity (mg/g)
$Q_{influent\ (d)}$	influent flowrate of aeration tank (m^3/d)
$Q_{influent\ (h)}$	influent flowrate of aeration tank (m^3/h)
SCADA	Supervisory Control and Data Acquisition
SMX	sulfamethoxazole
SRT	sludge retention time
SS	suspended solids
SS(e)	suspended solids in effluent of clarifier (kg/m^3)
SS(i)	suspended solids in influent of aeration tank (kg/m^3)
T °C	temperature in aeration tank
TETR	tetracycline
TOC	total organic carbon
$V_{aeration\ tank}$	total volume of aeration tank (anoxic+aerobic, m^3)
V_{WAS}	flowrate of removed waste activated sludge from clarifier (m^3/d)
WW	wastewater
WWTP	wastewater treatment plant
$WWTP_{removal}$	removal rate in WWTP
Zn	zinc

1 Background

1.1 Heavy metals and their sources

Heavy metals are defined as metals with a density of more than 5 g/cm^3 and toxic to living organisms at low concentrations (Kobielska, Howarth, Farha, & Nayak, 2018a). Heavy metals are the elements of the earth of natural origin, with some of them serving as necessary trace elements for us in a dissolved form (Chipasa, 2003a; Ramrakhiani, Ghosh, Sarkar, & Majumdar, 2016). Heavy metals are mainly used in electronics industry, plastics industry as stabilisers in PVC, paints, anti-corrosion agents, cosmetics, etc., from where they reach the environment by being carried by air, stormwater or wastewater (González-Acevedo, García-Zarate, Núñez-Zarco, & Anda-Martín, 2018; Kobielska et al., 2018a; Sani, Gaya, & Abubakar, 2016). But heavy metals may also be released into the environment through natural processes such as erosion, where as a result of the weathering of rocks, heavy metals are released, thereby reaching the water circle (Kobielska et al., 2018a).

The ever more stringent requirements applicable to the industries that discharge their effluents into the sewer system and to the municipal wastewater treatment plants, and the fact that heavy metals are avoided already in the product development stage have reduced the load of heavy metals in many cities. But the treatment plants often receive also stormwater carrying a variety of heavy metals, such as Zn and Cu (Charters, Cochrane, & O'Sullivan, 2016; Goonetilleke et al., 2017). Charters (2016) found in her study, in which she examined copper and galvanized roofs, that the runoff from these roofs contained copper and zinc in concentrations ranging from 397 to 1970 μg/l and from 1663 to 7860 μg/l, respectively (Charters et al., 2016). Also, heavy metals are carried to the sewer system with precipitation, bringing metals contained in car emissions, and higher concentrations of heavy metals have also been observed in coal-fired power plant fumes falling on the ground with precipitation (Bernard, Jimoh, & Odigure, 2013; Gunawardana, Goonetilleke, Egodawatta, Dawes, & Kokot, 2012). Precipitation is also the transporter of heavy metals contained in brake pads and car tyres. Since the stormwater volumes are very large, a separate treatment of that water would be economically impossible (Goonetilleke et al., 2017; Gunawardana et al., 2012).

The main sources of heavy metals contained in wastewater include cosmetics, pharmaceuticals and, in small quantities, food (Sani et al., 2016; Ullah et al., 2013). Sani (2016) found in his study, in which he examined the cosmetics, such as skin lightening creams, lipsticks and face powders, that these products contained the following heavy metals, starting from the highest concentration on the left: Mn>Ni>Cu>Cd>Pb>Cr (Sani et al., 2016).

Table 1.1 Sources of various heavy metals (González-Acevedo et al., 2018; Kobielska et al., 2018a; Sani et al., 2016; Tahri et al., 2017).

Heavy metal	**Anthropogenic sources**
Zn	Anti-corrosion agents, roofs, road barriers, PVC stabilizers, skin creams, welding, rubber industry, pharmaceutical products, paints
Ni	Anti-corrosion agents, roofs, road barriers, PVC stabilizers, skin creams, welding, rubber industry, pharmaceutical products, paints
Pb	Plastic, various alloys, Pb batteries
Cu	Roofs, water pipes, kitchen appliances, alloys, cosmetics, pharmaceutical products
Cr	Wood industry, cooling water piping protection, plating, textile and leather industry, colour pigments
Cd	Plastic stabilizers, Ni-Cd batteries, coal burning

Table 1.1 lists the main sources of heavy metals. Zn is widely used as an anti-corrosion agent and a stabiliser in PVC, and also in various cosmetics where it should inhibit the growth of bacteria, i.e. have a disinfecting effect (Kobielska et al., 2018a). The dermatologists believe that many of the cosmetics are harmful rather than helpful, because more than 10 000 different substances are in use, many of which are associated with cancer, malformations, and compounds hindering the child development. The analyses of cosmetics have shown that, for example, the lipsticks contained the following heavy metals, in the ranking starting from the highest concentration: Fe>Pb>Cu>Zn>Ni>Co>Cd>Cr (Ullah et al., 2013). In particular, the problem of these compounds is that they are in direct contact with people, because they are spread on skin or lips. Heavy metals react with amino acids of proteins and -COOH, $-NH_2$ or -SH that disturb the cell functions or destroy them. A survey carried out in the USA revealed that 63% of the girls in the age of 7-19 regularly use lipstick (Ullah et al., 2013) and it follows from Table 1.1 that the plastics industry is one of the industries, requiring more attention with regards to heavy metals, because some of the plastic products contain e.g. Zn, Ni, and Cd, which increase the load to the environment, also as a direct pollution, e.g. by means of microplastics.

1.1.1 Spread and impact of heavy metals in the environment

Heavy metals are mainly introduced into the environment by the air or water, but the main source of heavy metals is the soil, i.e. the water only has a role of transporting heavy metals and increasing their mobility (Geng, Wang, Luo &, 2015). If heavy metals that spread in the air mainly put us at risk when the air is inhaled and heavy metals bioaccumulate in the body, then the route of heavy metals to the blood circulation mainly goes through the wastewater treatment plants, stormwater, and erosion of rocks (Goonetilleke et al., 2017; Kobielska et al., 2018a). The stability and high solubility of the heavy metal compounds also have a great role to play in this process (Burakov et al., 2018). Only ca 5% of heavy metal pollution in surface waters comes from the air pollution. Furthermore, indirect effect occurs where, for example, acid rains accelerate the erosion of rocks and the migration of heavy metals in the environment (Pan, Lu, & Lei, 2017; Weimar, 2014). Figure 1.1 illustrates the migration of heavy metals in the environment.

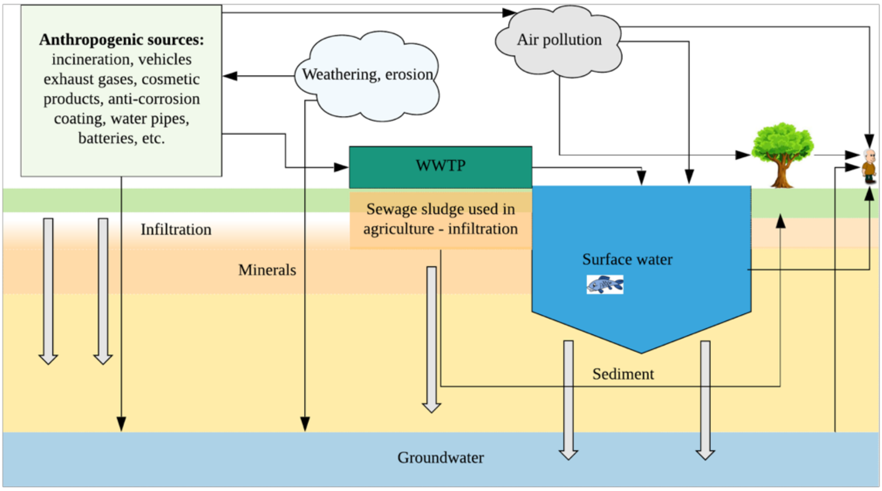


Figure 1.1 Migration of heavy metals in/to the environment *(Chowdhury, Mazumder, Al-Attas, & Husain, 2016; Kobielska et al., 2018a; Ma, Egodawatta, McGree, Liu, & Goonetilleke, 2016; Men et al., 2018; Napa, 2017).*

It follows from Figure 1.1 that heavy metals mainly get into the blood circulation in two ways: either directly through the wastewater treatment plants and stormwater outlets or through the air pollution, groundwater is polluted through infiltration. The load of heavy metals from infiltration can increase due to the compounds contained in rocks, and this may not be only from the anthropogenic sources. Tedoldi (2016) examined storm water outlets and infiltration, and found that when it came to the open ditches, then the stormwater caused point source pollution in the relatively narrow area, i.e. heavy metals concentrated in the immediate vicinity of the outlet. Earlier studies have confirmed that heavy metals accumulate in the top layers of soil and from there slowly infiltrate into the groundwater (Tedoldi et al., 2017). It follows from Figure 1.1 that through the water circle this pollution reaches the plants and, either directly or by means of food, the humans.

The greatest hazard is seen in Cd, Cr, As, Hg, Pb, Cu, and Zn, since the effects of these heavy metals on organisms have been identified (Burakov et al., 2018). For example, the use of Cd, Co, Cr, Ni, and Pb in cosmetics was prohibited with the Directive 76/768/EEC, after their DNA-mutating characteristics had been revealed, possibly leading to the development of cancer (Ullah et al., 2013). But Cu and Zn are still widely used in pharmaceuticals and cosmetics as inhibitors of bacterial growth, i.e. these compounds are used to prevent the proliferation of microorganisms (Ullah et al., 2013). Some of the heavy metals are known to be important trace elements for us, but may cause various health damage in larger quantities (Burakov et al., 2018; Kobielska et al., 2018a). While many of the heavy metals act as important catalysts for enzymes in the body, ensuring the activity of enzymes, then heavy metals in large quantities become toxic to our body, because the enzymes that otherwise degrade casein, gluten or other nutrients, make the non-toxic nutrients toxic to us (Abdel Salam, Reiad, & ElShafei, 2011).

The maximum contaminant limit (MCL) for common heavy metals and their effects on humans are presented in Table 1.2.

Table 1.2 Provisional maximum tolerable daily intake and effects of common heavy metals (Burakov et al., 2018; Kobielska et al., 2018a).

Heavy metal	**MCL (mg/l)**	**Toxicity/effect**
Zn	0.8	Affects the metabolism of cholesterol, causes depression, lethargy
Ni	0.2	Associated with asthma, chronic lung diseases, contact dermatitis, is carcinogenic
Pb	$6*10^{-3}$	Toxic, global problem, causes cerebral, renal and nervous disorders
Cu	0.25	Causes hepatic damage, insomnia, Wilson's disease
Cr	0.05	Cr^{+3} is not very harmful, Cr^{+6} is carcinogenic, causes diarrhoea, nausea, headache
Cd	0.01	Causes Itai-itai disease, renal disorders and damage, is carcinogenic

Following describes some of the more serious incidents where the local population seriously suffered from the consequences of heavy metal pollution in drinking water. After Cd contamination that occurred in Japan on Jinzu-Takahara River after the Second World War, osteoporosis was observed among the population (Yoshida, Hata, & Tonegawa, 1999). In Bangladesh, 200 000-270 000 fatal cancer cases are associated with Cd contaminated groundwater. In India, surface water was contaminated with high concentrations of Cd, Cr, Cu, Ni, Pb, and Zn due to the discharges of a wastewater treatment plant to its receiving water, causing asthma and different skin diseases, e.g. chromium ulcers, to large number of people. The area had nearly 240 leather tanning factories, ceramics industries and Cr factories (Smith, Lingas, & Rahman, 2000). In Pakistan, it was found that the concentration of As in drinking water, ranging from 35.2 to 158 μg/l, caused skin lesions, and increased As content was found in human hair and blood. In India, in the town of Buldana, a chronic renal insufficiency spread among the population, caused by Cd and Pb contamination from phosphorus fertilizers and pesticides (Chowdhury et al., 2016). Heavy metals have also been used as a weapon, e.g. in the First World War, and to commit murders, and we are still dealing today with the consequences of these contamination cases (Ullah et al., 2013).

1.2 Pharmaceutical residues and their sources

The whole area of research on pharmaceutical residues in the environment started in 1990 in Pakistan and India, where a steep, nearly 95% decline was observed in the white-backed vulture (Gyps africanus) population. Examining the causes of death of the birds, it was found that the deaths had been a consequence of renal insufficiency, so the various toxic compounds in the environment, as well as a climate change were analysed, but at first, the reasons for the organ failures could not be identified. Detection of the causes continued with the examination of the food chain of birds, which revealed that the dead vultures had been eating free-range livestock, who was continuously treated with diclofenac for the prevention of infections on animals in case they accidentally injure themselves, which is a common method applied in veterinary medicine. The concentrations of diclofenac found from the kidneys of the dead birds ranged from 0.051 to 0.063 µg/g. Before that case, no one had thought of the ecotoxicological impact of pharmaceuticals in the environment (Fent, Weston, & Caminada, 2006; Oaks et al., 2004).

In recent years, several studies have shown that the active ingredients and residues of different pharmaceuticals can be found from the aquatic environment within the detection range (µg/l and the ng/l). The highest concentrations were found for anti-inflammatory drugs (NSAID-s) and analgesics. For example, in Germany, ca 87.5 million prescriptions were issued in 2001, plus the pharmaceuticals sold over-the-counter (Cleuvers, 2004). The ever growing and ageing population and consequently higher consumption of pharmaceuticals make many scientists concern about whether and what kind of impact the pharmaceuticals can have on the environment (Cleuvers, 2004; Zhou, Zhang, Banks, Grover, & Jiang, 2009). For example, by today, 131 different pharmaceuticals have been detected in surface waters and groundwater sources in Germany (Weber et al., 2014). One of the problems that the scientists also have to face is analysing the pharmaceutical metabolites, because the majority of pharmaceuticals degrade, either in the metabolic system of the body or later in the environment, and form new compounds which are difficult to analyse, because we cannot predict the types of molecules forming under certain conditions. That is to say, without knowing what we are looking for, it is almost impossible to detect it, and it is even less possible to assess its impact on the environment (Ericson, Thorsén, & Kumblad, 2010; Langenhoff et al., 2013).

To control this problem, the EU has included diclofenac, 17-alpha-ethinylestradiol (EE2), 17-beta-estradiol (E2), estrone (E1), and macrolide in the watchlist of antibiotics, with the maximum permitted detection limit of the method in the monitoring 10 ng/l, 0.035 ng/l, 0.4 ng/l and 90 ng/l, respectively (EU 2015/495.). Sweden has set for itself maximum permitted levels that characterize the status of aquatic environment, which are: 10 ng/l for diclofenac, 0.007 ng/l for EE2 and 0.08 ng/l for E2, respectively (HELCOM, 2017). Many studies have also highlighted the antibiotics, such as sulfamethoxazole and levofloxacin, that have a toxic effect on algae already at low concentrations, as being substances of concern (Santos et al., 2010; Q-Q. Zhang, Ying, Pan, Liu, & Zhao, 2015).

Table 1.3 Extract of the best-selling pharmaceuticals in Estonia, Finland, Germany and Sweden (together), and in Estonia and in Sweden (separately) (Fent et al., 2006; HELCOM, 2017).

Pharmaceutical	**kg/y**	**Estonia kg/y 2014**	**Sweden kg/y 2014**
Paracetamol	529 935	16 950	338 007
Sulfamethoxazole	-	470	1700
Metformin	346 888	18 800	135 00
Macrogol	273 687	980	54 400
Ibuprofen	180 208	15 100	14 400
Mesalazine	41 966	685	17 100
Diclofenac	12 062	593	8800

It follows from Table 1.3 that the most widely consumed pharmaceuticals include paracetamol and metformin. Paracetamol is a common analgesic, metformin is used for the treatment of diabetes, and macrogol helps in case of constipation. Mesalazine is used as an anti-inflammatory pharmaceutical, and diclofenac and ibuprofen mainly as analgesics; diclofenac also has an anti-inflammatory effect (Bradley et al., 2016; Fatta-Kassinos, 2010; HELCOM, 2017). Contraceptives and their increasing use are also seen as a problem. Worldwide studies have shown that, on average, ca 30 000 kg of contraceptives (E1, E2, E3) are released to the environment every year. This is combined with the natural hormones, e.g. cattle oestrogens, the quantity of which, released in USA and EU, is believed to be ca 83 000 kg/y, that is twice as much as in case of humans. And the scientists are convinced that the natural oestrogen reaching the environment affects the living organisms (Adeel, Song, Wang, Francis, & Yang, 2017).

Ericson (2010) examined the effluent of various wastewater treatment plants and the surroundings of their receiving waters in Sweden, and detected diclofenac ranging from 0.2 to 7.1 µg/l, and ibuprofen in the range between 0.1 and 0.2 µg/l, and different NSAID-s in concentrations of up to 24 µg/l (Ericson et al., 2010). HELCOM study that focussed both on the Baltic Sea and the wastewater treatment plants, found measurable concentrations of diclofenac, ibuprofen and sulfamethoxazole in certain points of the Baltic Sea (mainly near the Eastern shore of Sweden). Carbamazepine and primidone were detected in nearly all the measuring points (HELCOM, 2017).

1.2.1 Migration of pharmaceutical residues and impact on the environment

Pharmaceuticals reach the environment from various points and parts of their lifecycle, such as production, use, and handling after expiring. Studies have shown that the effluents of pharmaceutical industry usually contain concentrations of these compounds that are low or not measurable, and therefore, key attention is paid to the handling of expired pharmaceuticals and the use of pharmaceuticals (Cleuvers, 2004; Fent et al., 2006).

Figure 1.2 illustrates the simplified migration of pharmaceutical residues in the environment. Pharmaceutical molecules are designed to be strong and biologically active, to ensure they have a guaranteed effect, and therefore, many of the pharmaceuticals do not degrade in the body and are excreted in unchanged form (Heberer, 2002; Ternes, 1998). These features make the pharmaceuticals hazardous to the aquatic environment (Fent et al., 2006). In the case of pharmaceuticals, there are two main routes. In the first case, a person consumes certain pharmaceutical, which degrades partially in the body, but most of it is excreted with urine or faeces that are discharged to the treatment plant. Some of the pharmaceuticals degrade in the treatment plant, depending on the applied treatment process, but most of it leaves the treatment plant or accumulates in the sewage sludge. Compounds contained in the effluent reach the water bodies where they slowly accumulate. Sludge is often used for the greening purposes and in some countries even in agriculture, and therefore, the pharmaceuticals contained in the sludge may bioaccumulate in the plants, or infiltrate into the soil and even into groundwater (Fent et al., 2006; Lienert, Güdel, & Escher, 2007; Lillenberg, 2011; Miège, Choubert, Ribeiro, Eusèbe, & Coquery, 2009). The second way of releasing pharmaceuticals to the environment is by handling them incorrectly: people either flush the unused and expired pharmaceuticals down the drain from where they reach the wastewater treatment plant, or throw them away with domestic waste, which in the case of older landfills may infiltrate with leachate into the soil and reach the groundwater.

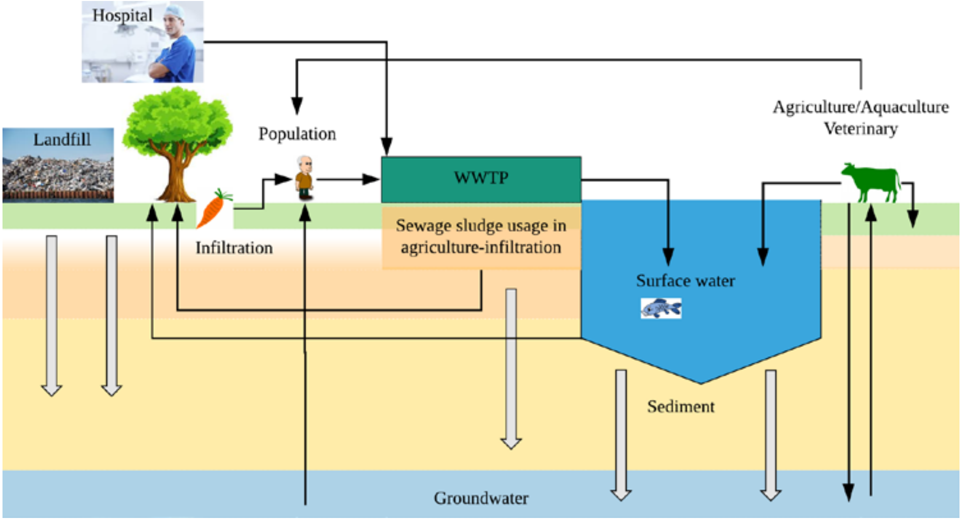


Figure 1.2 Migration of pharmaceuticals in the environment (Fent et al., 2006).

Since there are more than 3000 different active ingredients in use both for humans and in veterinary medicine, such as analgesics, NCAD-s, contraceptives, antibiotics, beta-blockers, lipid regulators, neuroactive compounds, etc., then it is difficult to identify the effect of all these pharmaceuticals and their interaction with the environment. And we need to add metabolites, which may also form hazardous compounds. Therefore, most of the studies focus on the active ingredients that are most widely used (Fent et al., 2006; He, Sutton, Rijnaarts, & Langenhoff, 2016; Margot et al., 2013).

Several methods have been developed to identify the pharmaceuticals that need the most attention, by assessing their impact on the environment and mapping the most hazardous compounds. Carlsson (2006) analysed the ecotoxicological effects of 27 different pharmaceuticals and found that the most hazardous compounds to the environment include diclofenac, ethinylestradiol, ibuprofen, metoprolol, norethisterone, oestriol and oxazepam (Carlsson, Johansson, Alvan, Bergman, & Kühler, 2006). Li (2016) confirmed this list of active ingredients that are hazardous to the environment, by adding only sulfamethoxazole (W. C. Li, 2014). But the ecotoxicological data obtained from these analyses may not always provide an adequate and necessary information if we want to know the long-term effects and the risks to the environment, since no specific rules apply on how to carry out and assess these ecotoxicological tests (Fent et al., 2006).

The main concern people have is related to the bio-accumulation of pharmaceuticals in our food, such as plants and animals, and their resistance to micro-organisms and antibiotic-resistant bacteria (Fent et al., 2006; Klatte, Schaefer, & Hempel, 2016; Skórczewski, Mudryk, Miranowicz, Perlinski, & Zdanowicz, 2014). It is difficult to assess the combined effects of various pharmaceutical residues in the body when, for example, Fent (2006) found that the mixture of many pharmaceuticals had a smaller ecotoxicological effect than the pure active ingredient (Fent et al., 2006).

1.3 Effects of heavy metals and pharmaceutical residues on the biological wastewater treatment

It follows from Figures 1.1 and 1.2 that a large part of the heavy metals and pharmaceutical residues reach the wastewater treatment plants. As the wastewater treatment process usually consists of mechanical, chemical and biological treatment, then it is the biological treatment that is the most-affected by various hazardous compounds. The biological treatment is designed to degrade organic matter (BOD) and perform the nitrogen and phosphorus removal. The nitrogen removal is a multiple-step process, performed by chemoautotrophs and heterotrophic micro-organisms, with chemoautotrophs being very sensitive to any changes in the environment, such as changes in temperature, light radiation, changes in loads, various hazardous compounds, etc (Henze, Loosdrecht, Ekama, & Brdjanovic, 2011). Therefore, the effects of heavy metals and pharmaceutical residues on the wastewater treatment process have started to gain more and more attention (Katsou et al., 2016; Sa & Engineering, 2010). Two aspects must be considered when looking at these effects: inhibiting effect and lethal effect, in case of the latter, it will take 2-8 weeks, depending on the water temperature, to recover the operation of the wastewater treatment plant (Antoniou et al., 1990; Hartmann, Skrobankova, & Drozdova, 2013).

1.3.1 Effects of heavy metals on the wastewater treatment

The direct effects of heavy metals on the micro-organisms have been separately examined for individual heavy metals. For example, Cr inhibits the metabolism of micro-organisms, causing a competition between the oxygen molecules and Cr. In the degradation of organic matter, both act as acceptors of electrons (Quintana, Olalla-Herrera, Ruiz-López, Moreno-Montoro, & Navarro-Alarcón, 2015).

Several reference methods are used to determine the effects of heavy metals on the biological treatment, such as ISO 9509:2006, ISO 8192-2006, and ISO 15522, all being based on measuring the oxygen consumption, i.e. in the case of inhibition, the metabolism of micro-organisms slows down or stops, thereby decreasing the oxygen consumption. Also, a bioluminescence test Mictorox is used, which measures the reduction in bioluminescence of *Vibrio fischeri* in the case of inhibition (Henze et al., 2011).

The main purpose of the biological wastewater treatment plant is the BOD, N and P removal, whereas the most sensitive process is the nitrification, which is carried out by two types of micro-organisms: ammonium oxidizing micro-organisms (AOB-s) and nitrite oxidizing micro-organisms (NOB-s).

$$NH_4^+ + 1{,}5O_2\ (AOBs) \rightarrow NO_2 - + H_2O + 2H^+ \tag{1}$$

$$NO_2 + 0{,}5O_2\ (NOBs) \rightarrow NO_3^- \tag{2}$$

The sensitivity lies in the growth rate of these micro-organisms, which is 0.9 and 0.5 for AOB-s and NOB-s, respectively, compared to, for example, the growth rate of 13.2 for heterotrophic micro-organisms that use carbon as an energy source. That is to say that the inhibition in the process is first observed as an increase in NO_2 concentration, because of the NNO bacteria being the most sensitive (Henze et al., 2011).

Series of studies have been conducted to determine the most hazardous heavy metal. Ong (2010) compared different studies and brought out the following ranking of heavy metals posing the greatest hazard to the wildlife: Cd>Cu>Zn>Cr>Pb, and according to another study: Cd>Cr>Cu>Pb>Zn with Zn being the least hazardous (Ong, Toorisaka, Hirata, & Hano, 2010).

When examining the effects of individual heavy metals on the activated sludge process it was found that, for example, 1 mg/l of Cu did not have any effect, in the case of Cr^{+6} it was revealed that the small concentrations even stimulated the growth of bacteria, but ca 80-160 mg/l was a lethal dose. Stimulatory effect was observed also in the case of small concentrations of Cr^{+3}, but the lethal dose for micro-organisms remained in the range of 160-320 mg/l. For Zn, the studies showed no effects on the micro-organisms in the wastewater treatment plant even at high concentrations (100 mg/l). However, very little is known about the combined effect of low concentrations of heavy metals (Özbelge, Özbelge, & Altinten, 2007).

The direct effect of heavy metals on the treatment process depends on many factors, such as temperature (micro-organisms recover faster at higher temperatures), mixed liquor suspended solids (MLSS) (most of the heavy metals are adsorbed by sludge), pH (which determines whether a heavy metal is dissolved in water or in the form of an insoluble compound). The dissolved compounds are biologically available to the plants (Huang et al., 2016; Ong et al., 2010; Oviedo, Márquez, & Alonso, 2002).

1.3.2 Effects of pharmaceutical residues on the wastewater treatment

The concentrations of incorrectly handled pharmaceuticals and pharmaceutical residues excreted from human metabolic system in the influent of the wastewater treatment plant usually remain in the range between µg/l and ng/l and have no direct effects on the biological treatment of the wastewater treatment plant. Widely used wastewater treatment technologies are not specifically designed to remove pharmaceuticals, just a small part of them is biodegraded – only ca 4 active ingredients out of 35 degrade 90% (Katsou et al., 2016).

However, the pharmaceutical concentrations in wastewater discharged from hospitals and livestock farms are many times higher, reaching even as high as 100-500 mg/l in the case of hospitals. In wastewater discharged from livestock farms, large quantities of tetracycline (TETR-100-1000 mg/l), doxycycline (DOX-0.5-16 mg/l) and amoxicillin (AMO-0.5-64 mg/l) have been measured. These measurements are in most cases taken from anaerobic wastewater without any prior biodegradation (Larsson, de Pedro, & Paxeus, 2007; K. Li, Yediler, Yang, Schulte-Hostede, & Wong, 2008). Several earlier studies have been conducted on the effects of pharmaceutical residues on the anaerobic digesters, but little is known about their effects on aerobic and anoxic processes, such as nitrification and denitrification (Katsou et al., 2016; Tang et al., 2011). The studies reveal that antibiotics inhibit the NOB bacteria and the anammox process, and that antibacterial pharmaceutical TETR has an inhibiting effect on Gram-negative bacteria. In the case of nitrification, it was found that the concentration of TETR at 200 mg/l fully inhibits the NOB bacteria (Halling-Sørensen, 2001).

Katsou (2014) has carried out the most comprehensive study of the effects of different pharmaceuticals on the biological wastewater treatment (2014). She found that a 250 mg/l dose of ibuprofen and paracetamol had the strongest inhibiting effect (99%) on the nitrification performed by NNO. In the case of biological phosphorus removal process, it was found that all the examined pharmaceuticals (paracetamol, DOX, TETR, ibuprofen, AMO) inhibited the phosphorus removal by >45%, and the inhibition at lower concentrations (e.g. DOX and TETR) was revealed in the case of combined effect of various pharmaceuticals (Katsou et al., 2016).

1.4 Removal of heavy metals and pharmaceutical residues from wastewater

The most common type of wastewater treatment plant is a plug-flow activated sludge plant (Figure 1.3), which involves the mechanical treatment where larger insoluble particles and small portion of nutrients and hazardous compounds adsorbed onto these particles are removed. In the next stage, insoluble organic matter is removed in primary sedimentation tank to reduce the energy needed for biological treatment. Removed organic matter can be stabilised either anaerobically or by using a composting process. In the biological treatment stage, i.e. in the bioreactor, BOD removal and nitrogen removal take place, carried out by AOB and NOB bacteria. Phosphorus removal is carried out either biologically, chemically, or as a combination of the two (Gray, 2004; Henze et al., 2011).

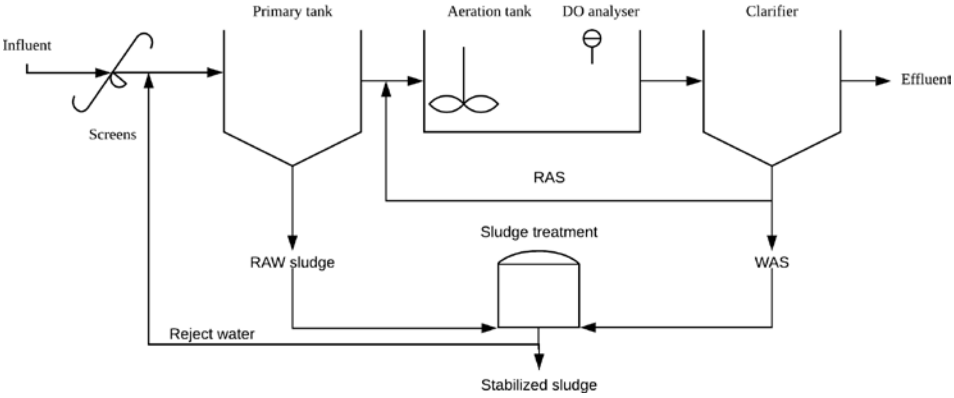


Figure 1.3 Plug-flow activated sludge plant.

Consequently, this type of wastewater treatment plants are not designed to remove hazardous compounds. A partial biodegradation of pharmaceuticals does take place, but most of the pharmaceuticals are either discharged with the effluent or accumulate in the sludge, thus reaching the environment (Carlsson et al., 2006; Haiba, 2017; Lillenberg, 2011). To a minor degree, studies have been conducted to find the ways to control these processes, for example, how to increase the adsorption of heavy metals to sludge or increase the degradation of pharmaceutical residues in the biological treatment. But due to the stringent maximum levels set for heavy metals (e.g. in Estonia, 50 µg/l for Zn, 34 µg/l for Ni, 15 µg/l for Cu, 5 µg/l for Cd, 50 µg/l for Cr, 10 µg/l for As, and 41 µg/l for Pb) and the lack of knowledge about the risks related to pharmaceutical residues, various studies have been carried out to find the best possible technological solution for their safe removal (Carletti, Pavan, Bolzonella, & Cavinato, 2003; HELCOM, 2017; Köhler et al., 2012; Lember, Pachel, & Loigu, 2017; Rattier, Reungoat, & Gernjak, 2012; Valitsus, n.d.).

1.4.1 Removal of heavy metals from wastewater

The removal of heavy metals from wastewater has become a necessity because of their toxic characteristics and accumulation in the environment. Also, particularly the industrial companies have economic motivators to reduce their energy consumption, water consumption, and environmental pollutants that are subject to taxes in many countries. For example, Cd, Hg, Pb, and Ni are listed as priority hazardous substances, subject to pollution charge, which is 28 026 EUR/t in Estonia for 2018.

In terms of technology, there are three ways to remove heavy metals: biological, physical and chemical removal. Each of these technologies has its advantages and disadvantages, for example, biological removal is not possible at high concentrations of heavy metals, because they suspend the metabolic activities of bacteria and therefore, the biosorption will not take place. The following solutions are applied to remove heavy metals: ion exchange, adsorption, filtering, electrodialysis, coagulation, membrane filtration, microbiological biosorption, biosorption with algae, etc.

Coagulation is the most commonly applied technology to remove heavy metals from wastewater. The aim of the coagulation is to coagulate the dissolved heavy metals into highly insoluble compounds, such as carbonates, sulphides and hydroxides. If normally the heavy metal compounds in water, often in the form of colloid particles, have the same density as water, then these particles do not settle but are at the state of equilibrium (Ghernaout, 2015). To increase the density, coagulant is added, forming compounds between the coagulant and heavy metals that are heavier than water and thereby able to settle. The coagulated heavy metals are removed with the sludge.

$$M^{+2}+2(OH)^{-}\leftrightarrow M(OH_2)\downarrow \tag{3}$$

where M^{+2} is a heavy metal to be removed and OH^{-} is a coagulant (Barakat, 2011).

The coagulation efficiency depends on many factors such as pH, temperature, alkalinity, mixing speed, type of coagulant, etc (Renault, Sancey, Badot, & Crini, 2009). Basically, the same coagulants, such as $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$, are used both for the drinking water and wastewater treatment. Coagulation does not enable to remove 100% of heavy metals, therefore, various technologies often have to be combined and the biggest disadvantage is the increased formation of waste activated sludge, containing higher concentrations of hazardous compounds than there would be without the coagulation (Carolin, Kumar, Saravanan, Joshiba, & Naushad, 2017; Yu, Han, & He, 2017).

Ion exchange is a separation process that separates different metal ions from wastewater. In simple terms, this means that in the ion exchanger, weaker metal is pushed out by stronger metal, i.e. the metals change places. This is a very effective solution and, as an advantage compared to the coagulation, no additional waste activated sludge is produced. The downside is that this method cannot be used for the treatment of wastewater containing high organic pollution, because the rapidly growing biofilm that emerges on the ion exchanger will prevent the work of the exchanger (Barakat, 2011). In the case of heavy metals, mainly cationic, acid or slightly alkaline ion exchange materials (resin) are used (Bilal et al., 2013). Among the natural materials, attention has mainly been on zeolites, which has enabled to achieve the treatment efficiency of even as high as 98% for e.g. Cu, Cd, Pb, and Zn (Carolin et al., 2017; Pepe, de Gennaro, Aprea, & Caputo, 2013).

Membrane filtration is ever-increasingly used for the separation of suspended solids and organic compounds, as well as inorganic compounds, e.g. heavy metals. Depending on the contaminants to be removed from wastewater, the size of the membrane pores is chosen, applying respectively either microfilters, ultrafiltration, nanofiltration, or a reverse osmosis. For the separation of heavy metals, ultrafiltration with the pore size ranging from 5 to 20 nm and molecular weight between 1000-100 000 Da is sufficient. Similarly to the coagulation, the treatment efficiency of the membrane filtration depends on the pH of water, because this determines the type of heavy metal compounds in water (dissolved, insoluble) (Carolin et al., 2017). The problem with the membrane filters is that they only concentrate the pollution and the retentate, i.e. the concentrate still needs a further processing (Barakat, 2011).

Biosorption is a technology gaining more and more popularity and being examined by numerous scientists today. The biggest advantage of this technology is seen in the fact that it is well-suited for removing namely the low concentrations of heavy metals. The treatment is similar to the adsorption processes, including a solid phase (sorbent) and a fluid phase (solvent). Both living biomass and dead biological material is used (Abdel

Salam et al., 2011; Amuda, Adelowo, & Ologunde, 2009; Mata, Blázquez, Ballester, González, & Mu, 2009). The advantage of using the dead mass is that it does not need any specific living conditions for the heavy metal removal to function, a filter-type device or a mixer and a later separation of biomass is enough. Biosorbents may include, for example, bacteria, algae, yeasts, husks, etc. The major advantage of these adsorbents is the low price, which makes their use attractive to many companies (Carolin et al., 2017). The main factors affecting the efficiency of sorption include temperature, pH, adsorbent dose, metal concentration, retention time of the process (Carolin et al., 2017). Following removal efficiencies have been achieved with the dead algae biomass: 64.7 mg/g for Cu, 64.6 mg/g for Cd, 68.9 mg/g for Pb. Dead biomass is usually more effective, because with the living biomass, the removal only functions in the growth phase of the algae, which is a slow process. Because the bacteria form a sticky material on their surface, their adsorbing characteristics are better than those of the algae. For example, in the case of *Escherichia coli*, the maximum removal found for Cr is 6329 mg/g (Carolin et al., 2017).

In addition to biosorption, better removal of heavy metals from wastewater under certain conditions has been observed also in the activated sludge process. For example, Özbelge (2005) found that the longer the retention time of the process, the higher the sorption of heavy metals in the sludge, but these tests were performed under laboratory conditions and with one heavy metal only (Özbelge, Özbelge, Tursun &, 2005). A correlation has also been found between the sludge retention time (SRT) and removal of heavy metals where longer sludge age increased the removal efficiency, however, after reaching a certain sludge age, the amount of heavy metals accumulating in the sludge may become so large that it starts to have an inhibiting effect on the biological treatment (Gulyás, Pitás, Fazekas, & Kárpáti, 2015; Ong et al., 2010; Sonali, Jayant, & Sunil, 2014). The correlation found between MLSS and removal of heavy metals indicates that greater MLSS reduces the removal of heavy metals, although one might assume that the greater mass will improve the removal. This correlation is probably caused by the screen effect between the biomass and heavy metals, which prevents the sorption (Hammaini, González, Ballester, Blázquez, & Muñoz, 2007; Wu, Zhang, & Wang, 2004).

Electrodialysis, in fact, is a membrane separation, where the ions move through the ion-selective membrane and moving force behind this is the electric potential. Two types of membranes, anionic and cationic membranes, are applied in electrodialysis (Barakat, 2011; Ebbers, Ottosen, & Jenssen, 2015). By electric potential, anions start moving towards the anode and cations start moving towards the cathode, and this way, water is cleaned from heavy metals that accumulate on the cationic membrane surface. Electrodialysis treatment has the advantage that even though water may have the toxic characteristics, this does not affect the treatment efficiency. The disadvantages include, similarly to the membrane filters, scaling and clogging that cover the membranes and thereby reduce the capacity of the process (Barakat, 2011; Carolin et al., 2017; Ebbers et al., 2015).

Adsorption is a process of separating the removable substance in the aqueous phase where it concentrates to the surface of an adsorbent, due to Van der Waals forces (Al-Saydeh, El-Naas, & Zaidi, 2017). Today, the adsorption process with activated carbon has become one of the most important methods of removing hazardous compounds, e.g. heavy metals, from wastewater and drinking water. Tests that were carried out on the pilot devices have shown that the adsorption process is characterised by the small operating costs and small biofouling, which therefore makes it one of the best possible future solutions for the removal of heavy metals in the wastewater treatment plant, because on the top on all, this process also ensures very high treatment efficiency (Barakat, 2011; Carolin et al., 2017; Zanin et al., 2017). The use of adsorption is difficult because of its sensitivity to temperature and pH, and since it is an equilibrium process, also to the concentration of the removed substance.

Activated carbon is a form of carbon that has been processed in the course of various processes, so as to make the material as porous as possible. This is achieved by heating the material in anaerob environment up to 1000 °C, which increases the size of pores, i.e. the inner surface, and by the further cleaning of pores with water vapour. Activated carbon is mainly produced from biomass, such as wood, coconut shells, coal or lignite, but scientists keep looking for new materials that could be used to produce good absorbents in a cheap and efficient way. Good absorbing characteristics of the activated carbon come from its large pores and the surface area of the pores. Although the activated carbon adsorption is a physical process without any chemical bonds, the bond created is, however, still very strong (Davis, 2010; Henze et al., 2011).

Mainly two types of activated carbon are used in the water treatment: powdered activated carbon (PAC) and granulated activated carbon (GAC). The PAC is mostly produced by grinding the GAC and it is characterized by the larger surface area compared to GAC. Figure 1.4 illustrates how the surface area depends on the size of the faction of activated carbon.

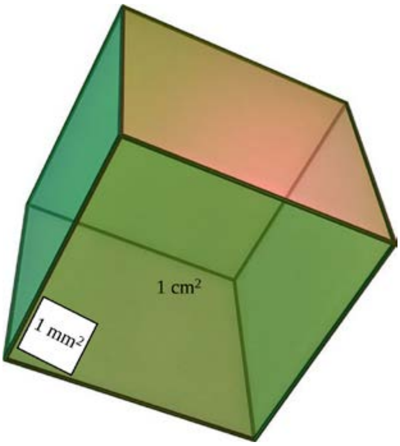


Figure 1.4 Total surface area of the big cube is 6 cm^2, if the cube is broken into 6 mm^2 cubes, the total surface area of all the cubes is 10 000 cm^2.

It follows from Figure 1.4 that breaking the originally 6 cm^2 GAC into a 6 mm^2 GAC will increase the total working surface area of PAC to 10 000 cm^2. Because the characteristics of the activated carbon depend on the size of the working surface, this example demonstrates well why PAC is a more effective adsorbent than GAC.

According to different studies, the following removal efficiencies have been found for the activated carbon adsorption, e.g. 61 mg/g for Cu, 22 mg/g for Cd, 29 mg/g for Zn, 33 mg/g for Ni, and 10 mg/g for Cr (Ong et al., 2010). However, the results are highly dependent on the characteristics of water outlined above and therefore vary a lot.

1.4.2 Removal of pharmaceutical residues from wastewater

While there are no maximum permitted levels established for pharmaceutical residues, a lot of work has already been done in developing technologies for their removal. The main technologies that have been used in the attemtps to remove the pharmaceutical residues include oxidation (O_3, H_2O_2), adsorption, TiO_2+UV, Fenton, membrane filtration (Alvarez-Corena, Bergendahl, & Hart, 2016; Giannakis et al., 2015; Meinel, Ruhl, Sperlich, Zietzschmann, & Jekel, 2015). However, if the aim is to remove these compounds in the municipal wastewater treatment plant, then the most realistic technologies include O_3 or activated carbon, or their combination, because other technologies would appear as too expensive for such volumes of water (Beltrán, Pocostales, Alvarez, & Oropesa, 2009; Margot et al., 2013).

Advanced oxidation, either with H_2O_2 or O_3, is one of the most common processes to remove pharmaceutical residues. It has been found that already small, 3-8 mg/l doses of O_3 oxidize most of the pharmaceuticals. However, the biggest disadvantage is the formation of unknow by-products, which may pose a potential hazard to the environment, the advantage, however, is that some of these by-products are biodegradable (Margot et al., 2013).

Adsorption of pharmaceuticals works in the same way as adsorption of heavy metals. The studies that have been carried out with both GAC and PAC found that the most effective PAC dose to remove these micropollutants is 10-20 mg/l. As some pharmaceuticals may have too large molecules for adsorption, then it is necessary to combine this process with deep oxidation (Margot et al., 2013; Nam et al., 2015; Okeola & Odebunmi, 2010). Margot (2013) carried out a study, comparing the processes with O_3 and PAC, where it appeared that, for example, the amount of diclofenac decreased 94% with ozonation and 69% with PAC, and the amount of sulfamethoxazole 93% and 64%, respectively. But in the case of ozonation, unknown by-products may have been formed (Margot et al., 2013). Meinel (2015) carried out a pilot-scale testing where he found the removal efficiency for diclofenac 30 µg/g (PAC), which is almost 1000 times lower compared to that of heavy metals (Meinel et al., 2015).

1.4.3 Combined removal of hazardous compounds from wastewater

The wastewater treatment plants are designed, first of all, to remove N, P, BOD and SS, but the increasingly high demands on the effluent discharged from the wastewater treatment plants means installing a further treatment stage that would cope with both heavy metals and various organic micropollutants, such as pharmaceutical residues, pesticides, herbicides, etc. So far, the majority of the studies have focused on providing solutions to individual problems, but lacked an integrated view on the problems. Therefore, it is important to find a method or a combination of wastewater treatment methods that would cope with the removal of all the substances listed above, where applicable. Table 1.4 compares the most widely used technologies to remove heavy metals and organic substances.

- (-) means that the method cannot be applied to remove the compounds;
- (+/-) indicates that some of the problematic compounds are partly reduced, but wastewater may need to undergo further treatment stage in order to meet the maximum levels;
- (+) efficiently removes the examined pollutants.

Table 1.4 Comparison of technological solutions to remove heavy metals and organic micropollutants (Carolin et al., 2017; Chipasa, 2003a; Fang et al., 2018; Giannakis et al., 2015; Hammaini et al., 2007; Meinel et al., 2015; Rattier et al., 2012; Wu et al., 2004).

Technology	**Heavy metals**		**Organic micropollutants**	
Advanced oxidation (O_3, H_2O_2)	-	does not remove heavy metals	+/-	oxidizes organic compounds, but by-products are formed with the unknown effects
Advanced oxidation (O_3, H_2O_2) + PAC/GAC	+	removes only in PAC/GAC stage	+	oxidizes organic compounds and by-products are removed with activated carbon
Adsorption (PAC/GAC)	+	removes most of the heavy metals, but control of the process is complicated and expensive	+/-	removes the majority of organic substances, problem with compounds that have large molecules and freely soluble compounds that adsorb less
Coagulation	+/-	many of the heavy metals can be removed, but it is often necessary to adjust the pH. Chemical sludge is formed.	-	indirect partial removal by sorption
Biosorption (micro-organisms)	+	the process is hard to control, but enables to move HeM from aqueous phase to sludge phase - sludge is formed, which needs	+/-	only possible if the compounds are not toxic

		separate processing, e.g. incineration.		
Electrodialysis	+	works well and is widely used in industrial wastewater treatment	-	does not work for removing the organic substances
Membrane filtration (UF, RO)	+/-	concentrates heavy metals, but further treatment of retentate, e.g. with GAC is needed	+/-	concentrates organic substances, but further treatment of retentate, e.g. with GAC is needed

It follows from Table 1.4 that advanced oxidation is effective in removing the organic pollutants, but this method does not remove the heavy metals and does not guarantee the full oxidation of organic pollutants (Epold, n.d.; Giannakis et al., 2015). That is to say, there is a risk that by-products are formed, which may react with other substances, forming even more hazardous compounds. To avoid this, it is important to combine the deep oxidation with the activated carbon adsorption, which removes most of the produced by-products (Margot et al., 2013; S. Zhang, Gitungo, Axe, Dyksen, & Raczko, 2016). Prior oxidation helps to improve the adsorption of large molecules, which may be otherwise poorly removed (S. Zhang et al., 2016). Coagulation only is suitable for the removal of heavy metals and only indirectly removes organic compounds due to the coagulation process where colloid particles stick together to form settling particles that are later removed (Carolin et al., 2017; Kobielska, Howarth, Farha, & Nayak, 2018b). Biosorption is relatively good in removing heavy metals, as long as the concentration is non-toxic, and to some degree, it also removes the organic substances (Carolin et al., 2017; Hammaini et al., 2007; Ramrakhiani et al., 2016). Electrodialysis is a technology only suitable for the removal of heavy metals, and does not allow to remove pharmaceutical residues (Carolin et al., 2017; Kobielska et al., 2018b). Membrane filter separates heavy metals and organic micropollutants, but produces a retentate, which needs further treatment, e.g. a advanced oxidation + activated carbon (Carolin et al., 2017; Hu, Shang, Deng, Heijman, & Rietveld, 2014).

2 Aims and objectives of the study

The aim of this doctoral thesis was to explore the release of hazardous compounds such as heavy metals and pharmaceutical residues into the wastewater treatment plant, and the impact of heavy metals on biological treatment, and to suggest the best possible technological solution for their removal. Earlier studies have focused on the individual removal of the examined compounds and there is a lack of materials on the combined treatment technologies that could be immediately implemented in the wastewater treatment plants. Also, there are no studies on the combined effects of heavy metals on the biological treatment that would have been carried out in an operating wastewater treatment plant. Little is also known about the sorption of heavy metals by the activated sludge and how to control this process.

The objectives of this doctoral thesis are:

- Develop load models for the pharmaceuticals diclofenac and ibuprofen found from the receiving waters of the largest wastewater treatment plants around the Baltic Sea and assess their possible effects on living organisms. (Paper I)
- Analyse the use of PAC for the removal of nonsteroidal anti-inflammatory pharmaceutical diclofenac and two antibiotics, sulfamethoxazole and levofloxacin, from wastewater. (Paper II, V)
- Analyse the load of heavy metals in the municipal wastewater treatment plant. (Paper III, IV, V)
- Examine the possibility to control the sorption of heavy metals in the existing activated sludge treatment plants. (Paper III)
- Assess whether the low concentrations of heavy metals have any combined effect on the efficiency of the biological wastewater treatment. (Paper III, IV)
- Suggest an optimum technological solution for removing heavy metals and hazardous organic compounds. (Paper II, V)

3 Methodology and tests

3.1 Development of load models for pharmaceutical residues (Paper I)

In order to understand the size of the loads of pharmaceutical residues that theoretically reach the Baltic Sea through the major wastewater treatment plants, a theoretical model of these loads was developed, estimating theoretical loads of diclofenac and ibuprofen contained in the effluents from Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare wastewater treatment plants in 2006-2014. These urban wastewater treatment plants provide wastewater services to ca 577 000 residents, which accounts for ca 44% of all the Estonian residents. The largest among the examined wastewater treatment plants was in Tallinn, with the p.e. of more than 410 000.

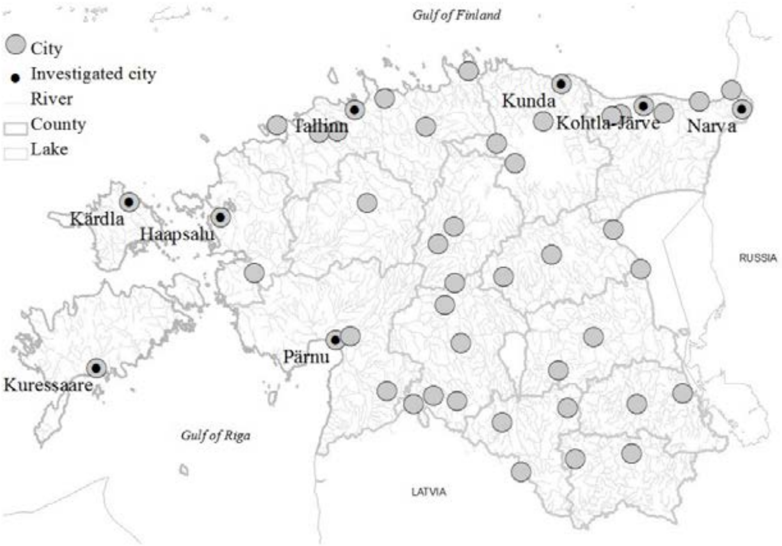


Figure 3.1 Location of the WWTP-s where loads and concentrations of diclofenac and ibuprofen in WWTP effluents were modelled.

Theoretical model developed considered the size of population, the annual examined consumption of pharmaceuticals, metabolic rate in the body, and the efficiency of the WWTP.

Consumption information on pharmaceuticals was obtained from the Estonian Agency of Medicines, in the form of raw data, i.e. the sales numbers of pharmaceuticals, not the amounts of active ingredients. The population data in the examined cities was obtained from the Statistics Estonia. Data concerning the WWTP-s was collected from the Estonian Environmental Register, which has the necessary information on the treatment processes used and the flow volumes (m^3/d) treated in each of the cities.

3.1.1 Data analysis

Total amounts of active ingredient for diclofenac and ibuprofen were calculated based on the amount or concentration of active ingredient indicated on the package leaflet. For example, diclofenac is widely used in the form of a gel where the content of active ingredient is 5%. Both pharmaceuticals also contained carriers that should improve the effects of the product, but these do not pose any risk to the environment, because in most cases, these were easily degradable compounds (except for complex pharmaceuticals, which contain a number of pharmaceuticals). Thus, a pure active ingredient had to be calculated for all the pharmaceuticals that the Agency of Medicines had provided information about.

Since the city-specific consumption information on pharmaceuticals in Estonia is not available, a simplification had to done by calculating the use of active ingredient per capita for the years 2006-2014, by using the formula no 4.

$$K_{yearly\text{-}u} = \frac{Consumption\ of\ pharmaceutical}{Population} \tag{4}$$

In order to find the amounts of pharmaceuticals for each of the cities under review, the consumption of pharmaceutical per capita, calculated by using the formula no 4, was multiplied by the number of residents in the city, based on the actual number of residents in each of the cities for the specific year.

To calculate the loads of diclofenac and ibuprofen, a theoretical model was developed in MS Excel, which calculated the average theoretical concentration of these compounds released to the Baltic Sea over the research period. Two constants were applied in the model: the metabolism removal rate of the examined pharmaceuticals in human body ($M_{removal}$) and the removal rate in the activated sludge treatment plant ($WWTP_{removal}$). These constants were found by Lienert (2007) and Miége (2009) in the course of their studies. Lienert examined the degradation of pharmaceuticals in the human body and found the constants. Miége (2009) analysed various earlier studies and found the diclofenac removal efficiency on the basis of 37 WWTP-s and the average ibuprofen removal efficiency in the activated sludge treatment plant on the basis of 51 WWTP-s (Miège et al, 2009). For both pharmaceuticals, this study used data that had been collected from 37 WWTP-s, and the constants calculated based on that are presented in Table 3.1.

Table 3.1 Removal rates for diclofenac and ibuprofen used in the model.

	$M_{removal}$ (1-$M_{removal}$)	**$WWTP_{removal}$ (1-$WWTP_{removal}$)**
Diclofenac	0.84 (0.78-0.94)[1]	0.32 (0.19)[3]
Ibuprofen	0.70 (0.71-0.51)[2]	0.74 (0.29)[4]

[1] minimum and maximum values are in the brackets (Laak, Aa, Houtman, Stoks, & Wezel, 2010; Lienert et al., 2007)

[2] standard deviation in the brackets (Laak et al., 2010; Miège et al., 2009)

[3] minimum and maximum values are in the brackets (Laak et al., 2010; Lienert et al., 2007)

[4] standard deviation in the brackets (Laak et al., 2010; Miège et al., 2009)

Using the constants presented in Table 3.1 and the following formula, annual loads of diclofenac and ibuprofen that reach the Baltic Sea after being discharged from the wastewater treatment plants, were found.

$$K_{yearly\text{-}load}=P_{population}*K_{yearly\text{-}u}*M_{removal}*WWTP_{removal} \quad (5)$$

where: $P_{population}$ is the size of population in the city analysed in year under review.

To assess the impact on wildlife it is also important to know the average concentration of pharmaceutical residues in the effluent ($K_{average\text{-}c}$), which also serves as a basis for the assessment of potential risks. Therefore, in addition, annual average flow volumes of the examined wastewater treatment plants were considered in order to find the respective concentrations, by using the formula no 6.

$$K_{average\text{-}c}=\frac{K_{yearly\text{-}load}}{Q_{flow}} \quad (6)$$

where: Q_{flow} is the average annual volume of wastewater, m^3.

3.2 Removal of pharmaceutical residues with activated carbon (Paper II)

Adsorption with the activated carbon is considered as having the greatest potential to remove the pharmaceutical residues from wastewater. Therefore, the removal of three pharmaceuticals with PAC was examined, including a nonsteroidal anti-inflammatory drug diclofenac (DCF) and two antibiotics, sulfamethoxazole (SMX) and levofloxacin (LFX). The results will be available to aid the engineers designing the technology to remove pharmaceutical residues.

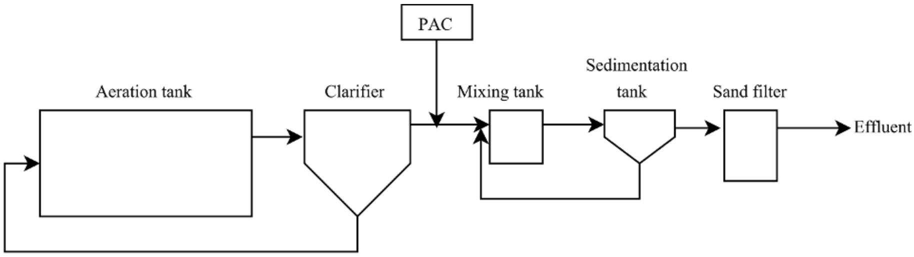


Figure 3.2 Possible technical solution for PAC dosing in the conventional municipal WWTP.

The tests carried out feed into the technological scheme illustrated in Figure 3.2 where PAC is dosed into the effluent of the existing activated sludge plant and is later removed by means of settling and/or a sand filter.

The pharmaceutical solutions necessary for the tests were prepared by using ultrapure water (ELGA) and the pharmaceuticals DCF ($C_{14}H_{10}Cl_2NNaO_2$), SMX ($C_{10}H_{11}N_3O_3S$) and LFX ($C_{20}H_{24}O_2$), respectively. All of the pharmaceuticals used had the Sigma-Aldrich laboratory quality. The removal efficiency was measured with TOC, and since the tests were carried out separately for each of the active ingredients, then it could be assumed that the total TOC was caused by the examined pharmaceutical. To verify this, a test was also carried out by using ELGA water and PAC only.

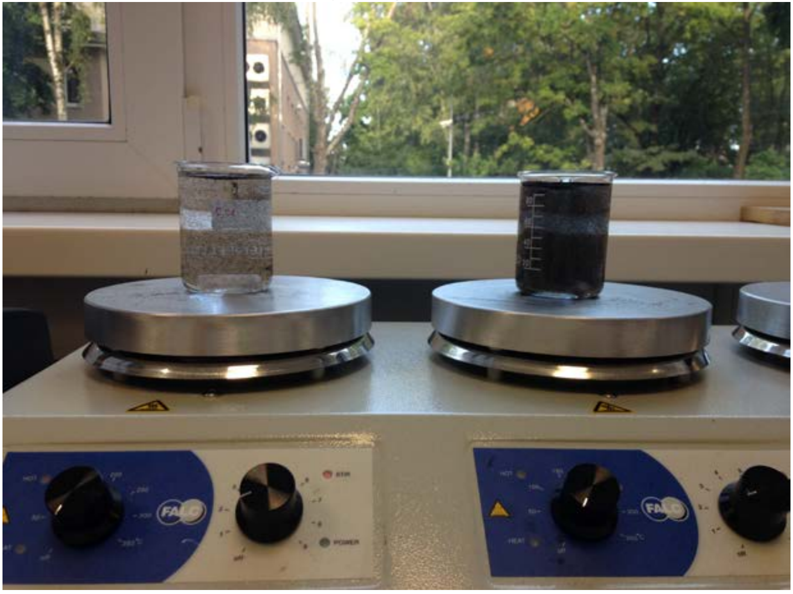


Figure 3.3 Concept of batch tests to remove the pharmaceuticals with PAC.

In order to find the time dependence of adsorption efficiency, 100 ml of test solution and 0.05 g of PAC (filter material, coal powder by Silcarbon, Lach-Ner, M 12.01 g/mol) were added to the 100 ml beaker and the resulting solution was mixed at room temperature, using a 150 rpm magnetic stirrer, taking samples in every 5, 10, 30, 60 and 120 minutes (until reaching the equilibrium concentration). The same test was also repeated, in order to find the dependence of adsorption efficiency on PAC dose.

3.2.1 Data analysis

The removal efficiency E % was calculated, using the following formula:

$$E\ \%=\frac{C_0-C_n}{C_0}\cdot 100\ \% \tag{7}$$

where: C_0 is the initial concentration of adsorbate, C_n is the final concentration of adsorbate, and C_e is the equilibrium concentration of adsorbate.

To describe the process of adsorption, Freundliche isotherms were prepared. These show us the correlation between the amount of adsorbate that is adsorbed per adsorbent unit and the equilibrium concentration of adsorbate q_e.

$$q_e = K \cdot C_e^{1/n} \tag{8}$$

where: K is the Freundlich adsorption constant (mg/g) and n is the heterogeneity factor. K and n are indicators denoting the adsorption capacity and intensity.

Maximum adsorption capacity qe_{max} depending on the process HRT was calculated by using the following formula.

$$qe_{max} = \left(\frac{1}{q}\right) \cdot m_s \tag{9}$$

where: q is the amount of adsorbent (g), m_s is the weight of adsorbed adsorbate (mg), and qe_{max} is the maximum adsorption capacity (mg/g).

3.3 Biological removal of heavy metals (Paper III)

Due to the new, lower maximum permitted levels for heavy metals imposed on the wastewater treatment plants, many of the WWTP-s find themselves in a difficult situation, trying to find a way how to meet these requirements. This study analyses the dependence of the loads of heavy metals and the removal efficiency of heavy metals on the main operating parameters, such as HRT, SRT, and MLSS, in an operating WWTP.

The load of the examined WWTP is ca 450 000 p.e. and the average incoming flow rate in the research period was 131 297 m^3/d. The treatment process consists of mechanical treatment with screens, sand traps and primary tanks. Biological treatment is carried out by means of an activated sludge process where 33% of the entire volume of the bioreactor is anoxic environment for the purposes of denitrification. In addition, subsequent post-denitrification is carried out in the fixed film reactor. The sludge that is removed in the course of the wastewater treatment process is anaerobically stabilised in the mesophilic digester and then dewatered. Phosphorus removal is carried out chemically, using $Fe_2(SO_4)_3$ as a coagulant. The average wastewater parameters of this treatment plant are presented in Table 3.2.

Table 3.2 Influent data of the examined WWTP (n = 1820).

Parameter	**mg/l**
BOD_7	190
COD	484
SS	349
P_{tot}	6.32
N_{tot}	49.64

The necessary samples for the study were collected and analysed in 2011-2016 at the interval of two weeks. The samples were taken from the influent and effluent of the bioreactor and from the dewatered sludge. The wastewater samples used were 24-hour averages where every hour, 200 ml of water was collected into one sample container. The content of heavy metals in the samples was determined by an accredited laboratory, by applying the ISO 17294-2:2003 standard (application of inductively coupled plasma mass spectrometry, ICP-MS). The heavy metals examined included Cr, Ni, Cu, Zn, As, and Pb (n = 118).

The necessary hydraulic process parameters for the analysis were logged automatically, using the Vera software, which recorded the hourly, as well daily operating data. In addition, the following activated sludge plant parameters were used in the study: HRT (formula no 10), MLSS (EVS-EN 872 standard "Water Quality.

Determination of Suspended Solids”), SRT (formula no 11). Further analyses were done on pH, DO, and T ° (C) of wastewater, and other parameters of the wastewater treatment plant, such as the daily amount of dewatered sludge, etc., which may have affected the results obtained.

$$HRT\ (h) = \frac{V_{aeration\ tank}\, m^3}{Q_{influent(h)} m^3/h} \tag{10}$$

$$SRT\ (d) = \frac{V_{aeration\ tank} m^3 * MLSS(a) kg/m^3 + Q_{influent(d)} m^3/d * SS(i)\ kg/m^3}{V_{WAS} m^3/d * MLSS(w) kg/m^3 + Q_{influent} m^3/d * SS(e)\ kg/m^3} \tag{11}$$

where:

$V_{aeration\ tank}$ - total volume of aeration tank (anoxic+aerobic), m^3
$Q_{influent\ (h)}$ - influent flowrate of aeration tank, m^3/h
$Q_{influent\ (d)}$ - influent flowrate of aeration tank, m^3/d
SS(i) - suspended solids in the influent of aeration tank, kg/m^3
MLSS(a) - mixed liquor suspended solids in aeration tank, kg/m^3
V_{WAS} - flowrate of the removed waste activated sludge from clarifier, m^3/d
MLSS(w) - mixed liquor suspended solids in waste activated sludge, kg/m^3
SS(e) - suspended solids in the effluent of clarifier, kg/m^3

The data were analysed, using MS Excel and GraphPad Prism software, applying the following principles:

1. Mass of heavy metals (HeM) removed in the activated sludge process was calculated by using the following correlation:

$$M = C_{HeM} * Q_{influent\ (d)} \tag{12}$$

$$M_{removal} = \left(M_{influent} - M_{effluent}\right) \tag{13}$$

where:

M - mass of heavy metal, mg
C_{HeM} - concentration of heavy metal in influent or effluent, mg/m^3
$M_{influent\ or\ effluent}$ - total mass of heavy metal in influent or effluent, mg

2. HRT and the corresponding $M_{removal}$ were sorted and presented as a linear function, where HRT is placed on the x-axis and $M_{removal}$ (mg) on the y-axis. In the case of HRT, only the data that fell in the range of 5-18 hours were used, because only very few data were available on HRT <5 h and >18 h (n<5).

3. In order to identify the correlation between SRT and HeM, SRT and $M_{removal}$ corresponding to that moment was sorted, similarly to HRT. In the case of SRT, data was used where SRT ranged from 11 to 24 days.

4. In order to identify the correlation between MLSS and $M_{removal}$ an analysis was carried out similar to that performed with SRT and HRT, where only MLSS values in the range of 3500-6000 mg/l were considered, since there were enough data. Number of repeated data points outside this range was small (n<10).

3.4 Combined effect of heavy metals on the wastewater treatment (Paper IV)

The aim of this study was to analyse the combined effect of Cd, Pb, Zn, Cu, Ni, Cr, Co, and Mn on the activated sludge process.

The necessary water samples for the analysis were collected from the influent and effluent of the WWTP in 2014-2017, using the automated sampler. The samples were analysed for heavy metals by an accredited laboratory, by applying the ISO 17294-2:2003 standard. The conceptual method of analysis is schematically shown in Figure 3.4.

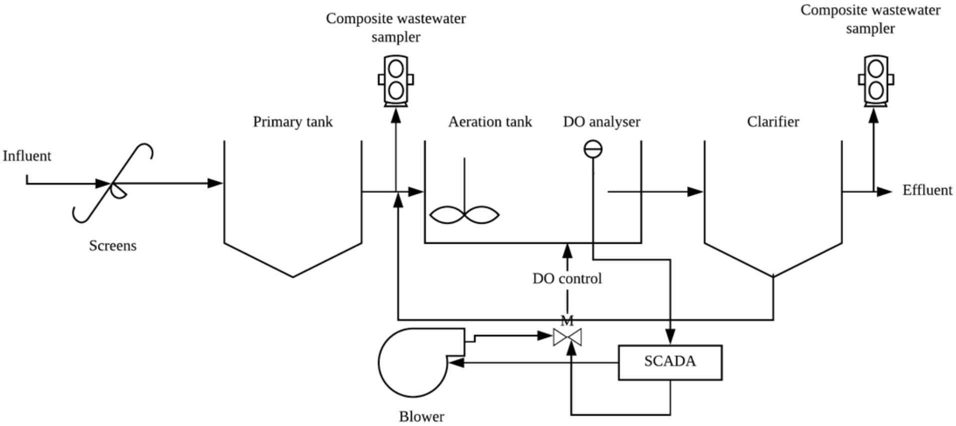


Figure 3.4 Flow diagram of the WWTP and the sampling points.

The necessary operational data for the process analysis were recorded automatically by the SCADA system used at the wastewater treatment plant. This necessary data included: HRT, wastewater temperature T °C, and air consumption of the biological treatment (m^3/d). Other necessary wastewater parameters such as N_{tot} removal efficiency and NH_4 removal efficiency were determined by means of EVS-EN ISO 11905 standard and SFS 3032, respectively.

Table 3.3 presents the examined parameters and their statistical characteristics. During the research period, e.g. the maximum air consumption (O_2) was 1 787 797 m^3/d. The maximum NH_4 removal rate (nitrification) was 99.5% and the minimum was 75.66%, i.e. the biological treatment of this wastewater treatment plant functioned properly during the research period. The average daily load of heavy metals was 22.12 kg/d.

Table 3.3 Core indicators of the research parameters (n = 45).

	Mean	**SD**	**Min**	**25%**	**Median**	**75%**	**Max**
O_2, 1000 m^3/d	1395.4	193.6	1053.8	1267.4	1350	1544.6	1787.8
HeM, kg	22.12	5.4	15.2	17.8	21.1	24.2	38
NH_4 removal efficiency, %	95.71	5.36	75.7	94.7	97.5	99.3	100
N_{tot} removal efficiency, %	84.21	5.8	69	81.1	84.9	88.1	93.6
HRT, h	12.9	2.0	8.6	11.7	13.2	14.4	17.1
T °C	13.5	3.0	9.2	10.8	12.3	16.5	18.6

3.5 Removal of hazardous compounds with activated carbon (Paper V)

The study described here compared various technological solutions for the use of PAC to remove heavy metals and TOC, illustrated by the example of an operating wastewater treatment plant. The theoretical part of the study demonstrated that this technology is best suited to remove heavy metals, as well as organic micropollutants. The TOC was used as a sum parameter of micropollutants, without examining any specific organic micropollutants.

The technological scheme of the examined wastewater treatment plant included the following: screens, primary tank, bioreactor, clarifier. The following average parameters characterised the activated sludge process: MLSS 4200 mg/l, SRT 16 days, F/M 0.05 and average HRT 8 h.

During the laboratory tests, in the first test scheme (Test 1), the removal of heavy metals and TOC in the course of the advanced wastewater treatment was examined, with PAC (coal filter material, coal powder by Silcarbon, Lach-Ner, M 12.01 g/mol) being dosed into the effluent of the wastewater treatment plant and subsequently removed either with a disc filter or with a clarifier. In the second test scheme (Test 2, APAC), a model of the wastewater treatment plant was built, consisting of an anoxic zone, aerobic zone and a clarifier. The principles of the test schemes are shown in Figure 3.5.

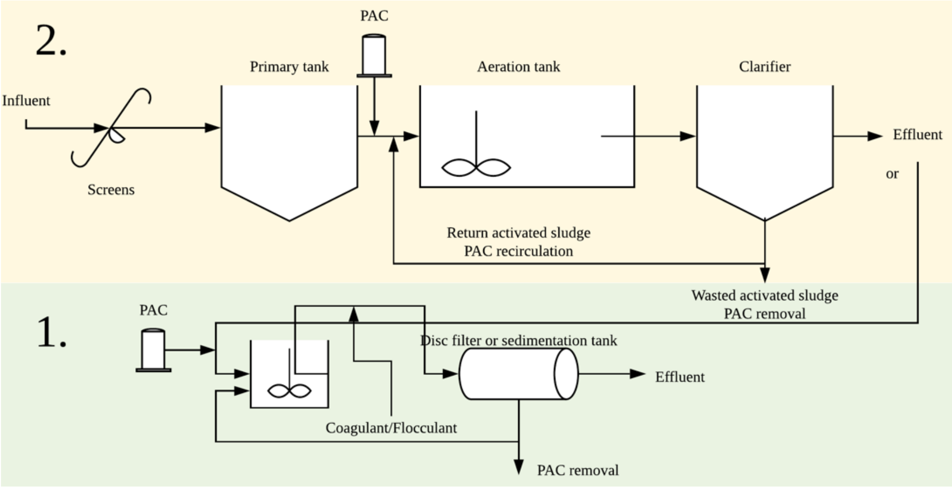


Figure 3.5 Principles of the concept of tests carried out. In Test 1, PAC was dosed into the effluent (after clarifier) of an operating wastewater treatment plant, and in Test 2, PAC was dosed into the bioreactor of a WWTP model.

For the determination of heavy metals (Zn, Cu, As, Pb, Cr, and Ni), ISO 17294-2:2003 was applied, and other parameters were determined by the following Hach Lange standard methods: TOC/DOC - LCK 380, N_{tot} - LCK 238, P_{tot} - LCK 348, PO_4 - LCK 348, NH_4 - LCK 305, NO_2 - LCK 341, NO_3 - LCK 339. In addition, water temperature, pH, and conductivity were registered.

Test 1 was conducted by applying a batch testing procedure on a 1000 ml of effluent, adding PAC in concentrations of 10, 25, 50 and 100 mg/l, respectively, and mixing the obtained reactor at 250 rpm to avoid the settling of PAC and to ensure its exposure to the substances it adsorbs. In order to assess the effect of the retention time on the adsorption process, 10 mg/l of PAC was dosed and the samples were taken at the following intervals: 5 min, 10 min, 20 min, 60 min, and 90 min. In order to examine the effect of different doses, the samples were analysed after 10 min of retention time, because technically, it would be difficult to achieve a retention time longer than this in case of a municipal WWTP. The effluent samples were filtrated through a 10 µm filter paper, imitating the disc/cloth media filter that is widely used.

Figure 3.6 APAC test where PAC was dosed into the first, anoxic reactor.

The model test was carried out on the model of the wastewater treatment plant where the volume of the anoxic reactor was 3800 ml, volume of the aerobic reactor 10 800 ml, and HRT of the whole process was adjusted to 8 h, which was the average retention time in the bioreactor of the examined wastewater treatment plant. MLSS of the activated sludge used in the model was 4200 mg/l, which was determined by applying the EVS-EN 872 standard. The return sludge ratio was adjusted to 180%. Before and after the test, the following parameters were determined: pH, electrical conductivity, temperature, Zn, Cu, As, Pb, Cr, Ni, N_{tot}, P_{tot}, PO_4, NH_4, and TOC.

It was not possible to assess in the model test the heavy metals and TOC that were already present in the activated sludge and possibly emerged as a result of the PAC process, which is also the case in a real situation. The analysis provides a good overview of correlation between the heavy metals and TOC and the the respective PAC doses.

4 Results and discussion

4.1 Pharmaceutical residues in Estonia and their removal in the wastewater treatment plant (Paper I, II, V)

Due to the hazard of pharmaceutical residues, many countries have decided to search for the best possible technological solutions to remove pharmaceutical residues and are planning to build in the near future so-called quaternary treatment stages attached to the existing wastewater treatment plants, that would have the capacity of removing various hazardous organic compounds. The results of this study provide an input to the dimensioning and operating of such technologies.

4.1.1 Modelling the loads of pharmaceutical residues

Figure 4.1 shows the consumption of diclofenac and ibuprofen in Estonia from 2006 to 2014. A remarkable decrease, 19.9%, was found in diclofenac consumption, whereas in the case of ibuprofen it was just the opposite - 14.1% increase in the consumption was discovered. The increase of the usage of some pharmaceuticals can be connected with population aging (Arnold, Brown, Ankley, Sumpter, & Arnold, 2014). The decreasing usage of diclofenac can be connected with changes in the law during this period; some common diclofenac pharmaceuticals have required a prescription since 2007. The second reason behind this can be the announcement made by the European Medicines Agency, stating that diclofenac as an analgesic is no safer compared to ibuprofen because it can cause cardiovascular diseases, such as heart attack and stroke. In Germany, a remarkable 116% increase in the consumption of ibuprofen was recorded from 2002 to 2009, whereas for diclofenac, the increase was only 4% (Bergmann & Weber, 2011). In Finland, for a comparison, 119 000 kg of ibuprofen and 1050 kg of diclofenac was consumed in 2014 (HELCOM, 2017).

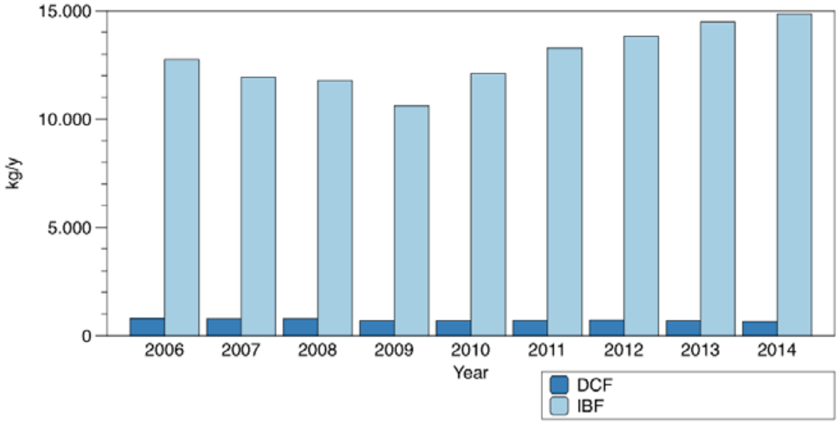


Figure 4.1 Consumption of diclofenac and ibuprofen in Estonia from 2006 to 2014.

In Figure 4.2, the modelled discharge loads for diclofenac for Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare are outlined. The main loads of diclofenac residues originating from the three largest cities Tallinn, Narva and Pärnu amount to the total average yearly amount of 30 kg. In Pärnu, a 23.1% decrease in the total load of diclofenac is observed. Narva has seen a 26% decrease and Haapsalu 24.7%, respectively.

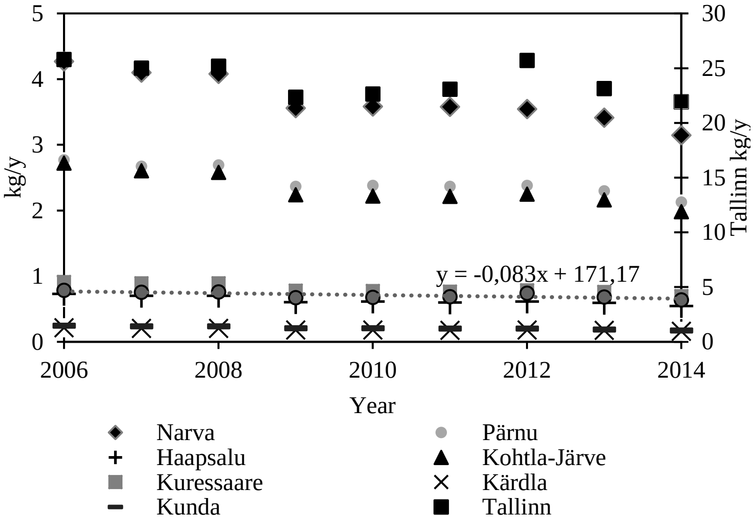


Figure 4.2 Modelled discharge loads of diclofenac residues into the Baltic Sea from the major cities in the time period between 2006 and 2014.

In Figure 4.3, the discharge rates for ibuprofen residues to the Baltic Sea are shown. The discharge rates for ibuprofen increased by more than 15% from 2006 to 2014. From 2006 to 2010, a drop in the consumption of all these cities was found, which was due to the usage of ibuprofen. In Narva, Pärnu, Haapsalu, Kohtla-Järve, Kärdla and Kunda, an average 7.5% increase in the discharge loads for ibuprofen was found. In Tallinn, the consumption rates have increased from 293 kg to 361 kg in connection with the growing consumption rates in Estonia and with the growing population trend in Tallinn.

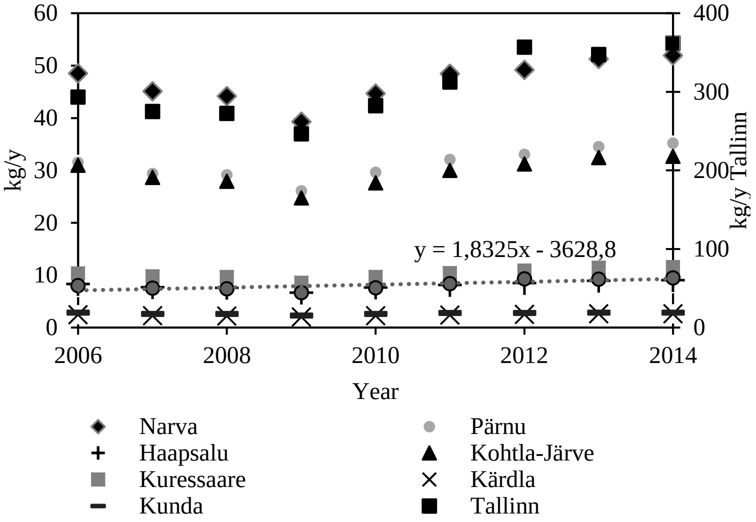


Figure 4.3 Modelled discharge loads of ibuprofen residues into the Baltic Sea from 2006 to 2014.

Figure 4.4 shows the modelled average annual concentrations of diclofenac residues in the effluent of the wastewater treatment plants examined in this study. The highest average concentrations were found in Kunda and Kärdla, with values of 1.4 and 1.5 µg/l, respectively. It can be explained by smaller flow rates per capita, which in turn results from a separated sewer system in use. In Estonia's largest city, Tallinn, a 17.8% decrease in diclofenac concentration was modelled. The average concentration in the cities under review has dropped from 1 to 0.8 µg/l (a 20% decrease). The German Ministry for the Environment analysed the effluent of 198 wastewater treatment plants in Germany and found diclofenac in various concentrations between 0.4 and 10 µg/l (Rohweder, 2003). In his article based on scientific journals from all around the world, Miége found that diclofenac concentrations in the effluent of 46 wastewater treatment plants varied from 0.035 to 1.72 µg/l (Miège et al., 2009). HELCOM (2017) report that gathers data from the Baltic Sea States, found that the average concentration of DFC in the influent of the wastewater treatment plants was 1 µg/l and maximum concentration 8 µg/l. The same report states that the average concentration of DCF in the effluent of the wastewater treatment plants was 0.8-1 µg/l and maximum concentration 11 µg/l, i.e. higher than in the influent (HELCOM, 2017). By comparing the modelled data of the present study with earlier studies, a rather good compatibility can be seen (Figure 4.4).

In her environmental risk assessment, Altmets found that a predicted environmental concentration of diclofenac of 0.59 µg/l has a high environmental risk because it is persistent and bioaccumulative (Altmets, 2012). The modelled data of the present study showed higher values in most of the WWTP outlets.

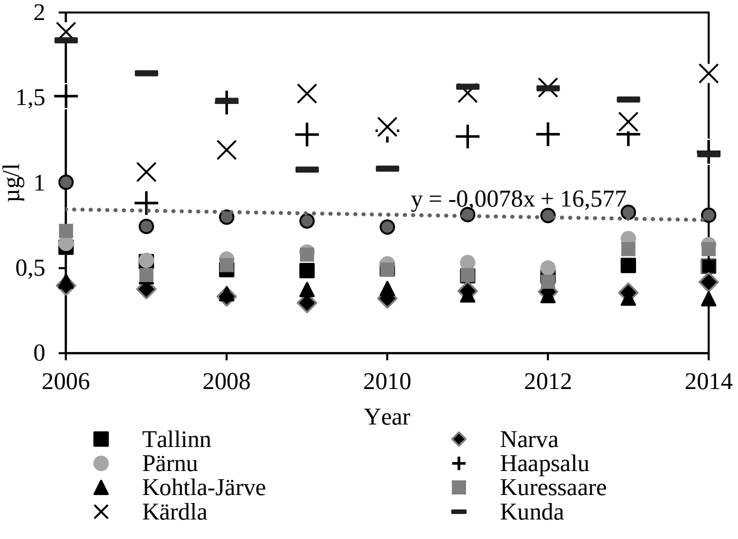


Figure 4.4 Modelled average diclofenac concentrations in the effluent of eight Estonian seaside WWTP-s, from 2006 to 2014.

In Figure 4.5, the modelling results of average ibuprofen residue concentrations in the effluent of eight WWTP-s of Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare are shown. Similarly to diclofenac, the highest average concentrations were found in Kunda (18.3 µg/l) and Kärdla (18.8 µg/l), due to smaller flow rates in the recent years. The average concentration of ibuprofen has increased in the eight described cities from 11.4 to 13.4 µg/l. Together, in all eight cities, an average 14.9% concentration increase for ibuprofen residues was seen. The previously described German report found ibuprofen in concentrations ranging from 0 to 3.7 µg/l in the effluent of 178 wastewater treatment plants (Rohweder, 2003). Miége in his study found ibuprofen ranging from 0.04 to 1.7 µg/l (Miège et al., 2009). In comparison to the modelling results obtained in the earlier studies, the present study observed that the theoretical model for ibuprofen is overrating the concentrations by more than 64%. The exaggeration can be due to a variety of possible reasons, such as the greater proportion of stormwater or higher accumulation into waste activated sludge, which is removed separately. At the same time, according to the HELCOM (2017) report, the average ibuprofen concentration in the influent of the wastewater treatment plants was ca 3 µg/l and maximum determined result 100 µg/l. The same report stated that the average concentration of ibuprofen in the effluent of the wastewater treatment plants was 2 µg/l and maximum determined result ca 80 µg/l. Considering that Estonia has the highest consumption of ibuprofen per resident among the Baltic Sea States, it can be concluded that the theoretical model is quite accurate in determining the specific substance (HELCOM, 2017).

In Altmets's environmental risk assessment for ibuprofen, the environmental risk was deemed to be insignificant (Altmets, 2012). Despite this, it is necessary to identify the real values for ibuprofen, since the model of the present study showed rather high concentrations.

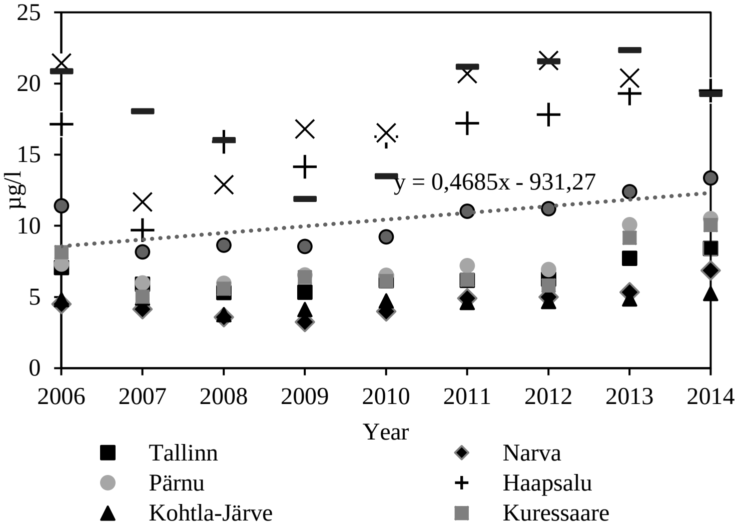


Figure 4.5 Modelled average ibuprofen concentrations in the effluent of eight Estonian seaside WWTP-s from 2006 to 2014.

In Estonia, the annual consumption of diclofenac has decreased from 804 to 644 kg and for ibuprofen it has grown from 12749 to 14836 kg in time period between 2006 and 2014. Diclofenac usage was rather decreasing, but an increasing trend was observed for ibuprofen, which is due to many reasons, such as aging population and longer life expectancy. In evaluating the risks on the environment, the concentration of pharmaceuticals in wastewater is more relevant than the consumption. The average concentration of diclofenac modelled for the research period in eight different cities was 0.8 µg/l and for ibuprofen 10.5 µg/l, respectively.

The environmental risk of diclofenac, based on different studies, has been categorised as high.

Using this modelled data, we are able to forecast the trends of consumption rates and concentrations of pharmaceutical residues in WWTP effluents. The model is not totally comparable with the real concentrations of diclofenac and ibuprofen, but it gives us a good overall picture and trend, and tells that we need to carry on with studies in this field.

4.1.2 Removal of pharmaceutical residues and organic pollutants by adsorption

As demonstrated in the theoretical part above, the best technological solution for removing pharmaceutical residues and organic pollutants is by using activated carbon PAC or GAC. The present study examines the use of PAC for the removal of three pharmaceutical residues and suggests the optimum dose and location for the application of adsorption through the tests carried out with actual wastewater.

In Figure 4.6, the results of the adsorption studies are shown, where the adsorption efficiency dependant on time and adsorbent dosage were examined. The best results were achieved in LFX removal, where within 5 minutes, 77% had already been removed, while the highest removal rate achieved was 94% after 60 minutes of retention time. The equilibrium concentration was reached in 60 minutes. 0.03 g/100 ml was determined to be the preferable PAC dosage for this LFX concentration, for which an 86% adsorption efficiency was achieved. A similar, 93% removal efficiency was reported by L. Lima (2004) (Lima, Aquino, Afonso, & Libanio, 2004). In higher PAC concentrations, the removal capacity remains similar, which means that at the initial examined concentration the higher PAC dose would only increase adsorbent consumption without significantly increasing the treatment efficiency. Rapid adsorption is an indicator that we need significantly shorter retention times when creating a treatment stage with specific activated carbon for LFX, compared to other pharmaceuticals. Therefore, the first stage may be dimensioned smaller when doing the design for the multistage filters. After a retention time of 120 minutes, the concentration of the substance to be removed even increased and the removal efficiency dropped by 2%. Similar rises in concentrations have also been reported by E. Chang (2015), suggesting that it is due to the continuous changes in the adsorbent and adsorbate equilibrium (Chang et al., 2015).

In the case of DCF, the adsorption process was significantly slower. 45% of DCF was removed in 5 minutes and, just like with LFX, the equilibrium concentration was achieved in 60 minutes with 82% of the initial concentration being removed. A 70% removal efficiency for DCF was achieved by L. Lima (2004) in a similar study (Lima et al., 2004). The highest adsorption capacity was achieved with PAC dosage of 0.1 g/100 ml, which is 70% higher than that of LFX. For DCF removal, we need longer contact time and higher PAC dosage than for LFX removal. The greatest difference can be seen in Figure 4.6 (b). While DCF usually adsorbs better than SMX, with different PAC concentrations it can be observed that the removal efficiency is lower than in other tests where fixed amounts of PAC (0.05 g/100 ml) are used. DCF only adsorbs better than SMX at 0.05 g/100 ml.

SMX has the lowest adsorption capacity. 31% of SMX was removed in the first five minutes. The equilibrium between adsorbate and adsorbent was reached in 60 minutes and the removal efficiency was 68%. The same result was also achieved by L. Lima (2004) (Lima et al., 2004). The most effective SMX removal was attained with a PAC concentration of 0.075 g/100 ml. The poor adsorption of SMX was also confirmed by an earlier study, in which the adsorption of SMX achieved was 76% worse than that of DCF (Nam et al., 2015).

Adsorption is influenced by many factors, such as porosity of the activated carbon, pH of the examined solution, and temperature. In the test of the present study, pH dropped from 7.6 to 6.3 after dosing PAC (0.05 g). B. Bhadra found that the adsorption capacity of diclofenac increases when the pH decreases (Bhadra, Seo, & Jhung, 2016). This is attributed to the surface charge of the activated carbon, which decreases when the pH falls and makes the adsorption more efficient (Bhadra et al., 2016). The adsorption is also influenced by the water solubility of the removable substance. The higher the solubility, the worse the removal rate by adsorption. In the present study, LFX proved insoluble in water, DCF poorly soluble (water solubility 2.37 mg/l) and SMX partly soluble (water solubility 610 mg/l). These study findings confirm the correlation between the water solubility and adsorption, where LFX was removed in higher amount than DCF and SMX (National Center for Biotechnology Information, 2016b, 2016c, 2016a).

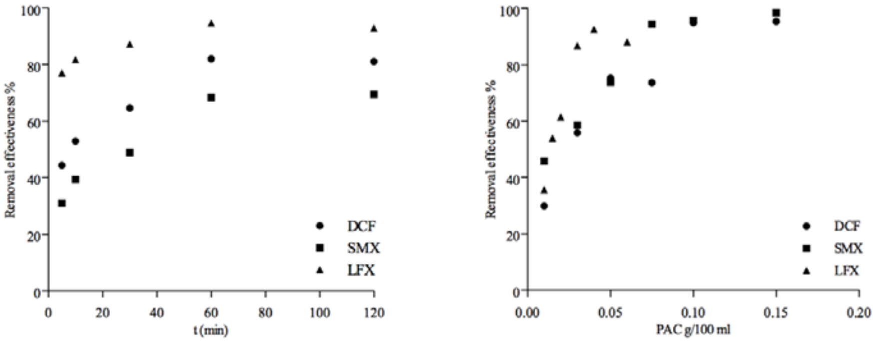


Figure 4.6 Removal efficiency dependent on adsorption time (a) and adsorbent dosage (b).

In Figure 4.7(a), we see the adsorption capacity of DCF, SMX and LFX dependant on time. LFX has the highest adsorption capacity as is also shown in Figure 4.6. The equilibrium was achieved in 60 minutes, with 324 mg of LFX per 1 gram of PAC being adsorbed. DCF has an adsorption capacity of 231 mg/g on the examined concentration, which is 29% lower than that of LFX. For SMX, the maximum adsorption potential in the same time was 185 mg/g, which is 43% less than that for LFX.

From Figure 4.7(b), K and n for DCF, SMX and LFX tests was found. K was determined from the intersection of the graph with the y-axis and n is equal to the slope of the graph. The higher K is the more effective adsorption process. With the n value, we can see the adsorption intensity and whether the adsorption process is integrated or not. When 1/n is higher than 1, it is uniform; the smaller the 1/n value, the greater the heterogeneity of the surface of PAC. If n is less than 1, then the process is unfavourable for adsorption

(Desta, 2013; Sekar, Sakthi, & Rengaraj, 2004). In Table 4.1, the results according to Figure 4.7 are shown.

Table 4.1 Freundlich parameters for DCF, SMX and LFX adsorption with PAC.

Parameter	**DCF**	**SMX**	**LFX**
K	23.8	34.3	106.1
1/n	0.4237	0.4115	0.1858
n	2.36	2.43	5.38
q_e	34.2	53.8	138.5
R^2	0.77038	0.80276	0.8855

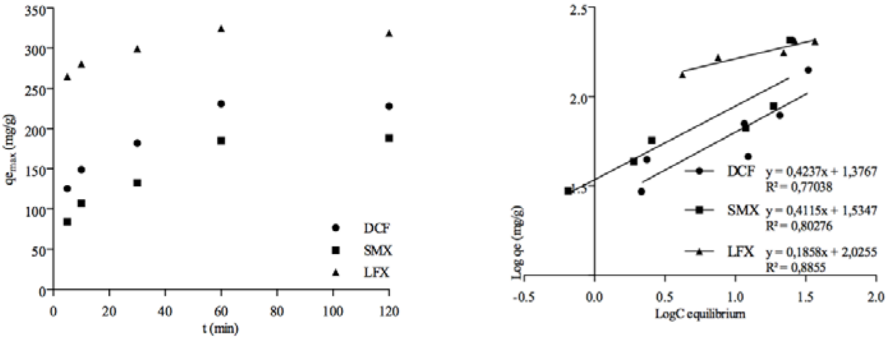


Figure 4.7 Maximum adsorption capacity qe_{max} (mg/g) dependent on time (a) and Freundlich adsorption isotherms (b).

The results show that the adsorption processes of DCF, SMX and LFX align with the Freundlich adsorption isotherm. As the previous discussion already showed, LFX has the highest adsorption capacity, as confirmed through the K, qe and n values where it is higher than those of DCF and SMX. At the equilibrium concentration, the maximum adsorption capacities were 106.8, 34.3 and 23.8 for LFX, SMX and DCF, respectively. Though DCF was otherwise better adsorbable than SMX, the reason for the low qe of DCF was explained above in Figure 4.6. In reviewing other similar studies where different adsorbents were used, K was found to be 2.26 in one study and 44.9 in another, which demonstrated that adsorption processes largely depend on the adsorbent being used (Larous & Meniai, 2016; Nam et al., 2015).

Tests with actual wastewater were carried out to compare the removal of TOC with PAC by dosing the adsorbent either into the effluent from the clarifier or straight into the anoxic bioreactor. The TOC removal efficiencies at different PAC doses are presented in Figure 4.8.

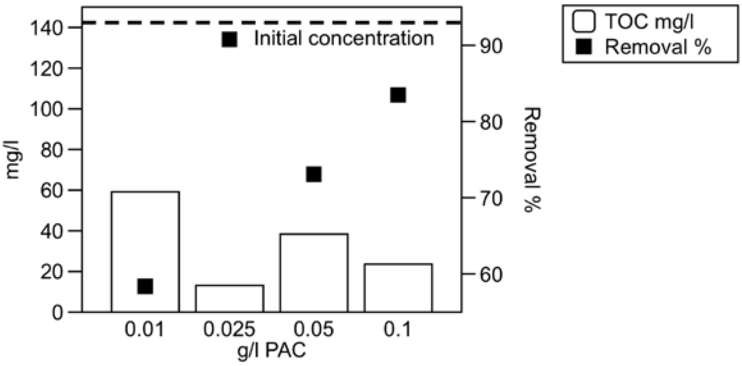


Figure 4.8 Test 1, where PAC was dosed into the effluent from the clarifiers in doses of 10, 25, 50, and 100 mg/l in order to determine the optimum dose and treatment efficiency ratio.

After dosing 10 mg/l of PAC the TOC initially dropped by 58%. A comparative test with the higher PAC dose of 25 mg/l resulted in a 90.8% TOC removal efficiency, which was also the most effective result of this test, because the TOC removal efficiency even started to drop at higher PAC doses, e.g. dosing 50 mg/l of PAC resulted in a 73% removal efficiency.

These test results confirm that the rest, appr. 10% of the organic compounds are not removable by applying adsorption with activated carbon due to their molecular characteristics (large molar mass and volume), and may require pre-ozonation of wastewater to break down larger molecules into smaller ones that would improve the adsorption (Margot et al., 2013).

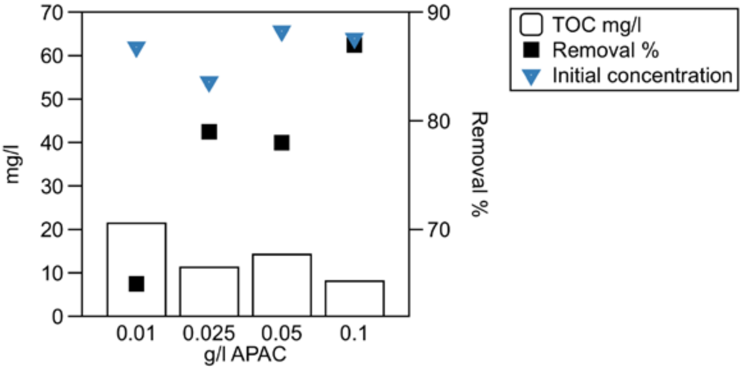


Figure 4.9 Test 2, where PAC was dosed into the bioreactor in doses of 10, 25, 50, and 100 mg/l in order to determine the optimum dose and treatment efficiency ratio.

Dosing 10 mg/l of APAC (Figure 4.9) reduced the TOC by approximately 65%. With increasing doses there was also an increase in the TOC adsorption of up to 87% (at APAC dose of 100 mg/l). In the case of the APAC process, the TOC removal was certainly enhanced by the biological processes, where heterotrophic micro-organisms used readily degradable dissolved organic matter in their vital functions (Çeçen, Semerci, & Geyik, 2010; Margot et al., 2013).

APAC tests showed that the rest, appr. 10-20% of the organic compounds that are not removable by applying adsorption with activated carbon due to their molecular characteristics, are biosorbed by biomass and are then removed with the sludge or degraded by micro-organisms due to the longer retention time.

Wang (2016) carried out similar test to examine the removal of TOC with PAC, using wastewater from chemical industry on an SBR pilot device. He found that PAC alone removed 38% of TOC and the APAC scheme resulted in 68% removal efficiency, which suggests that the rest of 32% of the organic compounds do not respond to absorption and are not readily biodegradable due to their molecular characteristics (Wang, Hu, Li, Wang, & Ji, 2016). Plus, any further removal of TOC would require e.g. a prior advanced oxidation of wastewater (Giannakis et al., 2015; Margot et al., 2013).

Higher efficiencies achieved in the removal of TOC, BOD, and N_{tot} when using APAC method are well-known but still unexplained to a large extent. It is known that the synergism of APAC method lies in the capacity of the PAC adsorption to sorb toxic substances and compounds that inhibit the activity of micro-organisms, thus improving the efficiency of biological process, which has been examined to some extent. Also, with the adsorption of metabolic end products the APAC process ensures higher treatment efficiency. In addition to synergism, the APAC method improves the treatment efficiency by extending HRT of the target compounds in the system, because these are adsorbed by the sludge. Therefore, the removal efficiency for the removed compounds (N_{tot}, P_{tot}, BOD, HeM) does not depend so much on HRT as it normally does in the biological treatment process.

The comparison of Test 1 and Test 2 is presented in Figure 4.10, illustrating the removal of TOC per 1 g of PAC.

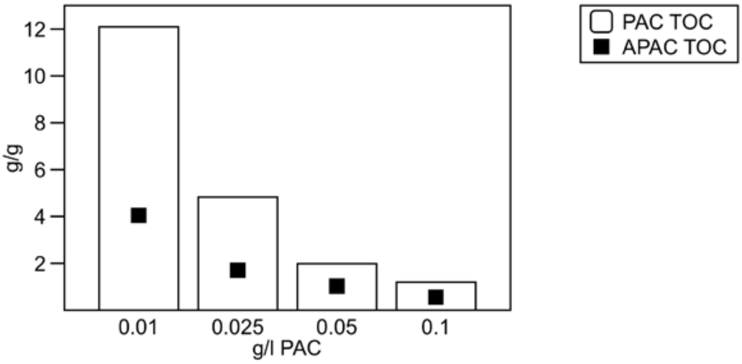


Figure 4.10 Removal of TOC per 1 g of PAC (Qe) in Test 1 and Test 2.

In Test 1, the most effective PAC dose was 10 mg/l, with a respective TOC removal of 12096 mg/g, and in Test 2, where the same PAC dose proved to be the most effective, the achieved removal was 4060 mg/g. 10 mg/l was also identified as the most effective dose to remove organic matter in the study by Margot (2013), where he pointed out that a higher dose will increase the treatment efficiency to some extent, but given the increasing operating costs, it would not be justified (Margot et al., 2013). Higher removal efficiency is likely to result from the additional sorption by biomass, which increases the removal of TOC, and from the longer retention time of the process (Abdel Salam et al., 2011; Ong et al., 2010; Wang et al., 2016).

The results of comparing the tests that were carried out under controlled conditions (Figure 4.7(a)) and the tests carried out with actual wastewater (Figure 4.10), applying HRT of 10 min for both, are presented in Table 4.2.

Table 4.2 Comparison of tests to remove TOC per 1 g of PAC.

	DCF mg/g	**SMX mg/g**	**LFX mg/g**	**PAC TOC g/g**	**APAC TOC g/g**
Qe	149.1	106.8	280.8	12.1	4.1

It follows from Table 4.2 that under controlled conditions, the average qe (mg/g) was 178.9 mg/g (DCF, SMX, LFX), whereas in case of PAC and APAC, the average qe reached 8.1 mg/g. This means that the adsorption capacity under real conditions is 95.5% lower than under conditions where only one compound is adsorbed. These results indicate that the large number of compounds contained in the wastewater, such as various organic compounds, heavy metals, salts, etc., significantly reduce the specific adsorption of organic compounds (Hu et al., 2014; Meidl, 1999; Wang et al., 2016).

For example, the average DCF load modelled for the effluent from the wastewater treatment plant in Tallinn was 23.8 kg/y, which means that, based on these tests, the necessary annual amount of PAC would be following:

Table 4.3 Annual amount of PAC necessary to remove diclofenac.

	DCF test	**PAC TOC test**	**APAC TOC test**
PAC kg/y	0.16	1.97	5.8

So, the table above shows that, based solely on the DCF removal, the amount of PAC necessary to adsorb DCF (23.8 kg/y) is 97.2% higher. The reasons behind this are explained under Table 4.2.

4.2 Heavy metals in wastewater and their removal in the wastewater treatment plant (Paper III, IV, V)

The removal of heavy metals in the wastewater treatment plant has mainly been a concern for industries who face high concentrations and are therefore required to pretreat their wastewater before they discharge it to the public sewer system or the receiving waters. The topic of removing heavy metals in the municipal wastewater treatment plant has not been addressed much before. However, since Estonia has imposed requirements for heavy metals that are quite strict compared to those set in other countries, the issue has become topical also for the non-industrial treatment plants. The following studies described here analyse the combined effect of heavy metals on the activated sludge plant and various solutions for the removal of heavy metals from wastewater. The main focus is on the combined effect of heavy metals, in order to identify whether any combined effect of low concentrations of heavy metals in the operating wastewater treatment plant can be observed and whether it is possible to control the removal of heavy metals by sorption through the process control.

4.2.1 Combined effect of heavy metals on the wastewater treatment process

The results of the correlation analysis are presented in Table 4.4 and Figure 4.11. The Pearson correlation coefficient *r* indicates the direction of the correlation (symbol) and its strength (on the scale $|r| = 0$ – no correlation up to $|r| = 1$ – strong correlation). If the test statistic $p<0.05$, then the correlation is deemed statistically significant on the confidence level 0.05.

Table 4.4 Pearson correlation coefficients (r) between variables with significance probabilities (p)

	HeM, kg/d		**HRT, h**		**T, °C**	
	r	***p***	***r***	***p***	***r***	***p***
NH_4 removal, %	-0,11	0,494	0,39	0,009	0,28	0,065
N_{tot} removal, %	-0,17	0,272	0,56	< 0,0001	0,41	0,006
O_2 to aeration, 1000 m^3/d	-0,26	0,085	0,21	0,173	0,13	0,389

The main objective of the analysis was to compose linear regression models, which would describe the combined effect of heavy metals on the biological wastewater treatment, considering three variables: temperature (T °C), retention time (HRT), and the load of heavy metals (HeM). It is well known that the nitrogen removal is mostly affected by the temperature and process retention time, thus making the effect of heavy metals mathematically insignificant, but significant in terms of treatment efficiency (Özbelge et al., 2007). N_{tot} removal efficiency was found to be best described by Model 1 (formula no 14):

$$N_{tot} = 83{,}69 + 1{,}78 \cdot HRT - 1{,}92 \cdot T°C - 1{,}15 \cdot HeM + 0{,}098 \cdot T°C \cdot HeM \qquad (14)$$

Table 4.4 demonstrates that for N_{tot}, significant correlations between HRT and T °C were found and the correlation between heavy metals was insignificant. However, Model 1 provides an adequate result in forecasting the effect of heavy metals as it considers the combined effect of various characteristics. Model 1 (formula no 14) shows that by increasing the volume of heavy metals by 1 kg/d, N_{tot} treatment efficiency drops by 1.052%. Based on the premise that the average nitrogen load in the examined WWTP is 6750 kg/d, a 1.052% drop in the treatment efficiency increases the load to the environment by 71.01 kg/d as an average. Furthermore, the inhibitory effect has a long-term impact on the wastewater treatment process, as the process recovery lasts 1-21 days, depending on the load of heavy metals and the temperature (Henze et al., 2011; You, Tsai, & Huang, 2009). Table 3.3 shows that the loads of heavy metals vary during the research period by 20.116 kg/d (SD is ±5.398), i.e. due to the combined effect of heavy metals, nitrogen removal efficiency also varies by 5.68%.

Since the examined WWTP is operating in carbon deficit, N_{tot} removal efficiency may not indicate as exact correlation as in the case of NH_4, because nitrification is the most sensitive process and the inhibitory effect can be observed fast (Henze et al., 2011). NH_4 removal efficiency can be forecasted with Model 2 (formula no 15):

$$NH_4=103.65+1.24 \cdot HRT-2.003 \cdot T°C-1.13 \cdot HeM+0.095 \cdot T°C \cdot HeM \qquad (15)$$

Model 2 shows that by increasing the load of heavy metals by 1 kg, the nitrification efficiency drops by 1.035%, i.e. the variability of NH_4 removal efficiency, as a result of the combined effect of heavy metals, is 5.55%. Earlier studies have examined the effect of individual heavy metals where the concentrations necessary for measuring the effect were ca 100 times higher than those of the combined effect (Özbelge et al., 2007; You et al., 2009).

In Models 1 and 2, the significance probability p is small, which suggests that the models are reliable. The description percentage of models (r^2, %) indicates the percentage of the variation of descriptive variables N_{tot} and NH_4 described by these models. As the models contain several variables, we must look at the percentage of the adjusted description because it considers the combined effects of the factor variables.

Table 4.5 Efficiency indicators of Models 1 and 2.

	Significance probability p	**Description percentage r^2,%**	**Adjusted description percentage r^2_{adj}, %**	**Standard error of the model, %**
Model 1	< 0.001	43	37	4.59
Model 2	0.0019	25	17	4.87

Models 1 and 2 are not well suited for separately evaluating the effects of temperature and process retention time on N_{tot} and NH_4 removal efficiency because of their multicollinearity, i.e. if there is a strong reciprocal correlation between the model arguments then their effects are also correlated and the evaluations received from the model may not be correct (e.g. a negative coefficient for T °C shows that an increase in temperature, when other parameters have been fixed, will cause a drop in nitrogen removal efficiency, which is not correct). Therefore, in comparison with basic linear regression models (see Table 4.6), Models 1 and 2 do not provide better results when separately evaluating the effects of temperature and the retention time.

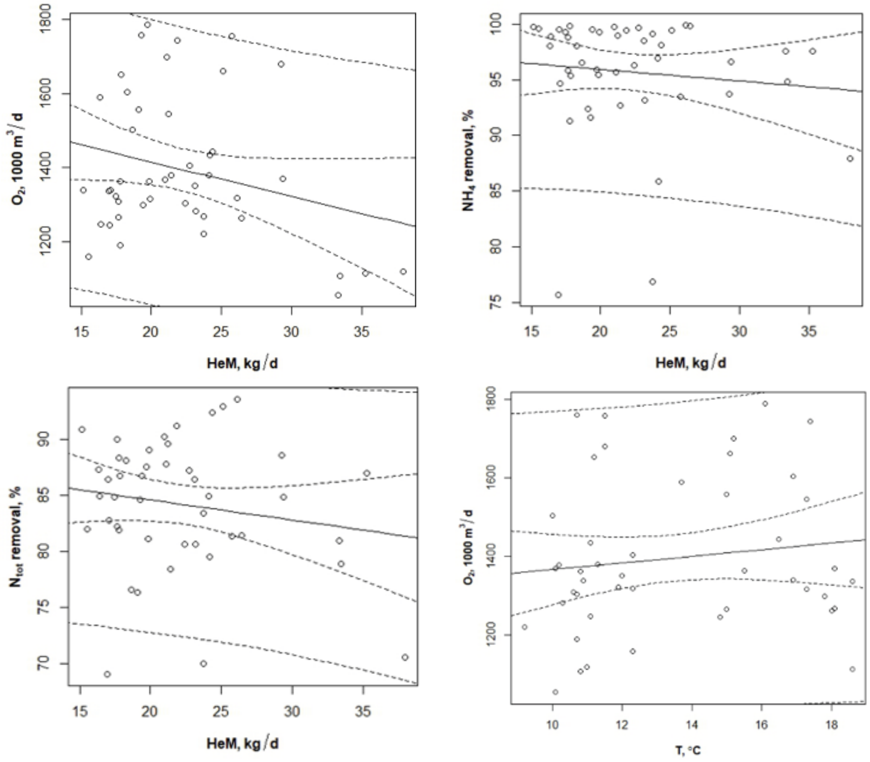
Table 4.6 Regression models describing the effect of temperature and retention time on N_{tot} and NH_4 removal efficiency.

Linear regression model	**Significance probability p**	**Description percentage r^2,%**	**Standard error of the model, %**
$N_{tot}=0.77\cdot T\ °C+73.73$ (16)	0.006	16.6	5.35
$N_{tot}=1.63\cdot HRT+63.22$ (17)	<0.0001	31.9	4.84
$NH_4=0.49\cdot T\ °C+89.11$ (18)	0.065	7.7	5.21
$NH_4=1.04\cdot HRT+82.41$ (19)	0.009	14.96	5.0

Modelling the volume of air consumed for biological treatment by using linear models with several factor variables did not give significantly better results in comparison with simple linear regression models. Therefore, these correlations are described with simple linear models. The regression models, which describe the combined effect of heavy metals, and the effect of retention time and temperature on the volume of air needed for biological treatment, are presented in Table 4.7. The models show that a 1 kg increase in the load of heavy metals reduces the amount of air used for biological treatment by approximately 9300 m^3/d, which suggests that the biological treatment is inhibited. Ong (2010) found similar results in a laboratory research, analysing the effect of individual heavy metals on the amount of air used for biological treatment, in order to thereby evaluate the inhibitory effect (Ong et al., 2010). At high Zn concentrations, the inhibitory effect was nearly 50% (Ong et al., 2010). The Models 1 and 2 demonstrated also similar results where, by increasing the load of heavy metals, the nitrogen removal efficiency dropped, i.e. less oxygen was used for nitrification because the bacterial metabolism was inhibited (You et al., 2009).

Table 4.7 Regression models describing the effect of heavy metals, retention time and temperature on the air consumption.

Linear regression model	**Significance probability *p***	**Description percentage r^2, %**	**Standard error of the model, m^3/d**
$O_2=-9.3 \cdot HeM+1601.14$ (20)	0.085	6.7	189.1
$O_2=20 \cdot HRT+1138.59$ (21)	0.173	4.3	191.5
$O_2=8.39 \cdot T\ °C+1282.4$ (22)	0.389	1.7	194.1



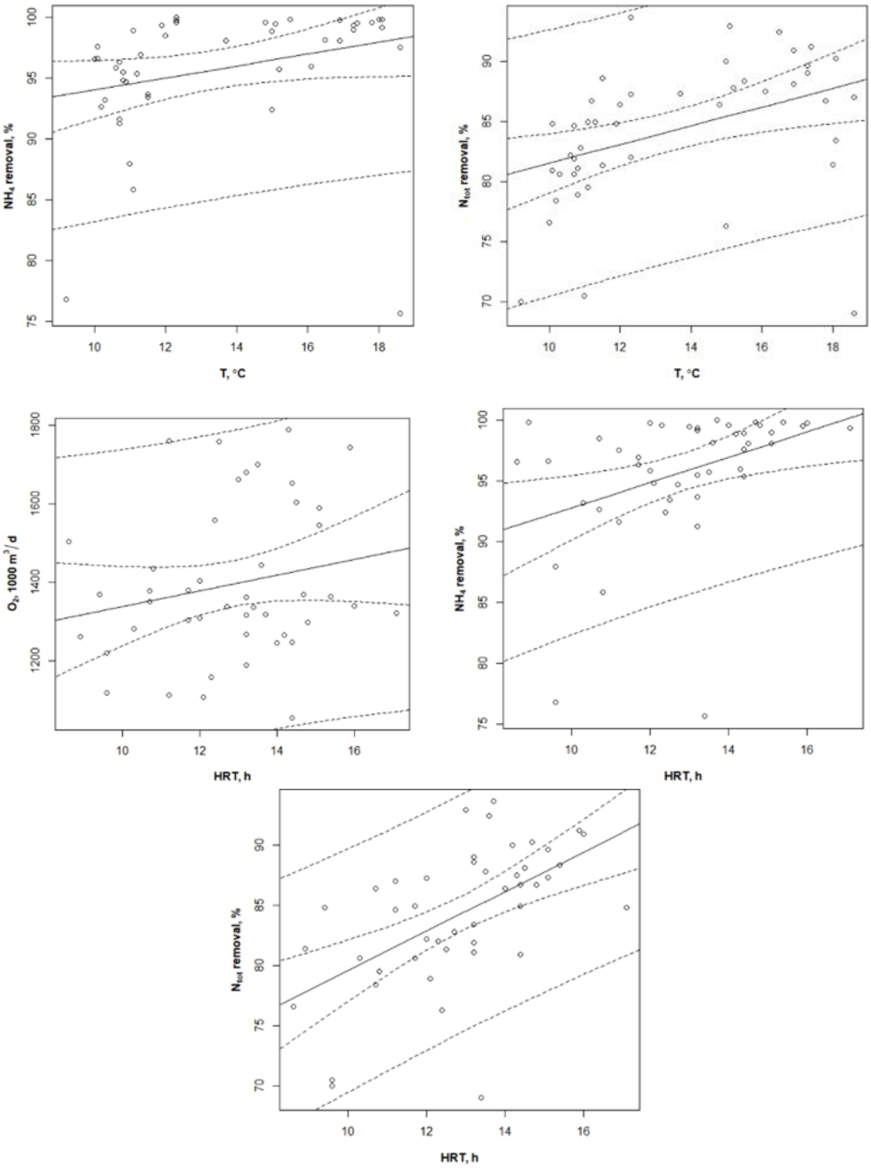


Figure 4.11 Scatter plots with regression lines and the lines showing 95% tolerance and the width of confidence intervals.

For illustration of statistical correlations, Figure 4.11 presents scatter plots with regression lines. The straight dotted lines mark the area where 95% of the measurement results should remain, and the curved dotted lines show where the real regression line with a 95% probability is located. The diagrams on the left in Figure 4.11 confirm that the effect of metals on N_{tot} and NH_4 removal efficiency and the air consumption is statistically insignificant because one of the possible positions of the real regression line is horizontal. The same situation also applies to the pairs air consumption and temperature, and air consumption and retention time. The scatter plots, which illustrate the effects of temperature and retention time on N_{tot} and NH_4 removal efficiency, on the other hand, confirm the existence of positive correlation. And the Models 1 and 2, taking account of the combined effect of three factors, gave adequate results where an increase in the load of heavy metals resulted in the drop of the treatment efficiency by 1.052% for N_{tot} and 1.035% for NH_4, respectively.

4.2.2 Removal of heavy metals in the activated sludge process

Figure 4.12 shows the average concentrations of 6 heavy metals in the influent and effluent of the wastewater treatment plant examined in 2011–2016. The highest influent concentrations were 108.27 µg/l for Zn and 45.18 µg/l for Cu. The reasons for this are partially explained also in Figure 1.1. As the examined wastewater treatment plant is partly receiving also storm water, the main sources of Zn include zinc roofing and street railings. Cu also originates from the roofing and from the water pipes widely used (Charters et al., 2016; Ma et al., 2016). In the research period, the removal efficiency was 84.7% for Zn and 82.7% for Cu. Similar results were also observed by Luo (2006) in the study where 94.1% of Cu and 75.3% of Zn were removed in the course of biological treatment under laboratory conditions (Luo et al., 2006). Hereby, the term "removal" refers to the removal of heavy metals from the aqueous phase, i.e. since the metals persist, the percentages cited above refer to the fact that in the wastewater treatment process, the difference between the influent and effluent parameters is due to the adsorption of Zn and Cu in the activated sludge or their biosorption in micro-organisms. As and Ni were the least-decreasing metals in the course of the examined wastewater treatment process, with a removal efficiency of 49.2% and 14.7%, respectively. These were also the elements with the lowest concentrations.

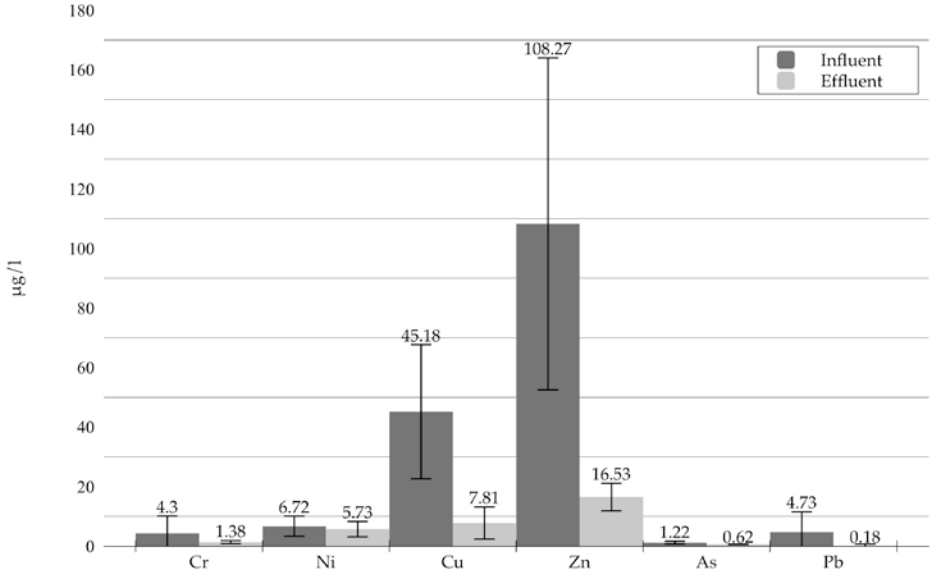


Figure 4.12 Average concentrations of heavy metals during a 5-year period in the influent and effluent of the examined wastewater treatment plant (n=118).

The study by Chipasa (2003) found that the higher the concentration of a heavy metal in the influent, the higher the removal efficiency, which was confirmed also in the present study (Chipasa, 2003b). The removal of heavy metals also depends on their water solubility at different pH values. In the present study, the pH value ranged from 7 to 9. Different studies point out that the better the water solubility of a heavy metal, the higher the biosorption and the smaller the physical adsorption (Dhokpande, 2013; Huang et al., 2016).

HRT is one of the key parameters in the activated sludge process: the longer the HRT, the more time micro-organisms have to aggregate the nutrients. This study allowed for a reliable analysis of HRT ranging from 5 to 18 h. The number of single days when the retention time was shorter or longer than the given range were not considered, as this was insufficient for the corresponding data analysis. The results are presented in Figure 4.13.

Figure 4.13 shows a strong linear correlation between HRT and the removal of heavy metals. The strongest correlation coefficient was found for Cu where R^2 was 0.9263 and the smallest given parameter of 0.7206 was found for Pb, respectively (Quintana et al., 2015). This correlation is good, considering how many different factors affect biological wastewater treatment and that any R^2 over 0.7 is considered as a strong linear correlation.

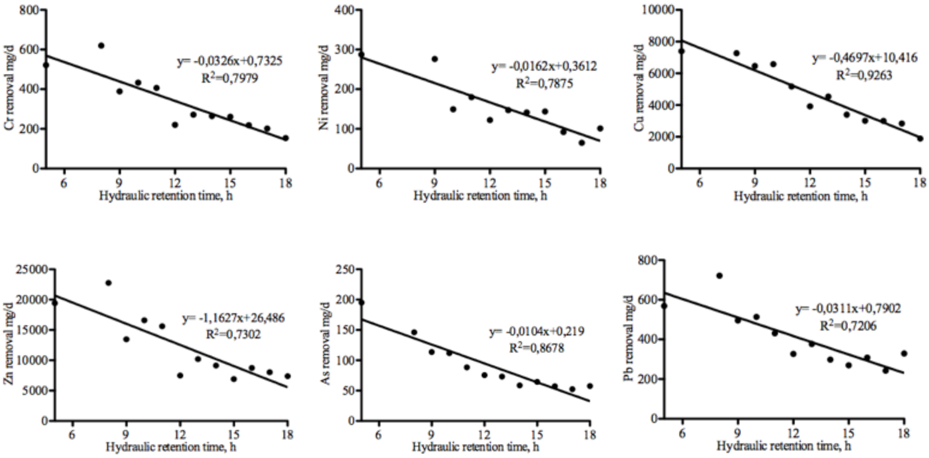


Figure 4.13 Dependence of removal of the examined heavy metals on HRT.

The study shows that the retention time mostly affects the removal of Cu. In the case of Cu, it was found that the removal rates for the minimum and maximum retention times examined were 7399.4 mgCu/d and 1883.7 mgCu/d, respectively, which makes a 74.5% difference in the removal efficiency (Figure 4.13). The removal of Pb was the least influenced by the retention time. During the minimum and maximum retention times, 568.9 mg/Pb/d and 329.1 mgPb/d, respectively, were adsorbed in the sludge, which makes a 42.2% difference in the removal efficiency. The respective differences between the minimum and maximum removal efficiencies were 70.6% for Cr, 64.9% for Ni, 62% for Zn and 70.5% for As. There are no clear answers to such linear correlation in publications to date, but according to different studies it can be explained by an inhibition of biological treatment caused by different heavy metal compounds. Malamis (2012) found in his study that already small concentrations of heavy metals (inhibition up to 49%, concentrations of heavy metals varied from 10.2 to 411.1 µg/l) cause significant inhibition of the heterotrophic biomass activity (Madoni, Davoli, & Guglielmi, 1999; Malamis, Katsou, Takopoulos, Demetriou, & Loizidou, 2012). Similar results were also found by Feng (2013) (Feng et al., 2013). In other words, longer retention time inhibits the metabolism in micro-organisms and reduces biological biosorption (Juliastuti, Baeyens, Creemers, Bixio, & Lodewyckx, 2003; You et al., 2009). Regarding Cu and Zn, Özbelge (2005) found an inverse correlation in the tests conducted in laboratory, where more heavy metals were aggregated in the sludge in the case of longer HRT (Özbelge et al., 2005). However, these tests used individual heavy metals with different initial concentrations, referring to the possibility that this may differ from the combined removal of heavy metals in an operating wastewater treatment plant.

The species composition of micro-organisms involved in the activated sludge process depends on the sludge age: the wastewater treatment plant, designed for removing only carbon, operates at SRT of less than 5 days, and the SRT for a treatment plant designed for nitrogen removal is more than 10 days. It is well known that the biosorption of heavy metals by different micro-organisms and the adsorption of activated sludge flocs formed in different micro-organisms can vary. Some micro-organisms produce a substance in their metabolism that will intensify the formation of activated sludge flocs and consequently, increase the adsorption of suspended solids. The higher the adsorption, the more of heavy metals will be removed from the wastewater.

The wastewater treatment plant under examination removes organic matter, N, as well as P from wastewater and therefore, SRT of more than 10 days is applied. Figure 4.14 presents the dependence of removal of heavy metals on SRT.

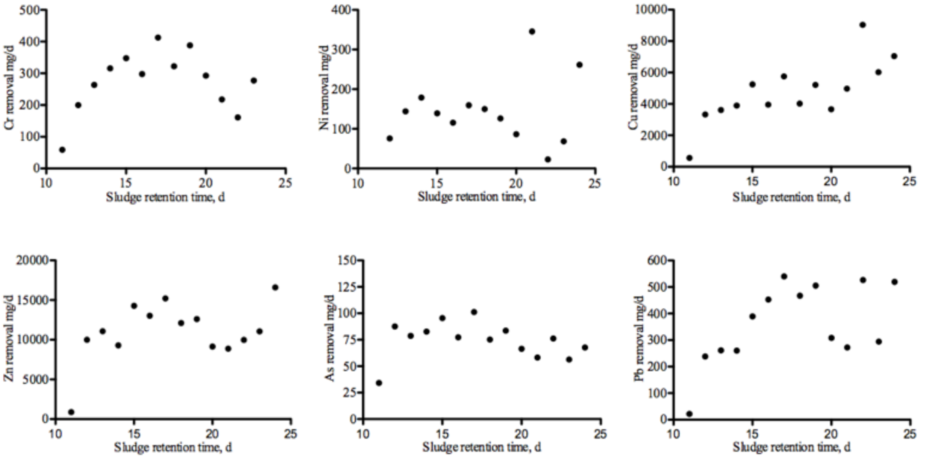


Figure 4.14 Dependence of removal of the examined heavy metals on SRT.

The dependence detected for SRT was not as strong as for HRT, however, it can be observed with all the examined metals that the highest amount of heavy metals is removed from the sludge that is 14 to 18 days old. The greatest dependence can be observed in the case of Cr, which clearly shows that the removal of Cr increases with the increasing sludge age and starts to drop again after 17 days. This dynamic can be explained by micro-organisms, characteristic to given sludge age, and by endogenous respiration caused by long SRT, causing the re-dissolution of aggregated heavy metals to increase. Similar hypothesis was also formulated by Gulyás (2015) (Gulyás et al., 2015). Study by Ong (2010) concluded that the longer the SRT, the more combined toxicity of heavy metals will start to inhibit biosorption and biological treatment (Ong et al., 2010). The review by Dhokpande (2014) found that the highest rate of heavy metals removal was achieved at the sludge age of 12 days (Sonali et al., 2014). However, as the operating wastewater treatment plant is a very complicated system, it is not possible to give a definite answer (Sonali et al., 2014). It can also be seen in Figure 4 that the removal capacity begins to increase starting from SRT of 23 days, but since the longest SRT at the wastewater treatment plant under examination was 24 days, the given dynamic could not be clearly proven.

While the species composition of the micro-organisms depends on SRT, the number of micro-organisms in the aeration tank depends on MLSS. The study examined rounded concentrations of MLSS in the range of 3500-6000 mg/l and the removed quantities of heavy metals in this range. The linear correlation between the analysed data is presented in Figure 4.15.

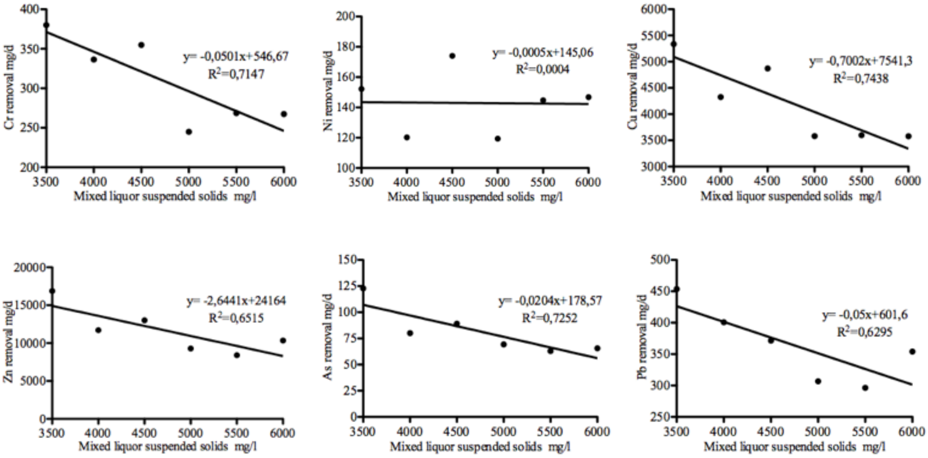


Figure 4.15 Dependence of removal of heavy metals on MLSS.

Figure 4.15 shows that MLSS mainly affected the removal of As, where the difference in the removal efficiency was 76.6%, which is also characterised by a strong R^2 of 0.7252. Similar dependence was also found for Zn and Cu, where the difference in the removal efficiency was 38.7% and 32.7%, and R^2 0.6515 and 0.7438, respectively. The smallest dependence was found for Ni, where difference between the removal rates at the minimum and maximum MLSS was 3.5% with no linear correlation identified either. The possible causes for the reduced removal of Ni are described at the beginning of chapter 4.2.2. However, the removal efficiency for all the examined heavy metals dropped when MLSS started to increase. The similar results were confirmed by Hammaini (2007) and Wu (2004) in their laboratory tests, where the sorption of heavy metals decreased with the increasing MLSS, explained by the screen effect where bigger biomass starts hindering the sorption (Hammaini et al., 2007; Wu et al., 2004).

4.2.3 Removal of heavy metals by adsorption

In Test 1, PAC was dosed into the effluent of an operating wastewater treatment in different concentrations, in order to find the optimal PAC dose for the removal of heavy metals. The retention time chosen for the process was 10 minutes, because it was the equilibrium concentration for most of the heavy metals. At the beginning of the test, the pH of the water was 7.22 and the higher the PAC dose added, the more alkaline was the pH of the test reactor; at 100 mg/l of PAC, the final pH was 7.5, i.e. PAC reduced the acidity of the water. The conductivity of the water before the test was 1200 μS/cm, and at the highest dose of PAC, the equilibrium value reached was 1191 μS/cm, i.e. the adsorption did not have significant effect on conductivity. The results of Test 1 are presented in Figure 4.16.

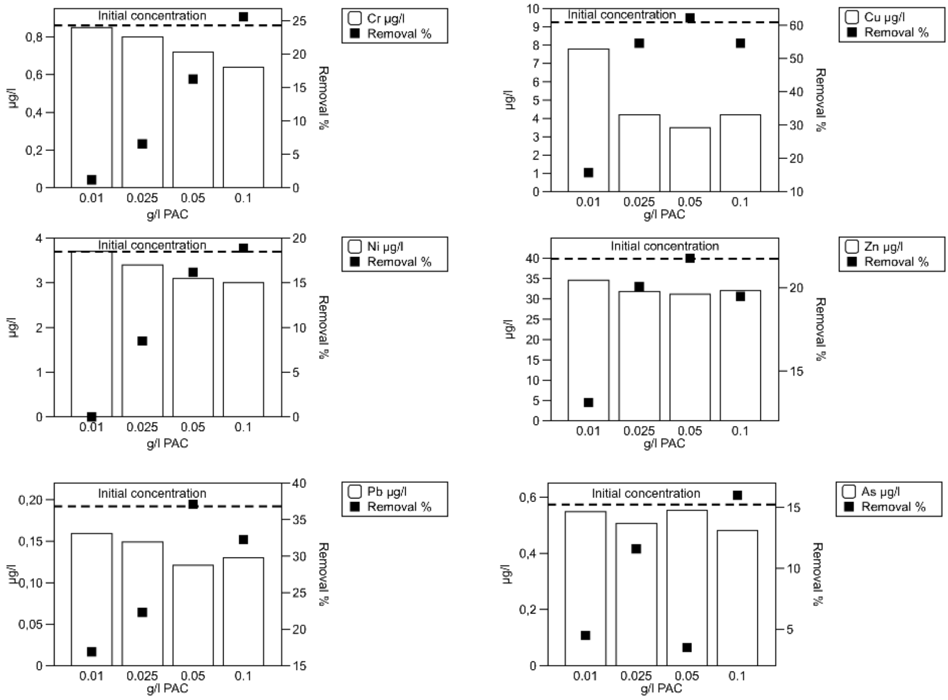


Figure 4.16 Test 1, where PAC was dosed into the effluent from the clarifiers in doses of 10, 25, 50, and 100 mg/l in order to determine the optimum dose and treatment efficiency ratio.

As for Cr, the initial concentration was 0.86 μg/l and the PAC concentrations dosed were 10, 25, 50 and 100 mg/l, respectively. The treatment efficiency increased linearly as the PAC doses increased, at 10 mg/l of PAC, 1.2% of Cr was removed, and at 100 mg/l of PAC, 25.6% of Cr was removed. The initial concentration of Cu was 9.25 μg/l and the removal efficiencies of the examined PAC doses were 15.7%, 54.6%, 62.2% and 54.6%, respectively. That is, the maximum Cu removal of the equilibrium system under review was achieved at 50 mg/l of PAC, and this started to drop again when dosing 100 mg/l of PAC. Similar dynamics of removal also occurred for Zn, where the maximum adsorption of 21.8% was achieved at 50 mg/l of PAC, and further increase in dosing did not increase the removal efficiency. It follows from Figure 4.16 that the best response to adsorption (max removal >30%) was achieved for Cu and Pb, where the maximum treatment efficiencies were 62.2% and 37.1%, respectively. Cr, Ni, Zn, and As did not respond to adsorption process so well, with the maximum treatment efficiencies of 25.6%, 18.9%, 21.8% and 16% achieved, respectively. For Cu, Zn, and Pb, the most effective dose was 50 mg/l of PAC, and for Cr, Ni, and As, 100 mg/l of PAC, respectively. Ong (2010) found in his batch tests, which were carried out with synthetic wastewater and at the initial heavy metal concentrations that were thousand times higher and with a retention time 30 times longer than in the present study, that the best response to PAC adsorption were achieved for Cu, Ni, and Zn, and the worst for Cd and Cr (Ong et al., 2010). The difference in the adsorption of heavy metals compared to this study is likely due to the additional compounds contained in actual wastewater, which also adsorb and reduce the specific adsorption of heavy metals. The study by Karnib (2014) found that the efficiency of adsorption at low concentrations of heavy metals (30 mg/l) is ranked as follows: Ni (90%), Cd (86%), Zn (83.6%), Pb (83%), and Cr (50.6%) (Karnib, Kabbani, Holail, & Olama, 2014). According to the results of the study described here, the same ranking is following: Ni>As>Zn>Cr>Cu>Pb. For a better comparison of the removal efficiencies, the data presented in Figure 4.18 are for the mass removed per 1 g of PAC.

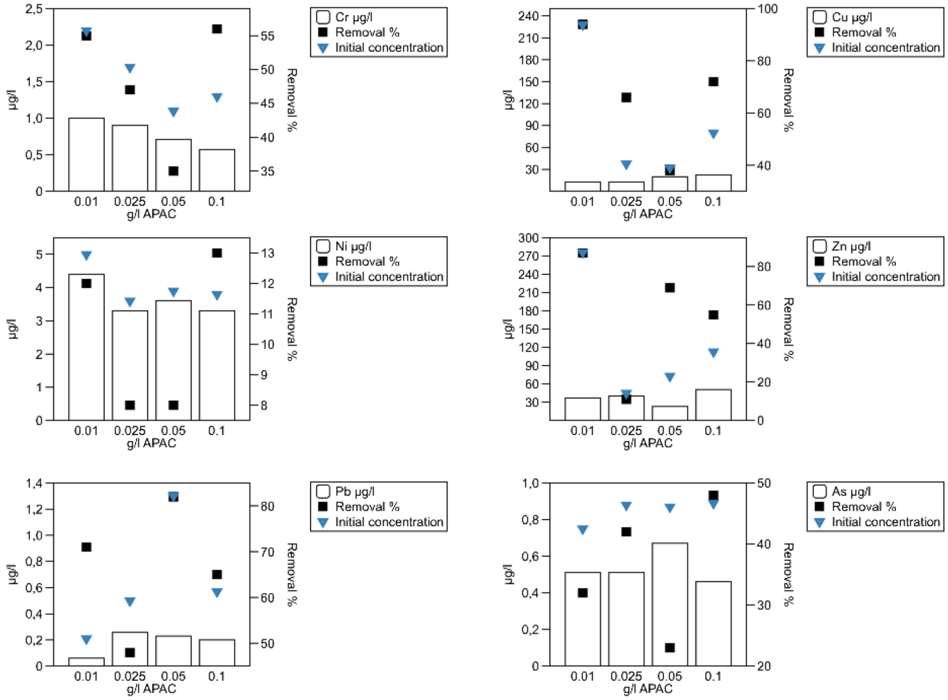


Figure 4.17 Test 2, where PAC was dosed into the bioreactor in doses of 10, 25, 50, and 100 mg/l in order to determine the optimum dose and treatment efficiency ratio.

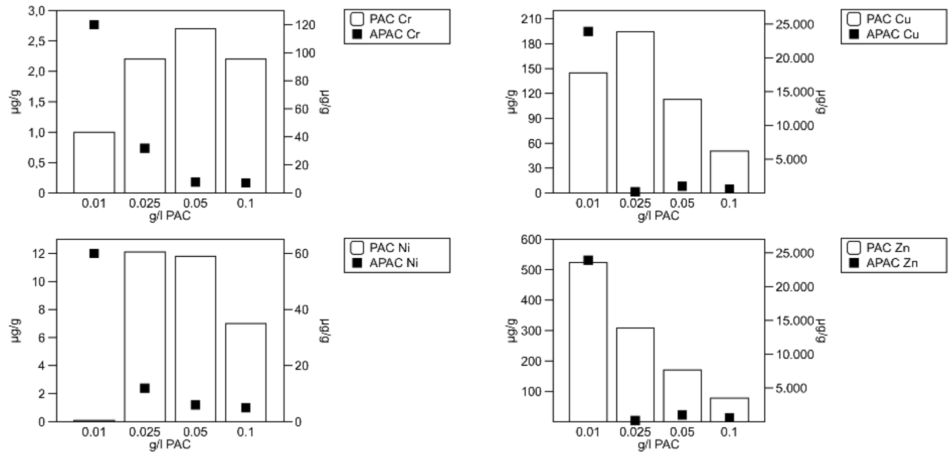
In Test 2, the pH in the bioreactor before dosing PAC was 7.32 and the conductivity as an average 1534 µS/cm. The pH in the bioreactor increased and conductivity dropped as the PAC doses were increased. At the maximum PAC dose of 100 mg/l, the pH increased to 7.49 and conductivity dropped to 1194 μS/cm, respectively. The decrease in the research parameters was due to absorption with PAC and the sorption by biomass which was not examined individually. But the sorption by biomass can be explained with a comparison of Test 1 and Test 2, the results of which are presented separately in Figure 4.18.

The removal efficiencies and the initial and final concentrations for the heavy metals analysed in APAC test are presented in Figure 4.17. For Cr, it was found that the smallest examined PAC dose (10 mg/l) already removed 55% of Cr and by increasing the PAC dose the treatment efficiency was not improved but rather aggravated. As for Cu, the initial concentration in the first series of tests was very high in comparison with other series, but with the PAC dose of 10 mg/l, a 94% removal efficiency was reached. The best response to the APAC process was achieved for Cr, Cu, Zn, Pb, and As, with the maximum removal efficiencies 55%, 94%, 87%, 82% and 48% achieved, respectively. The removal of Ni in this test was poorer compared to the other parameters, with the respective removal efficiency of 13%. The average treatment efficiency values for Test 1 and Test 2 are presented in Table 4.8.

Table 4.8 Average treatment efficiency in Test 1 and Test 2 (%).

	Cr	**Cu**	**Ni**	**Zn**	**Pb**	**As**
Test 1 PAC	12.4	10.9	46.8	18.6	8.9	27.2
Test 2 APAC	48.3	10.3	67.5	55.4	36.3	66.7

Table 4.8 shows that in terms of the removal efficiency, two different technological concepts for the removal of Cu and Ni proved to be similar, with a ±15% the same efficiency being achieved for each. At the same time, the differences in the case of Cr, Zn, Pb, and As were larger and in terms of the removal efficiency, the APAC process proved to be better with its results being over 2 times more effective. These better results in the treatment efficiency may have resulted from the biosorption or sorption where these specific heavy metals were adsorbed on the PAC surface and also by biomass (Carolin et al., 2017; Luo et al., 2006).



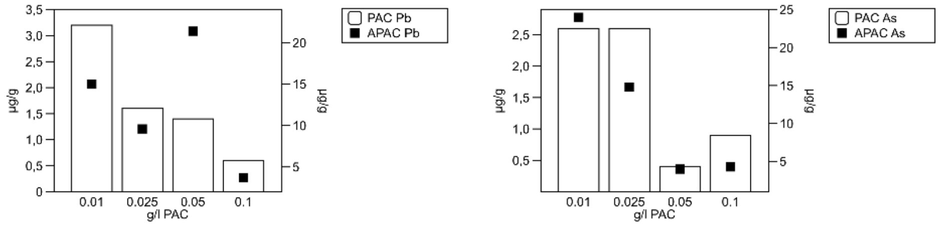


Figure 4.18 Removal of heavy metals per 1 g of PAC (Qe) in Test 1 and Test 2.

In order to compare the tests with different initial concentrations and to identify the most effective dosing point and dose of PAC, the removal of heavy metals (µg/g) per 1 g of PAC was identified. The results are presented in Figure 4.18. It follows from Figure 4.8 that the highest removal of Cr per 1 g of PAC was achieved at 50 mg/l of PAC in Test 1 and at 10 mg/l of PAC in Test 2 (APAC), with the removal of 2.7 µg/g and 120 µg/g, respectively. For Cu, the most effective dose in Test 1 proved to be 25 mg/l of PAC and 10 mg/l of PAC in Test 2, similarly to Cr. Ong (2010), in his tests carried out with synthetic wastewater, found the following Qe-s: Cu 61 mg/g, Cd 22 mg/g, Zn 29 mg/g, Ni 33 mg/g, Cr 10 mg/g. The big difference between the tests carried out with synthetic wastewater and actual wastewater indicate that the compounds contained in wastewater reduce the adsorption efficiency of heavy metals and the adsorption capacity depends on the concentration of the compounds found in the wastewater; the tests with synthetic wastewater have shown that higher concentration of heavy metals reduces the specific adsorption (Ong et al., 2010).

Based on the tests carried out, which consider the PAC dose and Qe, the most effective doses of PAC to remove the examined parameters are presented in Table 4.9. The data analysis also considered the rationality aspect, where 50% increase of the PAC dose is not justified in order to increase, for example, the removal efficiency of Ni by 2.7%.

Table 4.9 The most effective PAC dose (mg/l) depending on the dosing point.

	Cr	Cu	Ni	Zn	Pb	As
Test 1 PAC	50	25	50	25	50	25
Test 2 APAC	10	10	10	10	10	25

It follows from Table 4.9 that in Test 1, the most effective PAC dose was 34 mg/l, as an average, and in Test 2, 14 mg/l of PAC, respectively. Higher dose in the advanced wastewater treatment is likely to result from the small concentration of suspended solids and the low sorption. Whereas in the case of APAC, the circulation of unreacted PAC in the return activated sludge and the additional sorption by biomass are ensured. Leaving aside the costs of the sludge treatment, the first technological solution appears to be more expensive (Test 1) than the second, because the necessary PAC dose is higher, and furthermore, this means need for installing additional equipment to remove PAC (Celine, Scott, & Biller, 2017; Hu, Aarts, Shang, Heijman, & Rietveld, 2016). For the APAC process, only a PAC dosing unit needs to be added and PAC will be removed along with the waste activated sludge. But given the current technological level, this solution requires the waste activated sludge to be incinerated, because the separate removal of heavy metals and other micropollutants from the sludge is very complicated (Meinel et al., 2015; Weimar, 2014). One of the advantages of the APAC process appears to be also the improved nitrification. Several studies have demonstrated that PAC provides a good biofilm carrier for the various nitrifying micro-organisms, and also, positive effects have been observed on the phosphorus removal (Hu et al., 2014; Specchia & Gianetto, 1984). This was also observed in the present test where N_{tot} removal efficiency was 70.4% after dosing 10 mg/l of PAC and 88.7% when dosing 50 mg/l of PAC. Because for 8 hrs PAC could not act as a biofilm carrier, it can be assumed that PAC removed some of the inhibiting compounds in aqueous phase, and thereby improved nitrification and denitrification.

4.2.4 Removal of heavy metals from wastewater

Three options for removing heavy metals were discussed above: sorption in the activated sludge, dosing PAC in the advanced wastewater treatment, and APAC process with PAC being dosed into the bioreactor. In the following, these methods are analysed in order to find the optimal technological solution for removing heavy metals. Advantages and disadvantages of removing heavy metals by using biological removal and by adsorption with PAC are presented in Table 4.10.

Table 4.10 Removing heavy metals by using biological removal and by adsorption with PAC.

	Biological removal	**PAC**	**APAC**
Advantages	Does not require further investments. Easy to control the process (MLSS, SRT). Efficient in removing several heavy metals.	Easy to control the process.	Efficient in removing heavy metals. Dosing PAC is easy and does not require any additional space. More efficient compared to PAC process.
Disadvantages	Heavy metals accumulate in the activated sludge, which then cannot be directly reused. Heavy metals accumulating in the activated sludge inhibit nitrogen removal. Often not possible to control HRT in a flow-through system.	Requires further investments (flocculation chamber, disc filter, etc.) Treatment efficiency is unstable, because it is an equilibrium process. Installing additional equipment requires space. Less efficient compared to APAC process. PAC is irrecoverable.	Heavy metals and other hazardous compounds remain in the sewage sludge, so the sludge cannot be directly reused. PAC is irrecoverable.

It follows from Table 4.10 that removing heavy metals by using biological removal appears to be an efficient solution in the case of a wastewater treatment plant where sludge is incinerated. However, if the sludge is used in the circular economy, this solution is not suitable. In order to improve the treatment efficiency, a combination of the APAC process and biological sorption of heavy metals can be used, however, bearing in mind that a 1 kg/d increase in the load of heavy metals reduces the efficiency of nitrification by 1.035%. Earlier studies have shown that the APAC process reduces this effect because the hazardous compounds are aggregated with activated carbon, which reduces their mobility (Hu et al., 2014; Specchia & Gianetto, 1984).

Based on a more detailed analysis performed on an operating wastewater treatment plant, the necessary PAC dose would be 34 mg/l in the case of the PAC process and 14 mg/l in the case of the APAC process. If the average flow volume of that wastewater treatment plant is ca 136 000 m^3/d, the necessary amount of PAC would be:

- 4624 kg/d for the PAC process,
- 1904 kg/d for the APAC process.

At the average price for PAC, which is 0.89 EUR/kg, the daily costs would amount to 4115 EUR/d when using PAC and 1694.6 EUR/d when using APAC (this is without extra sludge treatment costs). In the case of APAC, sludge treatment adds extra costs which are difficult to estimate.

5 Conclusions

This doctoral thesis aimed to examine how the hazardous compounds, such as heavy metals and pharmaceutical residues, are released to the wastewater treatment plant, what is the effect of heavy metals on the biological treatment, and to suggest the best possible technological solution for their removal. The main focus was on the biological removal of heavy metals and the combined effect of heavy metals on the biological treatment, incl. nitrification.

The main results of the study are summarised as follows:

- The ageing population increases the consumption of pharmaceuticals in Estonia and consequently also the load to the environment. The modelling showed that the pharmaceuticals examined here do not cause any hazard to the environment at the current concentrations, however, the combined effect of various compounds and their long-term impact on living organisms cannot be excluded.
- The adsorption test results for diclofenac, sulfamethoxazole and levofloxacin removal showed that the best response to adsorption is achieved for levofloxacin and the worst response for sulfamethoxazole, respectively. These results can be used in dimensioning the treatment process for the removal of the said pharmaceuticals.
- The tests that were carried out with wastewater showed that the large number of compounds contained in wastewater have a direct impact on the removal of organic pollutants. Therefore, the amount of PAC dose needed in this study was higher than the doses applied in earlier studies that were carried out under controlled conditions (with synthetic wastewater). Wastewater was found to contain also some organic compounds that adsorb poorly and do not respond to this process; these compounds formed 6-16% of all TOC, and so the pre-ozonation of water to improve the adsorption of these compounds is not justified. Using PAC as an advanced wastewater treatment proved to be the most efficient in TOC removal.
- The analyse of the combined effect of heavy metals showed that even the small concentrations of heavy metals have an inhibitory effect on the biological treatment. With the load of heavy metals increasing by 1 kg, the nitrification efficiency dropped by 1.035%. The results of this study can be used in developing an automated inhibition detection, where inhibition is detected by monitoring the oxygen consumption which starts to drop with inhibition.
- The study of the biological removal of heavy metals demonstrated that the sorption of heavy metals can be controlled by means of HRT, MLSS and SRT. Longer retention time and higher MLSS reduce the sorption. As for SRT, it was found that the maximum sorption is achieved at 15-19 days for most of the examined heavy metals. However, it must be considered that the higher sorption of heavy metals by biomass inhibits the biological treatment.
- The highest efficiency of removing heavy metals with PAC is achieved in the APAC process. However, this process takes heavy metals from aqueous phase

to sludge phase and makes it difficult to reuse the sludge. Therefore, the APAC process is only suitable where sludge is incinerated.

- Using PAC in the advanced wastewater treatment for the removal of heavy metals is less efficient compared to APAC, but proves to be an optimal solution for reducing the environmental load of hazardous compounds and phosphorus when combined with the use of disc or sand filter.

In summary, the study found that the combined effect of heavy metals occurs at thousand times smaller concentrations than the effect of individual heavy metals. It also found that the movement of heavy metals between aqueous phase and sludge phase can be controlled with process parameters. Removing hazardous compounds by adsorption is simple in terms of technology, but the disadvantages include increasing investments and operating costs.

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Abstract

Harmful substances in wastewater, possible technical solutions for their removal

Hazardous compounds such as heavy metals and pharmaceutical residues have become a serious problem after being released into the environment, and this is faced by the engineers everywhere in the world. The amount of heavy metals released to the environment in the course of our daily living is significant. These amounts mainly come from the products such as car tyres, various coated materials, cosmetics, burning of oil shale, etc. We also have more than 3000 active ingredients in use and most of them reach the environment after being consumed by our metabolic system. One of the stops on the way of these hazardous compounds is the wastewater treatment plant. This study examines the loads of pharmaceutical residues received in the wastewater treatment plant and technologies for their removal. It also analyses the combined effect of heavy metals on an operating wastewater treatment plant and technologies for the biological removal of heavy metals. Furthermore, a comparison is made between applying the same technological solution to remove heavy metals by adsorption at two different dosing points – dosing PAC as an advanced wastewater treatment, after the existing treatment process, and dosing PAC straight into the bioreactor, where the adsorbed compounds are removed with sludge.

In order to estimate the size of the loads of pharmaceutical residues that reach the major wastewater treatment plants in Estonia, theoretical models were developed, considering the amounts of pharmaceuticals, their degradation in the body and their removal in the wastewater treatment plant. The study covered years 2006-2014 and found that during that time, for example, the consumption of diclofenac has dropped 19.9%, while the consumption of ibuprofen has gone up by 14.1%. Due to the ageing population, a significant increase has been observed in the consumption of pharmaceuticals. This theoretical model also showed that the average concentration of diclofenac in the effluent of the examined wastewater treatment plants ranged from 0.8 to 1 μg/l and from 11.4 to 13.4 μg/l in the case of ibuprofen. These concentrations do not pose any direct risk to the environment, but we cannot rule out the possibility that various compounds have a combined effect.

One of the technological solutions to remove pharmaceutical residues is by adsorption with activated carbon (PAC). The study analysed the removal of three pharmaceuticals – diclofenac, sulfamethoxazole and levofloxacin – with PAC. The tests revealed that the best response to adsorption is achieved in levofloxacin removal, where within 5 minutes of retention time, 77% of all the active ingredient had been removed, and after 60 minutes, 94% of all the active ingredient was removed. Sulfamethoxazole had the lowest adsorption capacity, with only 68% removal efficiency being achieved after 60 min of retention time. Based on these results, a (Freundliche) adsorption isotherm was prepared, serving as a basis for dimensioning the respective treatment process. Since this test was performed under controlled conditions, further tests were carried out with actual wastewater, using sum parameter TOC to determine the overall drop of organic compounds. A comparison was made between two technological

solutions, the PAC and the APAC process. The PAC process appeared as the most efficient, with an adsorption capacity per 1 g of PAC reaching 12096 mg/g, compared to that of the APAC process, which was 4060 mg/g, respectively.

The release of heavy metals to the wastewater treatment plant often cannot be avoided, but little is known about the combined effect of heavy metals. When earlier studies had focused on the concentration of individual heavy metals, this study revealed the combined effect of six heavy metals, including Zn, Ni, Pb, Cu, Cr and Cd. As a result of the respective inhibition modelling it was found that with the load of heavy metals increasing by 1 kg, the nitrification efficiency drops by 1.035%. As a result of this analysis, mathematical models were prepared that can be used for example in developing an automated system for the detection of inhibiting compounds.

The last section of the study compared various technological solutions to remove heavy metals in the wastewater treatment plant. The analysis made on the biological removal of heavy metals demonstrated that the sorption of heavy metals can be controlled by means of HRT, MLSS and SRT. Longer retention time and higher MLSS reduce the sorption, and as for SRT, the maximum sorption is achieved in 15-19 days. This knowledge is necessary if we need to send the maximum concentration of heavy metals to sludge, for example, when the sludge is incinerated, and vice a versa - if we wish to reuse the sludge and therefore reduce the percentage of heavy metals in the sludge by removing heavy metals in the advanced wastewater treatment, for example, with activated carbon.

In the first half of the study, the analysis was done to identify the best suited technological solution to remove heavy metals, revealing that this is adsorption with activated carbon. Laboratory tests were carried out to assess the suitability of the technology by comparing the advantages and disadvantages of two different PAC dosing points. The tests revealed that the highest efficiency of removing heavy metals with PAC is achieved in the APAC process that is supported by biosorption. The APAC process is, as an average, 67.5% more efficient, but the disadvantage of this process is the accumulation of heavy metals into sludge. Therefore, higher PAC costs have to be considered if we wish to reuse the sludge.

Further studies will be needed on various organic compounds contained in TOC, because the tests with wastewater that were carried out in this study did not allow to identify which of the compounds in wastewater exactly responded well to adsorption and which did not. This further information would provide clarity on if the PAC process should be preceded by, for example, deep oxidation. However, all in all, when it comes to heavy metals and hazardous compounds, then the results achieved will support the decision making of people working in the wastewater treatment plants.

Lühikokkuvõte

Ohtlikud ained reovees, võimalikud tehnilised lahendused nende eemaldamiseks

Ohtlike ühendite nagu ravimijääkide ja raskmetallide sattumine keskkonda on muutunud tõsiseks probleemiks, millega insenerid üle maailma silmitsi seisavad. Meie igapäeva tegemiste käigus vabaneb keskkonda märkimisväärne kogus raskmetalle, mis satuvad sinna põhiliselt toodetest nagu rehvid, vastava pindega materjalidest, kosmeetikatoodetest, põlevkivi põletamisest jne. Samuti on kasutusel üle 3000 ravimitoimaine, millest suur osa jõuab peale tarbimist läbi meie ainevahetuse keskkonda. Üks punkt sel teekonnal, mida mainitud ohtlikud ühendid läbivad, on reoveepuhasti. Antud uuringu käigus uuritakse diklofenaki ja ibuprofeeni koormusi reoveepuhastis ja diklofenaki, sulfametoksasooli ja levofloksatsiini eemaldamise tehnoloogiad. Lisaks analüüsitakse raskmetallide kombineeritud koosmõju töötavale reoveepuhastile ja raskmetallide bioloogilisi eemaldustehnoloogiad. Täiendavalt võrreldakse ühte tehnoloogilist lahendust raskmetallide eemaldamiseks adsorptsiooni abil kahes erinevas doseerimispunktis: PAC doseerimine järelpuhastusena peale olemasolevat puhastusprotsessi ja PAC doseerimine otse bioreaktorisse, kust adsorbeerunud ühendid eemaldatakse reoveesettega.

Eesti suurimate reoveepuhastite ravimite koormuste teadasaamiseks koostati teoreetilised mudelid, mis arvestasid ravimite kogustega, nende lagunemisega organismis ja nende eemaldamisega reoveepuhastis. Uuringus käsitleti perioodi 2006-2014 ja leiti, et näiteks diklofenaki tarbimine on antud perioodil 19.9% vähenenud, kuid ibuprofeeni kasutamine samas 14.1% tõusnud. Seoses elanikkonna vananemisega on täheldatud ravimite kasutamise märkimisväärset tõusu. Teoreetiline mudel näitas lisaks, et uuritud reoveepuhastite keskmine diklofenaki kontsentratsioon väljundis jäi vahemikku 0.8-1 μg/l ja ibuprofeeni puhul 11.4-13.4 μg/l. Antud kontsentratsioonid keskkonnale otsest ohtu ei kujuta, kuid välistada ei saa erinevate ühendite koosmõju.

Üks tehnoloogiline lahendus ravimijääkide eemaldamiseks on adsorptsioon aktiivsöe abil (PAC). Uuringus analüüsiti kolme ravimi - diklofenaki, sulfametoksasooli ja levofloksatsiini - eemaldamist aktiivöe abil. Katsetest selgus, et kõige paremini allub adsorptsioonile levofloksatsiini, mille puhul 5 min viibajaga oli eemaldatud 77% ja 60 min pärast 94% kogu toimainest. Kõige halvemini allus adsorptsioonile sulfametoksasool, mille eemaldusefektiivsus oli peale 60 min viibeaega vaid 68%. Saadud tulemuste põhjal koostati adsorptsiooni isotermin (Freundliche), mis on aluseks vastava puhastusprotsessi dimensioonimisel. Kuna antud katse toimus kontrollitud tingimustes, siis viidi täiendavalt läbi katsed reoveega, kus üldist orgaaniliste ainete vähenemist määrati summaparameetri TOC kaudu. Võrreldi kahte tehnoloogilist lahendust: PAC ja APAC protsessi. Kõige efektiivsemaks osutus 1 g PAC kohta PAC protsess, kus adsorptsioonivõimekus oli vastavalt 12096 mg/g kohta, APAC puhul 4060 mg/g.

Raskmetallide sattumine reoveepuhastisse on tihti vältimatu, kuid vähe on teada raskmetallide kombineeritud koosmõjust. Kui varasemad uuringud on keskendunud üksikute raskmetallide kontsentratsioonidele, siis antud uuringu käigus selgus, et kuue raskmetalli Zn, Ni, Pb, Cu, Cr ja Cd kombineeritud koosmõju on olemas. Vastava

inhibitsiooni modelleerimise tulemusena leiti, et 1 kg/d raskmetallide koormuse tõus vähendab nitrifikatsiooni efektiivsust 1.035%. Analüüsi tulemusena koostati matemaatilised mudelid, mida on võimalik kasutada näiteks inhibeerivate ühendite tuvastamise süsteemi automatiseerimiseks.

Töö viimases osas võrreldi erinevaid tehnoloogilisi lahendusi raskmetallide eemaldamiseks reoveepuhastis. Analüüsiti raskmetallide bioloogilist eemaldust, kus leiti, et raskmetallide sorptsiooni on võimalik juhtida HRT, MLSS ja SRT kaudu. Sorptsioon väheneb pikema HRT ja kõrgema MLSS korral ning kõrgeim sorptsioon saavutatakse SRT korral, mis on 15-19 päeva. Antud teadmised osutuvad vajalikuks, kui on tarvis suunata võimalikult suures kontsentratsioonis raskmetalle settesse, näiteks sette põletamise korral, ja vastupidi, kui soovime setet taaskasutada ja seeläbi raskmetallide osakaalu settes vähendada, eemaldades raskmetallid järelpuhastuses näiteks aktiivsöe abil.

Antud uurimistöö esimeses pooles analüüsiti, missugune tehnoloogiline lahendus on raskmetallide eemaldamiseks kõige sobilikum ning leiti, et see on adsorptsioon aktiivsöe abil. Tehnoloogia sobilikkuse hindamiseks viidi läbi laboratoorsed katsed, kus hinnati kahe erineva PAC doseerimispunkti eeliseid ja puuduseid. Analüüsi käigus selgus, et raskmetallide eemaldamiseks on kõige efektiivsem APAC protsess, kus raskmetallide eemaldust toetab lisaks biosorptsioon. Keskmiselt oli APAC protsess 67.5% efektiivsem, kuid antud protsessi puuduseks on raskmetallide akumuleerumine reoveesettesse. Seega, kui soovime reoveesetet taaskasutada, siis peame arvestama kõrgema PAC kuluga.

Edasist uurimist vajaksid TOC sisalduvad erinevad orgaanilised ained, sest antud uuringus läbiviidud katsetest reoveega ei olnud võimalik välja selgitada, missugused ühendid täpsemalt reovees allusid hästi adsorptsioonile, missugused mitte. Täiendav informatsioon annaks selgust, kas PAC protsessile peaks eelnema näiteks süvaoksüdatsioon. Kokkuvõttes on saadud tulemused abiks reoveepuhastitega tegelevatele inimestele raskmetallide ja ohtlike ühenditega seonduvate otsuste tegemisel.

Appendix

Paper I

Lember, E.; Pachel, K.; Loigu, E. (2016). Modelling diclofenac and ibuprofen residues in major Estonian seaside cities. Journal of Water Security, 2 (2), 1−7.10.15544/jws.2016.002.

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MODELLING DICLOFENAC AND IBUPROFEN RESIDUES IN MAJOR ESTONIAN SEASIDE CITIES

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Abstract. A theoretical model was developed to model the fate of two common pharmaceutical residues: diclofenac and ibuprofen in eight Estonian seaside cities that discharge their wastewaters directly into the Baltic Sea. The consumption rates of the active ingredients of diclofenac and ibuprofen from 2006-2014 were analysed. A decrease of 19.9% for diclofenac consumption and an increase of 14.1% for ibuprofen were found. The fate of diclofenac and ibuprofen were modelled by considering the human metabolism removal rate for pharmaceuticals, the removal rate of diclofenac and ibuprofen in activated sludge wastewater treatment plants (WWTP) and annual flow rates. An average decrease from 1 to 0.8 µg/l (decrease of 20%) for diclofenac and an increase from 11.4 to 13.4 µg/l (increase of 14.9%) for ibuprofen for the concentration in the effluents of the WWTP were modelled. The model gives us a good overview about the theoretical concentrations of pharmaceutical residues in the environment and is helpful for evaluating environmental impacts.

Keywords: *diclofenac residues, fate of pharmaceuticals, ibuprofen residue, modelling pharmaceuticals, pharmaceutical residues in the environment.*

Introduction

Pharmaceuticals used in human and veterinary medicine have become an important public health issue in recent years and are an emerging environmental problem, since they pose a threat to both the environment and humans. With an increasingly aging population over the world in recent years, a new problem has emerged: pharmaceutical residues in the environment (Zhou *et al*., 2009). Pharmaceutical residues have already been found in measurable concentrations (µg/l and ng/l) in lakes, seas, groundwater (diclofenac and ibuprofen in range of 0.03-0.06 µg/l and 0.004-0.4 µg/l accordingly) and drinking water and they have become an emerging environmental problem (Cleuvers, 2004; Fent *et al*., 2006; Li, 2014). There is no acute toxic effect of pharmaceuticals for humans, but the concerning issue is their chronic toxicity and bioaccumulation. Pharmaceuticals are constructed to be persistent, biologically active and to target specific metabolic pathways (Ternes, 1998; Heberer, 2002; Moreno-González *et al*., 2016).

In the 1990s in Pakistan, the incomprehensible dying of white-backed vultures (*Gyps africanus*), resulting in a 95% decrease in the population of vultures, was observed. In examining the reasons for the deaths, scientists investigated the primary food source of vultures, dead domestic livestock. A connection between the food source of vultures and the deaths was found, as diclofenac residue concentrations of 0.051-0.063 µg/g were detected when scientists analysed the kidneys of vultures (Oaks *et al*., 2004).

In other research, Dietrich and Prietz (1999) analysed the lethality and teratogenicity of diclofenac to zebrafish embryos. A lethal concentration of 489 ± 50 µg/l (LC_{50}/96h) and an effect concentration of 90 ± 20 µg/l (EC_{50}/96 h) was found (Dietrich *et al*., 1999; Schwaiger *et al*., 2004). An acute toxicity of ibuprofen for algae EC_{50} /96 h 7100 µg/l was reported by Halling-Sørensen and Carina Carlsson and reported for *Lepomis macrochirus* (bluegill) a LC_{50} of 173 mg/l (Carlsson *et al.,* 2006; Halling-Sørensen *et al*., 1998).

To date, there have been rather few studies that reported about pharmaceutical residues in the water environment in Estonia; hence, it is important to know the impact rate of pharmaceuticals in the Baltic Sea catchment area. The Baltic Sea is virtually a closed system, much like a lake, and very sensitive to the accumulation of different harmful substances. An important issue is that the Baltic Sea is an important source of food for Nordic countries, and the bioaccumulation of diclofenac and ibuprofen is known. Therefore, it is important to analyse the fate of different pharmaceuticals in the environment (Carlsson *et al*., 2006; Borecka *et al*., 2015; Moreno-González *et al*., 2016).

Stockholm University has found diclofenac and ibuprofen in different WWTP runoff areas in concentrations ranging from 0.2 to 7.1 µg/l and 0.1 to 0.2 µg/l and a total non-steroidal anti-inflammatory drugs (NSAID) concentration of 24 µg/l. In the same study, a bioaccumulation effect of NSAID on the blue mussel in the Baltic Sea was found (Ericson *et al*., 2010). Depending on various troubling studies, a new regional HELCOM status report is scheduled in February 2016, which will provide an extensive background to determine the possible harmful effects of pharmaceutical residues in the Baltic Sea. In Estonia, hazardous substances, including the content of priority substances in wastewater and stormwater effluents, should not exceed the environmental quality limit values of surface water bodies, as established by the Water Act. However, there are no limits determined for pharmaceuticals.

There are already many promising treatment technologies for pharmaceutical residues removal, such as membrane bioreactor (MBR), activated carbon, advanced oxidation, UV irradiation and TiO_2 photocatalysis (Köhler *et al*., 2012; Giannakis *et al*., 2015; He *et al*., 2016). The easiest way is activated sludge process optimisation. For ibuprofen, a higher hydraulic retention time and sludge age means it has a good biological degradation rate (Miège *et al*., 2009).

In this study, we concentrated on two widely used pharmaceuticals NSAID: diclofenac and ibuprofen. These two pharmaceuticals have been chosen because there is no need for a prescription to buy these drugs; they are therefore used in large amounts, and their negative effect on the environment is well known.

Several previously published different models have estimated the concentrations of pharmaceutical residues in the effluents of WWTP. There are two ways to look at a model: (Khan, Ongerth, 2004; Zhang et *al*., 2015)

a) as a closed system, such as a hospital;
b) as a fate model from the consumer to the environment.

In a mathematical model from the consumer to the environment, two important parameters should be taken into account: the metabolism removal rate in human body and the removal rates of WWTP. In WWTP, we examine two main processes resulting in a decrease in concentrations of diclofenac and ibuprofen: these are the absorption of suspended solids and biodegradation (Kümmerer *et al*., 1997; Fent *et al*., 2006). Ibuprofen is biodegradable and normally more than 70% is removed in a WWTP (Fent *et al*., 2006). That means that there are lower pharmaceutical residues concentrations in effluent, but higher concentrations in sludge, which is often used in agriculture(Lillenberg, 2011).

The aim of this study was to model the fate of ibuprofen and diclofenac in major Estonian seaside cities to assess the need for a treatment step at WWTP to reduce the pharmaceutical residues in the effluent of WWTP that are discharging wastewater directly into the Baltic Sea. A second aim was to analyse the trend of pharmaceutical residues in Estonia.

Material and Methods

Description of the model

A theoretical model was compiled to evaluate the concentrations of diclofenac and ibuprofen in the effluents of the Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare WWTP located close to the Baltic Sea, in the time period between 2006 and 2014. There are approximately 577,000 inhabitants in these chosen settlements, comprising 44% of whole Estonian population. The largest settlement is Tallinn with over 410,000 people. The model considers population, yearly consumption of diclofenac and ibuprofen, metabolism removal rates of drugs in the human body and WWTP removal rates.

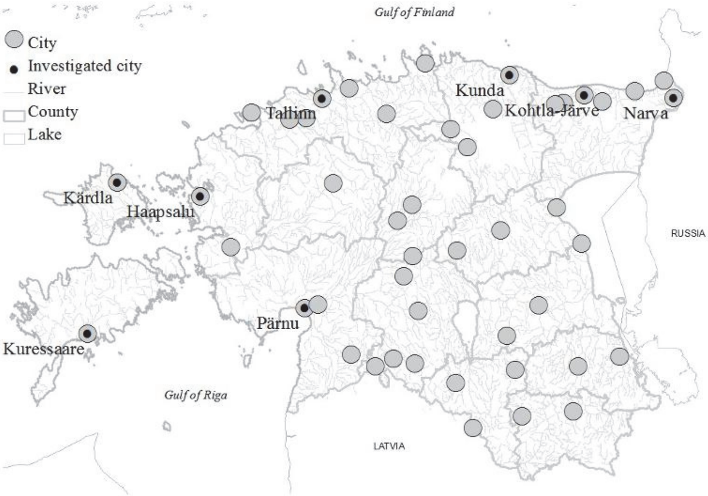

Fig. 1. Location of WWTP where diclofenac and ibuprofen loads and concentrations in WWTP effluents were modelled

Data collection

The population data for the time period between 2006 and 2014 for the eight cities of Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare were obtained from Statistics Estonia. Data about the consumption of diclofenac and ibuprofen were requested from the Estonian Agency of Medicine. Data about WWTP discharges were requested from National Water Use Database of the Estonian Environment Register.

Data analysis

The total amount of active substance for diclofenac and ibuprofen was calculated. As diclofenac is often sold as gel with an active substance concentration of 5%, there are also pharmaceuticals with ibuprofen content for injection.

Consumption of diclofenac and ibuprofen

As there are no separate data for the consumption of pharmaceuticals in Estonian settlements, a simplification was made. At first, the yearly consumption from 2006 to 2014 of the active substance of diclofenac and ibuprofen was calculated in ($K_{yearly\text{-}u}$) per person, using the entire Estonian consumption:

$$K_{yearly\text{-}u} = \frac{\textit{Consumption of pharmaceutical}}{\textit{Population}} \tag{1}$$

In order to calculate the consumption of diclofenac and ibuprofen for the study area cities, the population of these cities was multiplied with the consumption rate $K_{yearly\text{-}u}$.

Load calculation

A theoretical model in MS Excel was prepared to calculate the yearly loads and average concentration of diclofenac and ibuprofen in the Baltic Sea. In the model, two constants were used: the metabolism removal rate in the human body for diclofenac and ibuprofen ($M_{removal}$) and the removal rate in an activated sludge WWTP ($WWTP_{removal}$). The metabolism removal rate was studied and reported by Lienert (Lienert *et al*., 2007) and the removal rates in WWTP by Miége (Miège *et al*., 2009). In Miége's study, data on diclofenac removal from 37 WWTP and data on ibuprofen removal from 51 WWTP is reported (Miège *et al*., 2009). The average from these 37 WWTP was used to calculate the removal constant.

Table 1. Removal rates for diclofenac and ibuprofen used in model ($M_{removal}$ metabolism removal rate, $WWTP_{removal}$ WWTP removal rate)

	$M_{removal}$	$WWTP_{removal}$
Diclofenac	0.84 (0.78-0.94)[1]	0.32 (0.19)[3]
Ibuprofen	0.70 (0.71-0.51)[2]	0.74 (0.29)[4]

[1] (Lienert *et al*., 2007; ter Laak *et al*., 2010), minimum and maximum values are in the brackets.

[2] (Miège *et al*., 2009; ter Laak *et al*., 2010), standard deviation in the brackets.

[3] *(Lienert et al., 2007; ter Laak et al*., 2010), minimum and maximum values are in the brackets.

[4] (Miège *et al*., 2009; ter Laak *et al*., 2010), standard deviation in the brackets.

By using the model, the yearly load of diclofenac and ibuprofen from eight Estonian cities on the Baltic Sea was calculated as followed:

$$K_{yearly\text{-}load} = P_{population} * K_{yearly\text{-}u} * (1 - M_{removal}) * (1 - WWTP_{removal}) \tag{2}$$

$P_{population}$ is the population for Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare.

The concentration of different pharmaceuticals in wastewater plays an important role; therefore, a theoretical model was constructed to calculate the average concentrations $K_{average\text{-}c}$ of diclofenac and ibuprofen in the effluents of WWTP in Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare, using the following formula.

$$K_{average\text{-}c} = \frac{K_{yearly\text{-}load}}{Q_{flow}} \tag{3}$$

Q_{flow} is the annual wastewater volume to the Baltic Sea.

Results and Discussion

Figure 2 shows the consumption of diclofenac and ibuprofen in Estonia from 2006 to 2014.

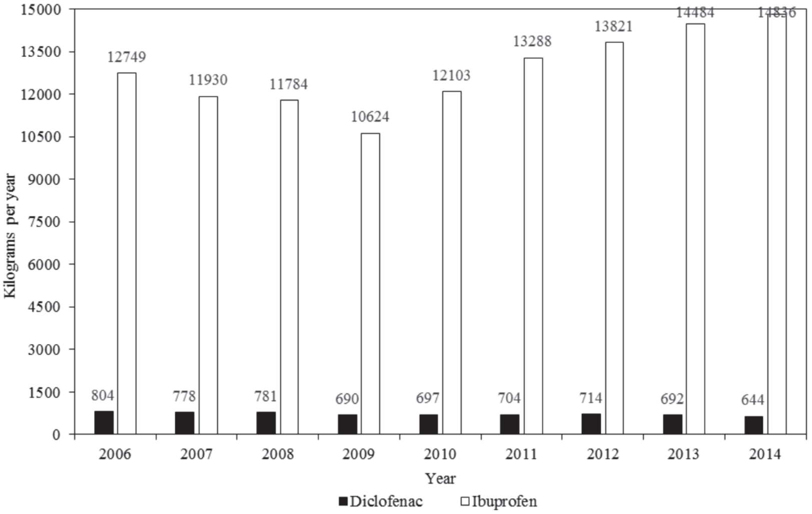

Fig. 2. Diclofenac and ibuprofen consumption in Estonia from 2006 to 2014

A remarkable decrease in diclofenac consumption of 19.9% was found, though it was just the opposite in the case of ibuprofen, as a consumption increase of 14.1% was discovered. The increase of the usage of some pharmaceuticals can be connected with population aging (Arnold *et al*., 2014). The decreasing usage of diclofenac can be connected with changes in the law during this period; some common diclofenac pharmaceuticals have required a prescription since 2007. A second reason can be the announcement from the European Medicines Agency that diclofenac is not a safer analgesic than ibuprofen, because it can cause cardiovascular diseases like heart attack and stroke. In Germany, a remarkable increase of 116% in the consumption of ibuprofen was recorded from 2002 to 2009, though it was only 4% for diclofenac (Bergmann, *et al*., 2011).

In Figure 3, the modelled discharge loads of diclofenac for Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare are outlined. The main loads of diclofenac residues originating from three largest cities of Tallinn, Narva and Pärnu amount to a total average yearly amount of 30 kg. In Pärnu, a decrease in the total load of diclofenac over 23.1% is observed. Narva has seen a decrease of 26% and Haapsalu of 24.7%.

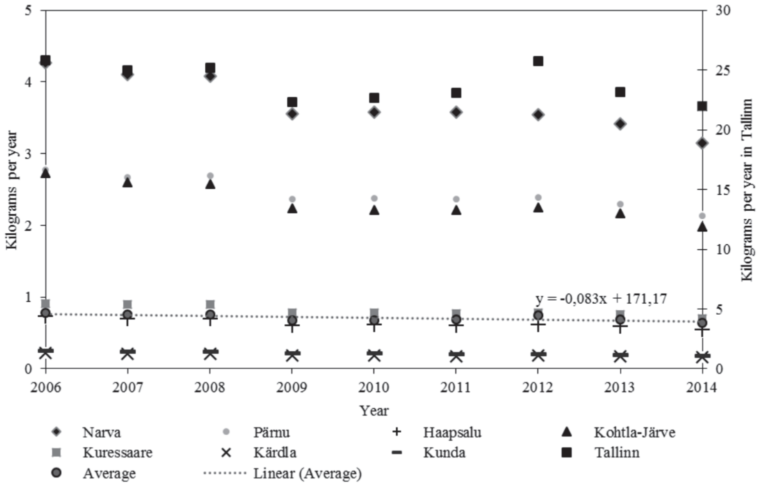

Fig. 3. Modelled discharge loads of diclofenac residues into the Baltic Sea from major cities in the time period between 2006 and 2014

In Figure 4, the discharge rates of ibuprofen residues to the Baltic Sea are shown. Ibuprofen discharge rates increased by more than 15% from 2006 to 2014. From 2006 to 2010, a decrease of consumption in all cities was found, which was due to the usage of ibuprofen.

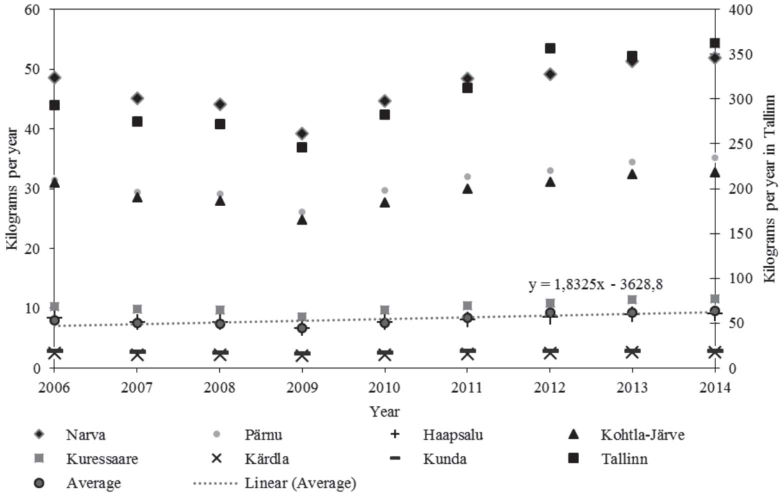

Fig. 4. Modelled discharge loads of ibuprofen residues into the Baltic Sea from 2006 to 2014

In Narva, Pärnu, Haapsalu, Kohtla-Järve, Kärdla and Kunda, an average increase of 7.5% for ibuprofen discharge loads was found. In Tallinn, the consumption rates have increased from 293 kg to 361 kg in connection with the growing consumption rates in Estonia and with the increasing population trend in Tallinn.

Figure 5 shows the modelled average annual concentrations of diclofenac residues in the effluents of WWTP covered by our research. The highest average concentrations were found in Kunda and Kärdla, with values of 1.4 and 1.5 µg/l, accordingly. It can be explained by smaller flow rates per capita, which in turn results from a separated sewer system in use. In Estonia's largest city, Tallinn, the decrease in diclofenac concentration of 17.8% was modelled. The average concentration in our research-enclosed cities has decreased from 1 to 0.8 µg/l (decrease of 20%). The German Ministry for the Environment analysed 198 WWTP effluents in Germany and found diclofenac in concentrations from 0.4 to 10 µg/l (Rohweder, 2003). In his article based on scientific journals around the world, Miége found a diclofenac concentration in the effluents of 46 WWTP from 0.035 to 1.72 µg/l (Miège *et al.*, 2009). By comparing our modelled data with prior studies, we see rather good compatibility (Figure 5).

Altmets found in her environmental risk assessment that a diclofenac predicted environmental concentration of 0.59 µg/l has a high environmental risk because it is persistent and bioaccumulative (Altmets, 2012). Our modelled data showed higher values in most of the WWTP outlets.

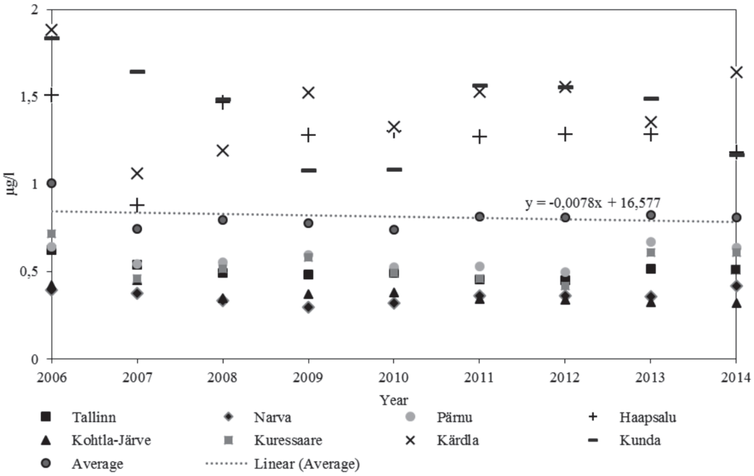

Fig. 5. Modelled average diclofenac concentrations in eight Estonian seaside WWTP effluents, from 2006 to 2014

In Figure 6, the modelling results of average ibuprofen residue concentrations in eight WWTP effluents of Tallinn, Narva, Kohtla-Järve, Kunda, Haapsalu, Pärnu, Kärdla and Kuressaare are shown.

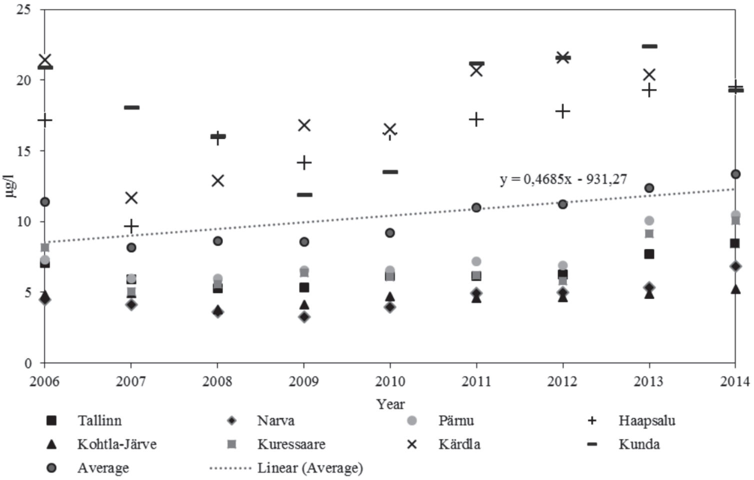

Fig. 6. Modelled average ibuprofen concentrations in eight Estonian seaside WWTP effluents from 2006 to 2014

Similar to diclofenac, the highest average concentrations are in Kunda and Kärdla, with 18.3 and 18.8 µg/l in connection with smaller flow rates in the recent years. The average concentration of ibuprofen has increased in the eight described cities from 11.4 to 13.4 µg/l. Together, in all eight cities, an average concentration increase for ibuprofen residues of 14.9% was seen. The previously described German report found ibuprofen in concentrations from 0 to 3.7 µg/l in the effluents of 178 WWTP (Rohweder, 2003). Miége in his study found ibuprofen in the range of 0.04 to 1.7 µg/l (Miège *et al*., 2009). In comparison to the modelling results obtained with the prior studies, we observed that the theoretical model for ibuprofen is overrating the concentrations by more than 64%. The exaggeration can be due to a variety of possible reasons such as the greater proportion of stormwater or higher accumulation into wasted activated sludge, which is removed separately.

In Altmets's environmental risk assessment for ibuprofen, the environmental risk was deemed to be insignificant (Altmets, 2012). Despite this, it is necessary to identify real values for ibuprofen, since our model showed rather high concentrations.

Conclusion

In Estonia, the consumption of diclofenac has decreased from 804 to 644 kg and for ibuprofen it has grown from 12749 to 14836 kg in time period between 2006 and 2014. Diclofenac usage was rather decreasing, but an increasing trend was observed for ibuprofen, which is due to many reasons such as aging population and longer life expectancy. To evaluate the risks for the environment, the concentration of the pharmaceuticals in the wastewater are more relevant than the consumption. For diclofenac in eight different cities on the studied period, an average concentration of 0.8 µg/l and for ibuprofen 10.5 µg/l was modelled.

The environmental risk of diclofenac, based on different studies has been categorised as high.

Using this modelled data, we are able to forecast the trends of consumption rates and concentrations of pharmaceutical residues in WWTP effluents. The model is not totally comparable with the real concentrations of diclofenac and ibuprofen, but it gives us a good overall picture and trend, as well the knowledge that we need to continue with this field of study.

A future study in Estonia is required to monitor in more detail the real concentrations of pharmaceutical residues in the effluents of WWTP and in the environment, with the aim of making a decision on an additional treatment step and treatment technology in WWTP for the removal of pharmaceuticals where it is deemed appropriate.

Acknowledgements

We wish to thank the Estonian Agency of Medicine for providing the statistical data about the consumption of diclofenac and ibuprofen.

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Paper II

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Adsorption of Diclofenac, Sulfamethoxazole and Levofloxacin with Powdered Activated Carbon

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Abstract. The presence of pharmaceutical residues in the receiving waterbodies of wastewater treatment plants (WWTP) and in the environment has become a global concern. We can now say for certain that, having metabolised in our bodies, partially modified or unmodified pharmaceuticals will reach WWTP. However, WWTP are not designed for the removal of such compounds. Only a small fraction of pharmaceuticals decompose during biological treatment or are adsorbed in sediment. Therefore, it is essential to find a treatment process that is capable of removing pharmaceutical residues. The aim of the present study was to research the removal of three pharmaceuticals found in the environment, namely diclofenac (DCF), sulfamethoxazole (SMX) and levofloxacin (LFX), through the use of powdered activated carbon (PAC). To this end, adsorption tests were conducted where the adsorption capacity was estimated according to the adsorbent dose and the residence time of the process. LFX had the highest adsorption rate: the removal effectiveness was 77% in a residence time of 5 minutes and in 60 minutes a stable indicator was achieved whereby 94% of LFX had become adsorbed. The worst adsorption property was observed for SMX, as 68% of SMX was adsorbed in a residence time of 60 minutes. According to the conducted tests, the Freundlich adsorption isotherms and constants characterising the adsorption were found where the DCF K was 23.8, the SMX K was 34.3 and the LFX K was 106.1. This test demonstrated that the pharmaceuticals selected for the experiment could easily be subjected to adsorption processes and could be removed by means of PAC.

Keywords: adsorption of pharmaceuticals, removal of pharmaceutical residues, diclofenac removal, sulfamethoxazole removal.

Conference topic: Water engineering.

Introduction

The presence of pharmaceuticals in the environment has become an important problem worldwide. In Germany, 131 different pharmaceuticals in sea and ground water have been found (Weber *et al.* 2014). Therefore, hundreds of scientific workgroups are working to understand the pathways of different human and veterinary drugs back into our food cycle (Miège *et al.* 2009; Li 2014; Białk-Bielińska *et al.* 2016) and to eliminate the long term effects of different pharmaceuticals on ecology (Fatta-Kassinos 2010; Klatte *et al.* 2016).

In examining different studies, one problem when searching for specific pharmaceuticals in the aquatic environment is that some pharmaceuticals are biologically degradable and form new chemical bonds (Langenhoff *et al.* 2013; Ericson *et al.* 2010). It makes analyses difficult because we simply don’t know what chemical substance we are looking for or what ecotoxic effect this new chemical substance can have.

Emission of pharmaceuticals

The first step in managing the occurrence of pharmaceuticals in the environment is to understand the path of pharmaceuticals in the environment and back into the food chain. The amounts and kinds of medicines depend on the population’s structure. Aging populations use more antibiotics and cardiovascular agents, while younger people use birth control pills. For different pharmaceuticals, the pathway can be different but a basic scheme is shown in Fig. 1 (Adamcza *et al*. 2012; Klatte *et al.* 2016; Weber *et al.* 2014).

In Fig. 1, the pathway of human and veterinary drugs is described. When we look the population box, we see two possibilities: the direct consumer who takes pharmaceuticals at home, including widely used medicines such as non-steroidal anti-inflammatory drugs (NSAID) and birth control pills. However, in hospitals, more effective and higher dosages of pharmaceuticals are used and are therefore described separately (Klatte *et al.* 2016). A third pathway is drugs that are used in veterinary medicine. Different antibiotics and NSAID are used to facilitate intensive animal farming (Oaks *et al.* 2004; Schwaiger *et al.* 2004). Some pharmaceuticals are not biologically degradable and pass through WWTP unchanged or are adsorbed to raw and activated sludge (ter Laak *et al.* 2010; Mohapatra *et al.* 2016). When the sludge is used as a fertiliser in agriculture, the pharmaceuticals can accumulate in plants (Lillenberg 2011; Nei *et al.* 2014). A similar cycle occurs with dung and fish faeces.

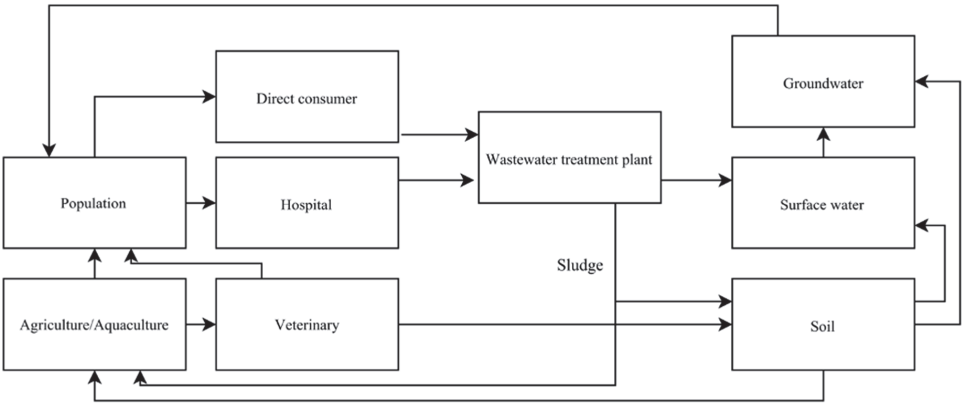

Fig. 1. Emission pathways of human and veterinary pharmaceuticals.

Risks for organisms and humans

The most widely known proven effect of pharmaceuticals on organisms is the major population collapse of white-backed vultures (Gyps africanus) in Pakistan and India in the early 1990s. The birds consumed the carcasses of cattle that had been treated regularly with NSAID diclofenac. For vultures, the concentration was high enough to cause kidney failure (Klatte *et al.* 2016; Oaks *et al.* 2004).

Various risk assessment methods have been developed in order to determine the most harmful drugs. In his research, Carlsson (2006) assessed the ecotoxicity risks of 27 different pharmaceuticals. Based on his study, the most dangerous drugs for the environment include diclofenac, ethinylestradiol, ibuprofen, metoprolol, norethisterone, oestriol and oxazepam (Carlsson *et al.* 2006; Lonappan *et al.* 2016). Li (2014) confirmed this data and added the antibiotic sulfamethoxazole to the list of ecotoxic pharmaceuticals (Li 2014; Sangion, Gramatica 2016).

For humans, the main concerns are bioaccumulation in our food, resistance to antibiotics and the toxicity of pharmaceutical mixtures and their effect on the human organism (Skórczewski *et al.* 2014; Fent *et al.* 2006; Klatte *et al.* 2016). Different studies show that the ecotoxic effect concentration of pharmaceutical mixtures are several times lower compared to pure active substances (Fent *et al.* 2006).

Removal of pharmaceuticals

In Fig. 1, we see two possible points for the removal of pharmaceutical residues: separately treating the effluent of hospitals or treating all water in a WWTP. Most European countries are examining ways to develop technology to remove pharmaceuticals at the WWTP stage because pharmaceutical residues are not the only problem (Nazari *et al.* 2016; Giannakis *et al.* 2015; Cruz-Morató *et al.* 2014). Many promising technologies to remove organic pollutions and heavy metals in the same treatment stage have already been determined.

In the advanced oxidation ozone, hydrogen peroxide or UV (UV+TiO2) is used to degrade pharmaceutical residues from wastewater. However, it is disturbing that we don't in fact know the degradation products and the possible derivatives that the residues can form (Giannakis *et al.* 2015; Alvarez-Corena *et al.* 2016).

The second possibility for treat drugs from water is membrane technology, often in combination with a bioreactor (aerobic membrane bioreactor- AMBR). While this doesn't degrade the pharmaceuticals, it can be used to concentrate the pollution after which you can use other technologies to remove the residues such as advanced oxidation or adsorption with activated carbon (Priya, Philip 2015; Arya *et al.* 2016).

The most promising technology is adsorption with activated carbon because it removes different types of organic pollutions and heavy metals (Wu *et al.* 2015; Karnib *et al.* 2014; Larous, Meniai 2016; Raki *et al.* 2015). There are three ways to add an adsorption step to an existing WWTP:

- Filtration through a granular activated carbon filter bed after secondary clarification. This removes pharmaceuticals from the effluent water, but adsorbed pharmaceuticals in the sludge are not eliminated (Chang et al. 2015; Lima et al. 2004; Rattier et al. 2012; Meinel et al. 2015).
- Adding PAC to the aeration tank. The adsorbed pharmaceuticals and heavy metals are removed with the waste activated sludge (WAS) (Zietzschmann et al. 2016; Chang et al. 2015). Because the concentration of harmful substances would be higher than normal in the sludge, the sludge wouldn't be immediately applicable for use in agriculture. One way is to use a struvite reactor for the dewatered sludge water and to subsequently burn the sludge in order to recover the phosphorous from the ash (Rattier et al. 2012; Meinel et al. 2015).

- Using PAC after clarifiers as a separate treatment step. This method requires more significant investment, because we need a mixing tank, a clarifier for PAC removal and sand filtration for final treatment (see Fig. 2) (Weimar 2014).

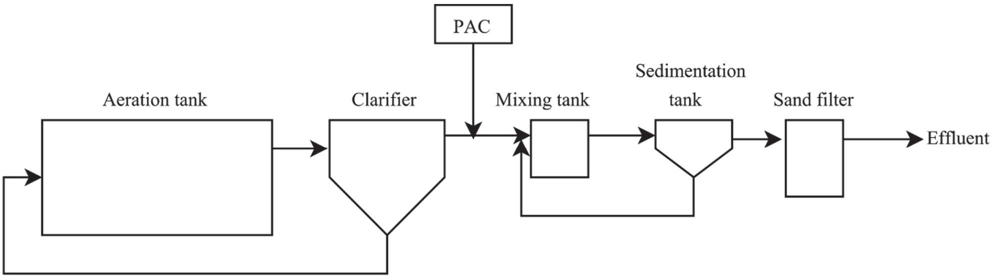

Fig. 2. Possible technical solution for PAC dosing in a conventional municipal WWTP (Weimar 2014).

The aim of this research was to study the removal potential of three common pharmaceuticals with PAC: non-steroidal anti-inflammatory drug diclofenac (DCF) and two antibiotics, sulfamethoxazole (SMX) and levofloxacin (LFX). To this end, different adsorption batch experiments were determined, and these provide information for process engineers on determining activated carbon treatment steps.

Materials and methods

For batch experiments, different solutions of DCF ($C_{14}H_{10}Cl_2NNaO_2$), SMX ($C_{10}H_{11}N_3O_3S$) and LFX ($C_{20}H_{24}O_2$) were prepared with ultrapure (ELGA) water and a known concentration of the pharmaceuticals under investigation (pH of all solutions was 7.6). All the pharmaceuticals were purchased from Sigma-Aldrich and are of lab quality. The concentration was measured as a TOC (total organic carbon). 100 ml of the solutions and 0.05 g of PAC (coal filter material silcarbon powder, Lach-Ner, M 12.01 g/mol) were mixed (stirring speed 150 rpm, at room temperature of 21.5 °C) and a sample was taken in intervals of 5, 10, 30, 60 and 120 minutes (when a stable value was achieved) in order to determine the adsorption capacity in relation to time. The same experiment was then repeated to discover the removal effectiveness and removal capacity, though different concentrations of PAC were added.

The removal effectiveness E % was calculated using the following equation:

$$E\ \% = \frac{C_0 - C_n}{C_0} \cdot 100\ \%, \tag{1}$$

where: C_0 is the initial concentration of adsorbate, C_n final concentration of adsorbate and C_e equilibrium concentration of adsorbate.

Freundlich adsorption isotherm was used to describe the adsorption process. It shows us the relationship between the adsorbate amount, what is adsorbed per unit adsorbent and the adsorbate equilibrium concentration qe (Sekar *et al.* 2004; Kumar, Kirthika 2009):

$$q_e = K \cdot C_e^{1/n}, \tag{2}$$

where: K is the Freundlich adsorption constant (mg/g) and n heterogeneity factor. K and n are the indicators denoting adsorption capability and intensity.

The maximum adsorption capacity $qe_{\max}$ dependent on time was calculated using the following relationship:

$$qe_{\max} = \left(\frac{1}{q}\right) \cdot m_s, \tag{3}$$

where: q is the amount of adsorbent (g), m_s weight of adsorbed adsorbate (mg) and $qe_{\max}$ maximum adsorption capacity (mg/g).

Results and discussion

Removal effectiveness

In Fig. 3, the results of the adsorption studies are shown, where the adsorption effectiveness dependant on time and adsorbent dosage were investigated. The best results were achieved in LFX removal; within 5 minutes, 77% percent had already been removed, while the highest removal rate was 94% after 60 minutes detention time. The equilibrium concentration was reached in 60 minutes. 0.03 g/100 ml was determined to be the preferable PAC dosage for this LFX concentration, for which the adsorption effectiveness was 86%. A similar removal effectiveness of 93% was reported by L. Lima (2004) (Lima *et al.* 2004). In higher PAC concentrations, the removal capacity stays similar, which means that at the initial concentration researched by us the higher PAC dose would only increase adsorbent consumption without significantly increasing the treatment effectiveness. Rapid adsorption is an indicator that we need significantly shorter residence times for creating a treatment stage of LFX with specific activated carbon than for other pharmaceuticals. Therefore, the planning of the first stage of multistage filters may be dimensioned smaller. After a residence time of 120 minutes, the concentration of the substance to be removed even increased and the removal effectiveness dropped by 2%. Similar rises in concentrations have also been reported by E. Chang (2015), suggesting that it is due to continuous changes in the adsorbent and adsorbate equilibrium (Chang *et al.* 2015).

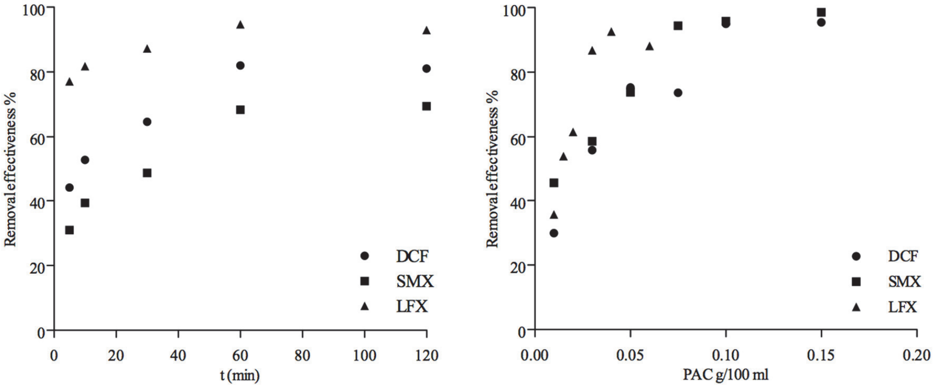

Fig. 3. Removal effectiveness depended on adsorption time (a) and adsorbent dosage (b)

In the case of DCF, the adsorption was significantly slower. 45% of DCF was removed in 5 minutes and, as with LFX, the equilibrium concentration was achieved in 60 minutes with 82% of the initial concentration removed. The removal efficiency of 70% for DCF was achieved by L. Lima (2004) in a similar study (Lima *et al.* 2004). The highest adsorption capacity was on PAC dosage of 0.1 g/100 ml, which is 70% higher than that of LFX. For DCF removal, we need longer contact time and higher PAC dosage than for LFX removal. The greatest difference can be seen in Fig. 3b. While diclofenac usually adsorbs better than SMX, with different PAC concentrations it can be observed that the removal effectiveness is lower than in other experiments where fixed amounts of PAC (0.05 g) are used. DCF only adsorbs better than SMX at 0.05 g.

SMX has the lowest adsorption capability. 31% of SMX was removed in the first five minutes. The equilibrium between adsorbate and adsorbent was reached in 60 minutes and the removal effectiveness was 68%. The same result was also achieved by L. Lima (2004) (Lima *et al.* 2004). The most effective SMX removal was attained with a PAC concentration of 0.075 g/100 ml. The poor adsorption of SMX was also confirmed by an earlier study, which found the adsorption of SMX was 76% worse than that of DCF (Nam *et al.* 2015).

Adsorption is influenced by many factors, such as porosity of the activated carbon, pH of the solution under study and temperature. In the case of the current test, pH dropped from 7.6 to 6.3 after PAC dosing (0.05 g). B. Bhadra (Bhadra *et al.* 2016) found that the adsorption capacity of diclofenac increases when the pH decreases. This is attributed to the surface charge of the activated carbon, which decreases when the pH falls and makes the adsorption more efficient (Bhadra *et al.* 2016). In addition, the adsorption is influenced by the solubility in water of the removable substance. The higher the solubility the worse the removal rate through adsorption. In our study, LFX turned out to be insoluble in water, DCF is poorly soluble (water solubility 2.37 mg/l) and SMX partly soluble (water solubility 610 mg/l). These study findings confirm the relationship between the water solubility and adsorption, where LFX was removed in higher amount than DCF and SMX (National Center for… 2016b, 2016a, 2016c).

Maximum adsorption capacity and Freundlich adsorption isotherm

In Fig. 4a, we see the adsorption capacity of DCF, SMX and LFX dependant on time. LFX has the highest adsorption capability as is also shown in Fig. 3. The equilibrium was achieved in 60 minutes, where 324 mg of LFX per 1 gram PAC was adsorbed. DCF has an adsorption capacity of 231 mg/g on the studied concentration, which is 29% lower than that of LFX. For SMX, the maximum adsorption potential in the same time was 185 mg/g, which is 43% less than that of LFX.

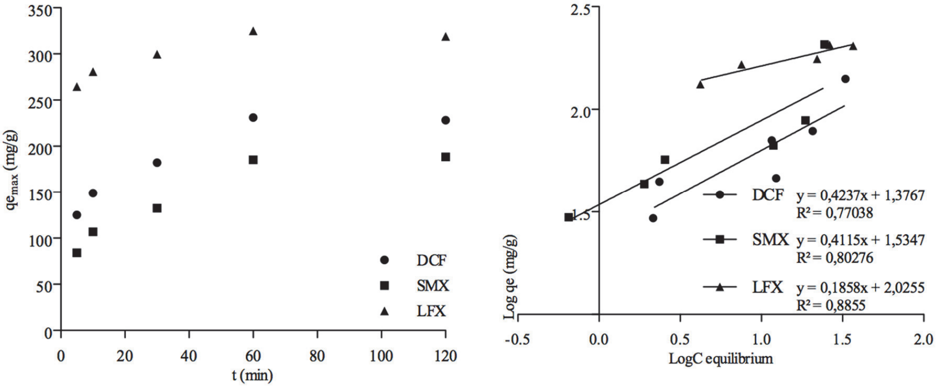

Fig. 4. The maximum adsorption capacity qe$_{max}$ (mg/g) dependent on time (a) and Freundlich adsorption isotherms (b)

From Fig. 4b, K and n for DCF, SMX and LFX experiments was found. K was determined from the intersection of the graph with the y-axis and n is equal to the slope of the graph (Okeola, Odebunmni 2010). The higher K is the more effective adsorption process. With the n value, we can see the adsorption intensity and whether the adsorption process is integrated or not. When 1/n is higher than 1, it is uniform; the smaller the 1/n value, the greater the heterogeneity of the surface of PAC. If n is under 1, then the process is unfavourable for adsorption (Sekar *et al.* 2004; Desta 2013). In Table 1, the results according to Fig. 3b are shown.

Table 1. Freundlich parameters for DCF, SMX and LFX adsorption with PAC

Parameter	DCF	SMX	LFX
K	23.8	34.3	106.1
1/n	0.4237	0.4115	0.1858
n	2.36	2.43	5.38
q_e	34.2	53.8	138.5
R^2	0.77038	0.80276	0.8855

The results show that the adsorption processes of DCF, SMX and LFX align with the Freundlich adsorption isotherm. As our previous discussion already showed, LFX has the highest adsorption capability, as confirmed through the K, qe and n values where it is higher than DCF and SMX. At the equilibrium concentration, the maximum adsorption capacities were 106.8, 34.3 and 23.8 for LFX, SMX and DCF, respectively. Though DCF was otherwise better adsorbable than SMX, the reason for the low qe of DCF was explained above in Fig. 2. In reviewing other similar studies where different adsorbents were used, K was found to be 2.26 in one study and 44.9 in another, which demonstrated that adsorption processes largely depend on the adsorbent being used (Larous, Meniai 2016; Nam *et al.* 2015).

The data from Table 1 is helpful in designing an activated carbon process for DCF, SMX and LFX removal. With these results, we can calculate the required amount of PAC and detention time for the adsorption.

Conclusion

The removal of three pharmaceuticals found in the environment was surveyed in this article. It was found that the pharmaceuticals selected for the study could be effectively subjected to adsorption processes, and they could be removed in a WWTP by adding an additional treatment process. LFX has the best adsorption property and SMX the poorest.

It should be taken into account that in wastewater there are in addition to pharmaceutical residues other substances that can influence the adsorption. Thus, the next step is pilot-scale experiments in an operating WWTP. This is a prerequisite for planning and designing a full-scale PAC treatment step.

Disclosure statement

I don't have any competing financial, professional, or personal interests from other parties in connection with this research.

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Combined effect of heavy metals on the activated sludge process

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Abstract. Migration of heavy metals in the environment is a serious problem for wastewater treatment plants (WWTP) and the environment as a whole. The combined effect of eight heavy metals on the biological wastewater treatment process was analysed in this research. The heavy metals examined were Cd, Pb, Zn, Cu, Ni, Cr, Co, and Mn. In order to evaluate their effect, mathematical models were created, taking into account the hydraulic retention time, the load of heavy metals (HeM), temperature, and the air consumption in aeration tanks in biological treatment. The modelling demonstrated that a 1 kg/d increase in the HeM reduced the nitrogen removal efficiency by 1.05% and the nitrification efficiency by 1.04%. Taking into account the variability of the HeM, this constituted a 5.68% change in the nitrogen removal efficiency for the examined WWTP. The air consumption in aeration tanks was taken as a basis for the assessment of the effect of the HeM on the entire biological treatment process, as a substantial part of the oxygen used for biological treatment is consumed by microorganisms and the inhibitory effect is observed as a decrease in the air consumption. Oxygen is consumed for the degradation of organic matter and nitrification. The modelling results showed that a 1 kg/d increase in the HeM reduced the air consumption by 9300 m^3/d in the aeration tanks due to the inhibition, causing a decrease in treatment efficiency.

Key words: heavy metals removal, inhibition, activated sludge process, heavy metals in wastewater treatment, modelling inhibition of nitrification.

1. INTRODUCTION

Entry of heavy metals into a wastewater treatment plant (WWTP) is often unavoidable. The main transmitters of hazardous substances are industrial effluents, domestic wastewater, stormwater, and the atmosphere [1–3]. While the imposition of increasingly stricter rules on industrial effluents directed to municipal WWTPs has improved the situation to some extent, the case concerning stormwater and domestic wastewater is more difficult to change [4]. In industrial production the reduction of hazardous substances starts at the production process, with alternative solutions with a smaller rate of heavy metals emission used where possible and, if necessary, a technological solution such as adsorption (activated carbon, zeolite), coagulation, membrane filtration, and ion exchange found for removing problematic compounds [5,6]. As to stormwater, a reduction is difficult to achieve because the water flow rates that need to be treated are too voluminous for modern technological solutions to handle, and the whole process would not be economically feasible [7]. For this reason, the first step in the stormwater treatment is to map the main sources of heavy metals and then find solutions for reducing the amount of heavy metals entering stormwater. The situation concerning domestic wastewater could be improved by changing consumer behaviour, but this has proved to be difficult.

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An ordinary municipal WWTP has three treatment stages: mechanical, biological, and chemical. While the first and the third stage use physical processes, the second, i.e. biological process, is carried out by microorganisms, which are often sensitive to environmental changes and hazardous substances. Therefore, even small concentrations of hazardous substances may considerably inhibit the efficiency of biological treatment [8].

1.1. Sources of heavy metals

As mentioned above, the main transporters of heavy metals include industrial effluents, stormwater, domestic wastewater, and the atmosphere where heavy metals are released mostly as a result of anthropogenic activity. Natural sources include the dissolution of heavy metals in rocks, for example. This way, Ni, Cb, Mn, Zn, and Cu easily enter the hydrological cycle, as these metals are found in water-soluble form in soil [9]. Estonia does not have many metallurgical, galvanic, or electronics industries that would cause heavy metal pollution. This is why most of the problems in Estonia in this field are connected with stormwater, the oil shale industry, and the households [10]. The fate of heavy metals in the environment is illustrated in Fig. 1 [1–4,9,10].

The heavy metals Zn and Cu are mainly released into stormwater from metal-coated items such as road barriers, roofs, particles from tyres and brake shoes, and exhaust gases of vehicles [4,11]. In a study of roofs coated with Cu and Zn, Charters [12] found the following concentrations of heavy metals in the stormwater runoff from the examined roofs: 397–1970 µg/L and 1663–7860 µg/L, respectively.

The atmospheric spreading of the heavy metals emitted into the air as a result of combustion processes, such as exhaust gases of vehicles and coal-fired power plants, also pose a problem. In the atmosphere, the pollutants are dispersed exponentially farther and enter the hydrological cycle again via precipitation; approximately 5% of the load of heavy metals (HeM) in surface water bodies comes from air pollution [13,14]. Likewise, acid rain and a decrease of the soil pH increase heavy metal leaching from rocks [14]. In addition, cosmetic products such as sunscreen creams, lipsticks, and face-powders as well as medicinal products also contain various heavy metals [15]. For instance, skin creams containing Zn are widely in use and therefore often enter the sewerage with domestic wastewater. Sani [16] analysed various cosmetic products and ranked the heavy metals contained therein, starting from the largest concentration: Mn > Ni > Cu > Cd > Pb > Cr.

Since in Estonia strict rules have been established for heavy metals, each factor that reduces their load, such as changing consumer behaviour, has an impact on the performance of WWTPs because the WWTPs are not currently capable of removing heavy metals. The following maximum levels of heavy metals for wastewater have been set in Estonia: 15 µg/L for Cu and 50 µg/L for Zn [17]. The main sources of heavy metals are listed in Table 1.

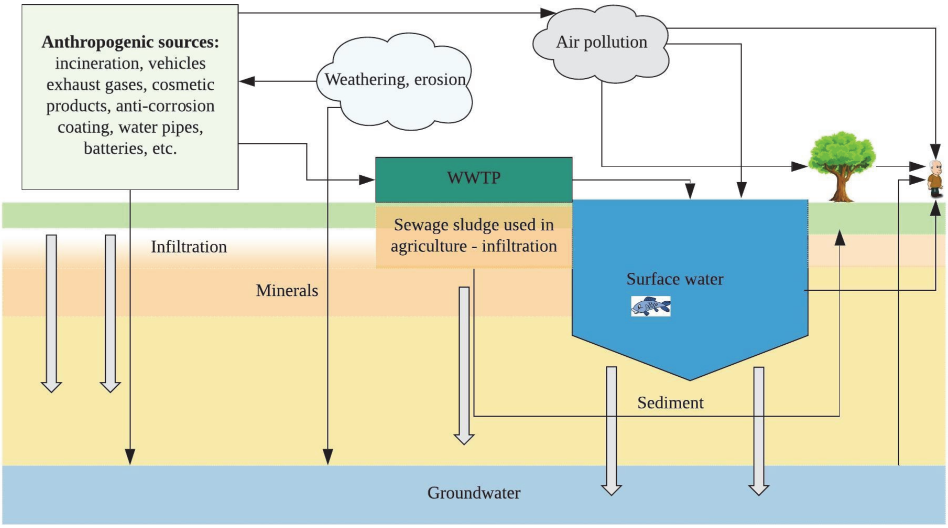

Fig. 1. Migration of heavy metals in/to the environment.

Table 1. Sources of various heavy metals [9,16,18,19]

Heavy metal	Anthropogenic sources
Zn	Anti-corrosion agents, roofs, road barriers, PVC stabilizer, skin creams, welding, rubber industry, medicinal products, paints
Ni	Electronics industry, metal industry, Ni–Cd batteries, dentures, metal cans
Pb	Plastic, various alloys, Pb batteries
Cu	Roofs, water pipes, kitchen appliances, alloys, cosmetic products, medicinal products
Cr	Wood industry, cooling water piping protection, plating, textile and leather industry, colour pigments
Cd	Plastic stabilizers, Ni–Cd batteries, coal burning

1.2. Toxicity of heavy metals

A lot of different research has been conducted on the toxicity of heavy metals on microorganisms, and standard methods have been developed for determining the direct effect thereof (ISO 9509:2006, ISO 8192-2006). Mainly respirometric tests are used where the toxic substance inhibits the metabolism of bacteria and the oxygen demand decreases. Another option is to use Mictorox® for measuring the bioluminescence of the microorganism *Vibrio fischeri* where the inhibitory substance causes a decrease of bioluminescence [20]. Attention must be paid to two different aspects with regard to toxicity: inhibitory effect and lethal effect. While in case of the lethal effect the entire biological process of the WWTP is destroyed and the process recovery may take 2–8 weeks depending on the composition and temperature of wastewater, the detection of an inhibitory effect is more complicated [21,22] because a sudden temperature change, a change in the wastewater composition, emission of a toxic chemical compound into the WWTP, and many other factors can have an inhibitory effect [23].

The main purpose of municipal WWTPs is to remove biological oxygen demand (BOD), N, and P. The most sensitive process is nitrification, which is performed by two types of microorganisms, i.e. ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) [20,24]:

$$NH_4^+ + 1.5O_2 \text{ (AOBs)} \rightarrow NO_2^- + H_2O + 2H^+,$$

$$NO_2 + 0.5O_2 \text{ (NOBs)} \rightarrow NO_3^-.$$

In the cases of AOB and NOB, the growth constants are 0.9 and 0.5, respectively, i.e. the most sensitive microorganisms in this process are NOB. For the bacteria that degrade organic matter this value is 13.2, that is, their recovery time is nearly 26 times faster than that of NOB [25].

It is difficult to say which of the heavy metals is the most hazardous, as their harmfulness depends on the form of the compound the metal occurs in the water. It is also important whether the compound is dissolved or insoluble. Dissolved compounds reach the metabolism of organisms more easily and may have a direct toxic effect. By conducting a risk assessment, Donnachie and co-authors [26] found that the following heavy metals have the greatest toxic effect on the rivers of England: Al > Cu > Ni > Zn > Fe > Cd > Pb > Cr > Mn. The metals listed in this ranking largely correlate with Sani's [16] research on heavy metals contained in cosmetic products. Therefore, cosmetic products may have an important role in the migration of heavy metals in the environment [16].

How a heavy metal directly affects the vital activity of a bacterium has been studied in the cases of Cr, Cu, and Ni, for example. In the case of Cr it was found that it inhibits the metabolism of bacteria, as there is a competition between the oxygen molecule and Cr where both act as acceptors of electrons (organic matter electron donors) in the chemical decomposition reaction of organic matter [27]. The antibacterial effect of Cu has been known for some time already. Besides, Cu is capable of binding and denaturating proteins [28]. In the case of Ni, a direct effect on the removal of suspended solids has been reported, as it reduces the bacteria's adsorption capacity. Also, a larger combined effect has been observed in the case of Ni in combination with various other heavy metals [19].

1.3. Combined effect of heavy metals

Heretofore, research has focused on the effect of individual heavy metals on living organisms, as well as on the biological treatment process in WWTPs. The effect of heavy metals depends on various factors, such as the bacterial culture participating in biological treatment, the age of sludge, hydraulic retention time (HRT), sludge concentration, pH, temperature, etc. [29–32]. Ong et al. [31] give the following ranking of the toxicity of the heavy metals for biological treatment: Cd > Cu > Zn > Cr > Pb, which differs from previously mentioned rankings as these have focused on the human organism. The effect on the wastewater treatment process is mainly the direct impact on the metabolism of microorganisms, but in the case of human beings the focus is mostly on the nervous system and cells [4,31].

We analysed the combined effect of eight heavy metals on the wastewater treatment to identify the combined effect of their load on nitrification, denitrification, and air consumption in the biological wastewater treatment process. The consumption of O_2 is an indicator of the inhibition of the biological treatment. Previous research has examined the effect of individual heavy metals, but there is little information on the combined effect of several heavy metals. For that reason, this research focuses on the combined effect of eight heavy metals with measurable concentrations – Cd, Pb, Zn, Cu, Ni, Cr, Co, and Mn – to model how much a total amount of 1 kg of different heavy metals reduces the treatment efficiency of nitrification and denitrification and how much it inhibits the O_2 consumption. The modelling also took into account the HRT and temperature, as their great effect on nitrogen removal is known.

2. MATERIALS AND METHODS

The data used in this research were collected from an operating municipal WWTP with an approximate load of 450 000 PE. The treatment process consists of the following stages: screens, sand traps, primary tanks, aeration tanks, and clarifiers. Raw sludge and wasted activated sludge are stabilized anaerobically at 37 °C.

The heavy metal samples necessary for the analyses were collected every two weeks during 2.5 years (2014–2016). The samples collected from the influent of the WWTP before biological treatment and from the effluent (Fig. 2) were averaged over 24 hours. The analyses were conducted in an accredited laboratory, where the ISO standard 17294-2:2003 (application of inductively coupled plasma mass spectrometry (ICP-MS)) was used for measuring Cd, Pb, Zn, Cu, Ni, Cr, Co, and Mn.

The process parameters necessary for the research were automatically logged using the VeRa drinking water and WWTP information software. The necessary parameters were the following: flow rate (m^3/d), wastewater temperature (T °C), HRT, pH, N_{tot} removal efficiency, NH_4 removal efficiency, and the O_2 consumption in the biological treatment in aeration tanks (m^3/d) (Table 2). As the examined WWTP operates under BOD deficit, BOD was not taken into account in the evaluation of the biological treatment, because methanol is dosed in the anoxic zone for denitrification. For data analysis R-statistical software was used, and the selected methods were correlation and regression analyses [33].

During the examined period, the maximum O_2 consumption in the aeration tanks was 1 787 797 m^3/d and the minimum was 1 053 780 m^3/d. The maximum nitrification efficiency was 99.95% and the minimum 75.7%, which indicates that the wastewater treatment process functioned properly during the examined period. On average, the load of heavy metals (HeM) was 22.12 kg/d (Table 2).

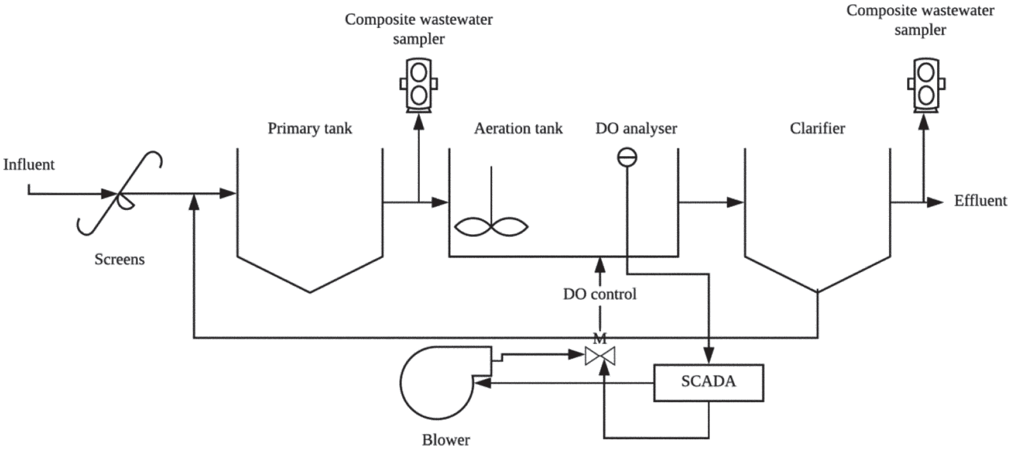

Fig. 2. Flow diagram of the WWTP and sampling points. DO – dissolved oxygen, SCADA – Supervisory Control and Data Acquisition.

Table 2. Core indicators of the research parameters ($n = 45$)

Indicator	Mean	SD	Min	25%	Median	75%	Max
O_2, 1000 m^3/d	1395.43	193.55	1053.78	1267.36	1349.99	1544.61	1787.8
HeM, kg	22.12	5.4	15.14	17.77	21.11	24.18	37.95
NH_4 removal efficiency, %	95.71	5.36	75.66	94.65	97.52	99.28	99.95
N_{tot} removal efficiency, %	84.21	5.79	69	81.1	84.9	88.1	93.6
HRT, h	12.84	2.0	8.6	11.7	13.2	14.4	17.1
T °C	13.48	3.03	9.2	10.8	12.3	16.5	18.6

3. RESULTS AND DISCUSSION

The results of the correlation analysis are presented in Table 3 and Fig. 3. The Pearson correlation coefficient r indicates the direction of the correlation (symbol) and its strength on the scale $|r| = 0$ (no correlation) up to $|r| = 1$ (strong correlation). If the test statistic $p < 0.05$, the correlation is deemed statistically significant on the confidence level 0.05.

The main objective of the analysis was to compose linear regression models that would describe the combined effect of heavy metals on biological wastewater treatment, taking into account three variables: T °C, HRT, and HeM. It is well known that nitrogen removal is mostly affected by the T °C and HRT, thus making the effect of heavy metals mathematically insignificant, but significant in terms of treatment efficiency [34]. The efficiency of N_{tot} removal was found to be best described by Model 1:

$$N_{tot} = 83.69 + 1.78 \cdot \mathrm{HRT} - 1.92 \cdot \mathrm{T\ °C} - 1.15 \cdot \mathrm{HeM} + 0.098 \cdot \mathrm{T\ °C} \cdot \mathrm{HeM}. \qquad (1)$$

Table 3 demonstrates that for N_{tot} removal, significant correlations were found with the HRT and T °C; but its correlation with heavy metals was not statistically significant. However, Model 1 provides an adequate result in forecasting the effect of heavy metals as it takes into account the interaction of various characteristics. Model 1 shows that by increasing the volume of heavy metals by 1 kg/d, N_{tot} treatment efficiency decreases by 1.05%. Based on the premise that the average nitrogen load in the examined WWTP is 6750 kg/d, a 1.05% decrease in its treatment efficiency would increase the load to the environment on average by 71.01 kg/d. In addition, the inhibitory effect has a long-term impact on the wastewater treatment process, as the process recovery lasts 1–21 days, depending on the HeM and the temperature [20,35]. Table 2 shows that the HeM levels varied during the examined period by 20.12 kg/d (SD ± 5.398), and due to the combined effect of heavy metals, N_{tot} removal efficiency varied by 5.68%.

Since the examined WWTP operates under carbon deficit, N_{tot} removal efficiency may not indicate as exact correlation as in the case of NH_4, because nitrification is the most sensitive process and the inhibitory effect can be observed fast [20]. The efficiency of NH_4 removal can be forecasted with Model 2:

$$NH_4 = 103.65 + 1.24 \cdot \mathrm{HRT} - 2.003 \cdot \mathrm{T\ °C} - 1.13 \cdot \mathrm{HeM} + 0.095 \cdot \mathrm{T\ °C} \cdot \mathrm{HeM}. \qquad (2)$$

Model 2 shows that by increasing the HeM by 1 kg, the nitrification efficiency decreases by 1.04%, or the variability of NH_4 removal efficiency as a result of the combined effect of heavy metals is 5.55%. Previous research has focused on the effect of individual heavy metals where the concentrations necessary for measuring the effect were ca 100 times higher than those of the combined effect [34,35].

In Models 1 and 2, the significance probability p is small (Table 4), which suggests that the models are reliable. The description percentage of models (r^2, %) indicates what percentage of the variation of the descriptive variables N_{tot} and NH_4 the given models describe.

Table 3. Pearson correlation coefficients (r) between variables with significance probabilities (p)

	HeM, kg/d		HRT, h		T °C	
	r	p	r	p	r	p
NH_4 removal, %	–0.11	0.494	0.39	0.009	0.28	0.065
N_{tot} removal, %	–0.17	0.272	0.56	<0.0001	0.41	0.006
O_2 to aeration, 1000 m^3/d	–0.26	0.085	0.21	0.173	0.13	0.389

Table 4. Efficiency indicators of Models 1 and 2

Model	Significance probability p	Description percentage r^2	Adjusted description percentage r_{adj}^2	Standard error of the model, %
Model 1	<0.001	43	37	4.59
Model 2	0.0019	25	17	4.87

As the models contain several variables, attention should be paid to the percentage of the adjusted description because it takes into account the combined effects of the factor variables.

Models 1 and 2 are not well suited for evaluating the effects of T °C and HRT on the N_{tot} and NH_4 removal efficiency separately because of their multicollinearity, i.e. if there is a strong reciprocal correlation between the model arguments, their effects are also correlated, and the evaluations received from the model may not be correct (e.g. a negative coefficient for T °C suggests that an increase in T °C with the other parameters fixed, will cause a decrease in the nitrogen removal efficiency, which is not correct). Therefore, Models 1 and 2 do not provide a better result in comparison with basic linear regression models (see Table 5) for the evaluation of the effects of T °C and HRT separately.

Modelling the volume of the air consumed for biological treatment (O_2) by using linear models with several factor variables did not give significantly better results in comparison with simple linear regression models. Therefore, these correlations are described with simple linear models. The regression models that describe the combined effect of HeM and the effect of HRT and T °C on the volume of air needed for biological treatment are presented in Table 6. The linear models showed that a 1 kg increase in the HeM reduced the O_2 by approximately 9300 m^3/d, which suggests that biological treatment is inhibited. Ong and co-authors [31] obtained similar results in a laboratory research when analysing the effect of individual HeM (concentrations varying between 0 and 50 mg/L) on the air consumption needed for biological treatment in order to evaluate the inhibitory effect. At high Zn concentrations, the inhibitory effect was nearly 50% [31]. Models 1 and 2 yielded similar results: by increasing the HeM, the nitrogen removal efficiency decreased or less oxygen was used for nitrification. The reason is that the bacterial metabolism was inhibited [35].

To illustrate statistical correlations, Fig. 3 presents scatter plots with regression lines. Figure 3 confirms that the effect of the HeM on the N_{tot} and NH_4 removal efficiency and on the O_2 is not statistically significant because one of the possible positions of the real regression line is horizontal. The same situation applies to the pairs O_2 and T °C, and O_2 and the HRT. The scatter plots that illustrate the effects of T °C and HRT on the N_{tot} and NH_4 removal efficiency confirm the existence of a positive correlation. However, Models 1 and 2, which take into account the combined effect of three factors, gave adequate results where an increase in the HeM resulted in a decrease in the treatment efficiency by 1.05% for N_{tot} and by 1.04% for NH_4.

Table 5. Regression models describing the effect of T °C and HRT on N_{tot} and NH_4 removal efficiency

Linear regression model		Significance probability p	Description percentage r^2	Standard error of the model, %
$N_{tot} = 0.77 \cdot T\ °C + 73.73$	(3)	0.006	16.6	5.35
$N_{tot} = 1.63 \cdot HRT + 63.22$	(4)	<0.0001	31.9	4.84
$NH_4 = 0.49 \cdot T\ °C + 89.11$	(5)	0.065	7.7	5.21
$NH_4 = 1.04 \cdot HRT + 82.41$	(6)	0.009	14.96	5.0

Table 6. Regression models describing the effect of HeM, HRT, and T °C on the O_2 in aeration tanks

Linear regression model		Significance probability p	Description percentage r^2	Standard error of the model, m^3/d
$O_2 = -9.3 \cdot HeM + 1601.14$	(7)	0.085	6.7	189.1
$O_2 = 20 \cdot HRT + 1138.59$	(8)	0.173	4.3	191.5
$O_2 = 8.39 \cdot T\ °C + 1282.4$	(9)	0.389	1.7	194.1

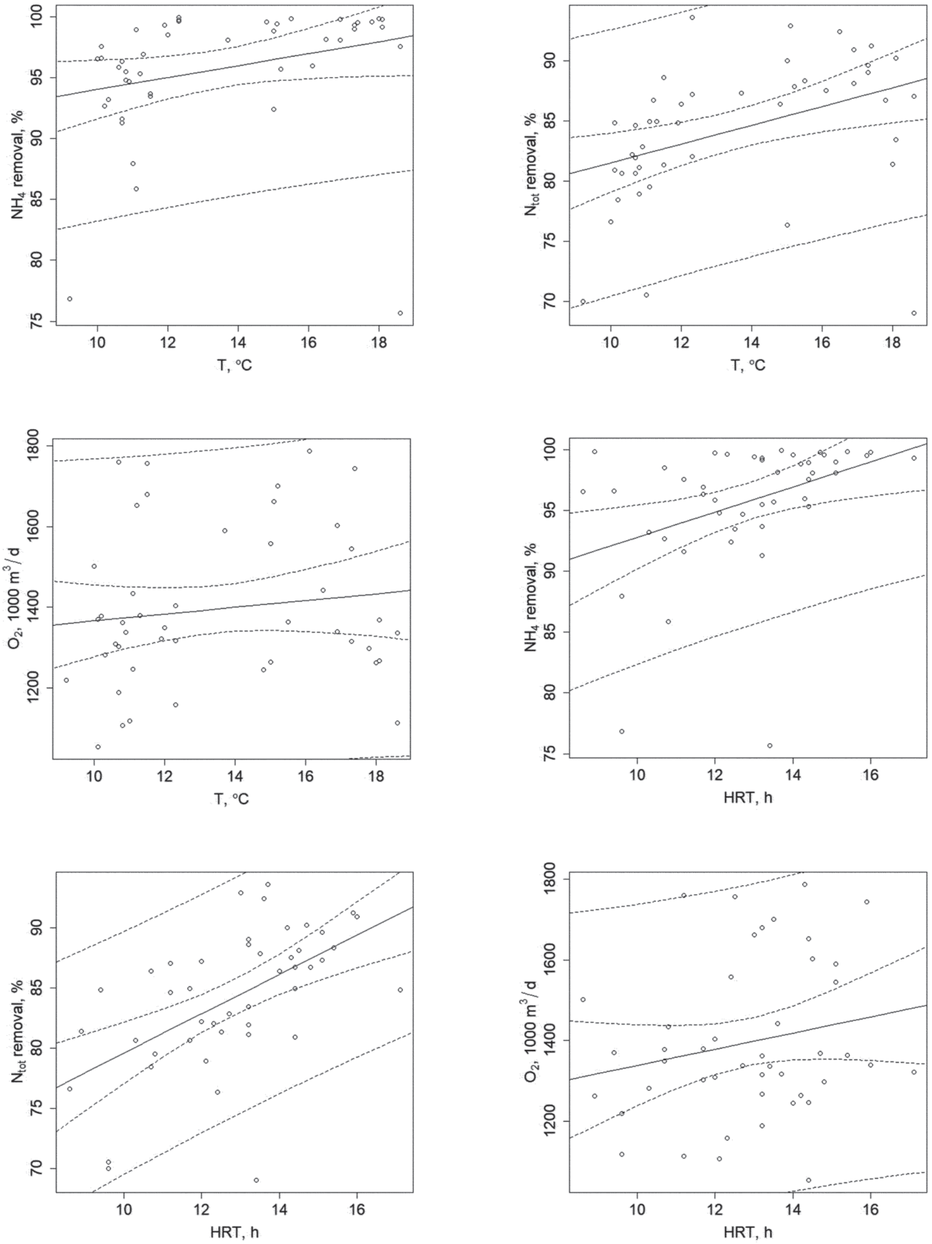

Fig. 3. Scatter plots with regression lines and the lines showing 95% tolerance and the width of confidence intervals. The straight dotted lines mark the area where 95% of the measurement results should remain, and the curved dotted lines show where the real regression line with a 95% probability is located. (*Continued on the next page.*)

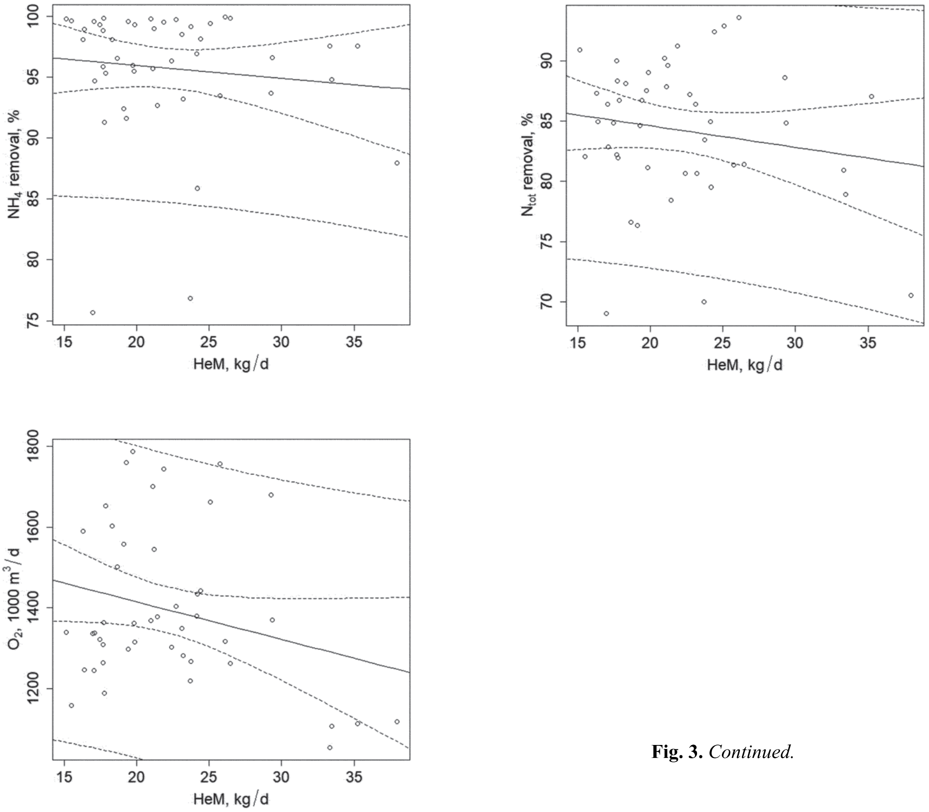

Fig. 3. *Continued.*

4. CONCLUSIONS

The combined effect of heavy metals on the biological treatment process of an operating WWTP was analysed in this research. In order to evaluate this effect, mathematical models were created, taking into account the HRT, T °C, and HeM; in the latter case eight different heavy metals as the total load were examined. Previous research has focused on the effect of individual heavy metals where the concentrations had to be exponentially higher in order to get measurable results.

The created mathematical models demonstrated that a combined effect of heavy metals exists also at lower concentrations, because a 1 kg/d increase in the HeM decreased the N_{tot} and NH_4 removal efficiency by 1.05% and 1.04%, respectively, and the air consumption in biological treatment was reduced by 9300 m^3/d. All the created models confirmed the inhibitory effect of heavy metals. Since the removal of nitrogen is a highly sensitive process, biological treatment monitoring is a significant outcome of this research, and the created mathematical models can be used, after some supplementation, for detecting inhibitory substances.

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Raskmetallide koosmõju aktiivmudaprotsessile

Erki Lember, Vitali Retšnoi, Karin Pachel ja Enn Loigu

Antud uuringus analüüsiti raskmetallide kombineeritud koosmõju töötavale reoveepuhasti bioloogilisele puhastusele. Mõju hindamiseks koostati matemaatilised mudelid, mis arvestasid protsessi viibeaja, temperatuuri ja raskmetallide koormusega, viimase puhul vaadeldi kaheksat erinevat raskmetalli kogu koormusena. Varasemad uuringud keskendusid üksikute raskmetallide mõjule, kus mõõdetavate tulemuste saamiseks pidid kontsentratsioonid palju suuremad olema.

Koostatud matemaatilised mudelid näitasid, et ka väikestel kontsentratsioonidel on raskmetallide kombineeritud mõju olemas, sest raskmetallide koormuse suurenemisel vähenesid N_{tot} ja NH_4 ärastusefektiivsus ning bioloogilises puhastuses tarbitud õhu kogus. Kõik koostatud mudelid kinnitasid raskmetallide inhibeerivat toimet. Kuna lämmastikuärastusprotsess on väga tundlik, on antud uuringul bioloogilise puhastuse seiramisel üks oluline väljund ehk koostatud matemaatilist mudelit on peale täiendamist võimalik kasutada inhibeerivate ainete tuvastamisel.

Paper V

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