Removal of hazardous substances in municipal wastewater treatment plants
Vallo Kõrgmaa, Mailis Laht, Riin Rebane, Erki Lember, Karin Pachel, Mait Kriipsalu, Taavo Tenno and Arvo Iital

ABSTRACT

Chemical pollution poses a threat to the aquatic environment and to human health. Wastewater treatment plants are the last defensive line between the aquatic environment and emissions of pollutants. This study focuses on identification of most relevant hazardous substances in Estonian municipal wastewater and their fate in the treatment process. During this study, seasonal wastewater and sewage sludge samples were collected from nine municipal wastewater treatment plants and analyzed for 282 hazardous substances, including EU ($n = 45$) and Estonian ($n = 31$) priority substances. Results of this study show that several substances that are subject to international restrictions (e.g. Stockholm Convention) are still present in untreated sewage. Wastewater treatment systems that had a greater level of complexity (TEC > 5) were more successful in removing hazardous substances. Statistical analyses showed that removal efficiency of organic hazardous substances had significant ($p$-value < 0.05) linear correlation with removal efficiencies of chemical oxygen demand (COD) and total suspended solids (TSS), but a monotonic relationship with operators’ competency. This study showed that operators’ competency had a strong influence on the stability of the wastewater treatment efficiency and removal of organic hazardous substances.

Key words | hazardous substances, municipal wastewater treatment, removal efficiency

HIGHLIGHTS

- Wide range of hazardous substances ($n = 282$) was analysed from nine wastewater treatment plants. Removal efficiencies for said substances were found.
- Wastewater treatment systems that had a greater level of complexity were more successful in removing hazardous substances. Statistical analyses showed that removal efficiency of organic hazardous substances had significant linear correlation with removal efficiencies of COD and TSS, but a monotonic relationship with operators’ competency.
- This study showed that operators’ competency had a strong influence on the stability of the wastewater treatment efficiency and removal of organic hazardous substances.

INTRODUCTION

In Europe, the Water Framework Directive (2000/60/EC) established provision for a list of Priority Substances (EC 2000). Directive 2008/105/EC laid down environmental quality standards (EQS) for the first 33 priority substances and eight other pollutants that were already regulated at Union level (EC 2008). Directive 2013/39/EU updated this list, concluding environmental quality standards to 45 priority substances (EC 2013). In addition to these
European-wide regulated substances Estonia has set quality standards (Minister of Environment 2019a) for six heavy metals (As, Ba, Cr, Sn, Zn, Cu), 11 pesticides (glyphosate, MCPA, chloromequat chloride, metazachlor, tebuconazole, dimethoate, clopyralid, spiroxamine, mancozeb, prothioconazole and 2,4-D), eight phenolic compounds (o-xylene, m,p-xylene, toluene) and for some other substances (C10-C40 hydrocarbons, fluorides). In order to ensure good quality of receiving bodies, Estonia has set quality standards for wastewater discharges (Minister of Environment 2019b) considering effluent from the wastewater treatment plants to be one of the most important point sources of hazardous substances to the aquatic environment (Clara et al. 2012).

There are two factors that basically define the effluent quality – characteristics of an influent and the performance of the municipal wastewater treatment plant (MWWTP). The performance of a WWTP depends on various technical and non-technical factors such as characteristics of influent wastewater and how well these are in accordance with the designed treatment process, operational and management practices, reliability of equipment and flexibility of the process (Hegg et al. 1979; Olsson 2012; Hao et al. 2015). Prasse et al. (2015) emphasized that as treatment technologies can also differ it is not clear to what extent the removal efficiencies of individual substances vary. Prasse et al. (2015) also outlined that chemical and biological assessment of wastewater treatment technologies were influenced by the sampling strategy and analytical methods used, therefore they suggested flow-proportional composite sampling in order to increase reliability. There are several articles available about removal of hazardous substances during the wastewater treatment process on a more general level (Clara et al. 2012; Gardner et al. 2013; Luo et al. 2014) or either focusing on certain substances (Clara et al. 2010; Pan et al. 2016; Ejhed et al. 2018), technologies (Gasperi et al. 2010; Gorito et al. 2017; Gruchlik et al. 2018) or small-scale solutions (Gros et al. 2017). According to Pomies et al. (2015) there are at least 18 models describing micropollutant removal in activated sludge processes available. Treatment technologies and conditions among MWWTPs can be standardized by indexes (Körgmaa et al. 2019), but influent characteristics are always community specific. Prasse et al. (2015) outlined that besides demographics on the sewer collection area and the number of facilities (e.g. hospitals, laundry services) that use specific hazardous substances, the proportion and composition of co-treated industrial wastewater has to be considered as having a great impact on certain substances in the influent.

In recent years there has been discussion on upgrading existing MWWTPs by adding tertiary treatment steps (e.g. filtration, ozonation) in order to reduce emissions of hazardous substances (Clara et al. 2012; Luo et al. 2014). Still, the decision about upgrading MWWTP should be made with regard to the situation where the control of influent wastewater is not possible and the ‘polluter pays’ principle does not have any desired effect. Whereas emissions of hazardous substances in industrial (indirect) discharges could be controlled by environmental permitting (2010/75/EU) (EC 2010) or by the contracting conditions between the industry and MWWTP (Finnish Water Utilities Association 2018), emissions in domestic wastewater are rather difficult to control. The mechanisms that are targeting reduction of the use of hazardous substances (e.g. REACH, Stockholm Convention) are working well on an industrial production level, but they are not capable of repealing emissions from widely used products that already contain prohibited hazardous substances.

In total, there are 668 municipal wastewater treatment plants in Estonia. 51.2% of the pollution load is treated in MWWTPs with capacity for more than 100,000 person equivalents (PEs) and 16.7% in MWWTPs that are less than 10,000 PEs. The variety of treatment technologies is also dependent on the plant’s capacity. The activated sludge (AS) process has been the process most commonly used (335 plug-flow and 62 sequencing batch reactors), followed by natural-based solutions (including 118 oxidation ponds and 22 constructed wetlands) and biofilm reactors (127 plants). Most of the MWWTPs are small – 503 MWWTPs have a capacity less than 300 PEs, 128 for 300–2,000 PEs, 20 for 2000–10,000 PEs, 15 for 10,000–100,000 PEs and two MWWTPs are designed for more than 100,000 PEs. Maximum concentrations of nitrogen and phosphorous in effluents are legally determined for MWWTPs exceeding 500 PEs in Estonia. The performance of MWWTPs has been varying over a wide scale based on a survey of 245 Estonian MWWTPs (Körgmaa et al. 2019).

This study aims to increase the knowledge on the occurrence and fate of hazardous substances relevant from the aquatic environment protection perspective (Directive 2000/60/EC) in municipal wastewater treatment plants. The studied substances belonged to a wide range of chemical groups; for example, phthalates, pesticides, halogenated flame retardants and volatile compounds (Appendix A). This study was a part of the inventory of sources and flows of priority hazardous substances in Estonia. In order to improve the understanding of removal efficiencies of hazardous substances during the wastewater treatment
process most widely used technologies in Estonia were included: constructed wetlands, soil beds, biofilm and activated sludge solutions. Additionally, the complexity of treatment plants and operators’ competence was evaluated to estimate possible gaps between technological potential and achieved pollutant removal rate.

**MATERIALS AND METHODS**

**Selection of wastewater treatment plants**

This study involved nine MWWTPs (see Table 1) that were selected according to the following criteria: (a) loading – this study covered 59.7% of the pollution load from MWWTPs in Estonia; (b) treatment technology selection covered most widely used solutions in Estonia, including small-scale solutions (e.g. biofilm reactors, constructed wetlands) as well as an activated sludge process (continuous flow and sequencing batch reactors (SBRs)); and (c) industrial load had to be less than 50% in order to minimize the impact of industrial wastewaters.

**Table 1 | Simplified description of selected wastewater treatment plants**

<table>
<thead>
<tr>
<th>Plant capacity (PE)</th>
<th>Primary treatment</th>
<th>Biological treatment</th>
<th>N-removal</th>
<th>P-removal</th>
<th>Effluent polishing</th>
<th>Sludge treatment</th>
<th>Complexity</th>
<th>Operator</th>
</tr>
</thead>
<tbody>
<tr>
<td>A &lt;300</td>
<td>Septic tank</td>
<td>Constructed wetland</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>3.3</td>
<td>0.6</td>
</tr>
<tr>
<td>B 300–1,999</td>
<td>Screen + septic tank</td>
<td>Oxidation pond</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>4.4</td>
<td>6.6</td>
</tr>
<tr>
<td>C 300–1,999</td>
<td>Screen + septic tank + grit separator</td>
<td>Biofilm</td>
<td>No</td>
<td>Chemical</td>
<td>Oxidation pond</td>
<td>No</td>
<td>4.9</td>
<td>0.8</td>
</tr>
<tr>
<td>D 2,000–9,999</td>
<td>Screen + grit separator</td>
<td>SBR</td>
<td>Yes</td>
<td>Biological + chemical</td>
<td>No</td>
<td>Composting</td>
<td>6.4</td>
<td>7.5</td>
</tr>
<tr>
<td>E 10,000–99,999</td>
<td>Screen + grit separator</td>
<td>SBR</td>
<td>Yes</td>
<td>Chemical</td>
<td>No</td>
<td>Composting</td>
<td>6.9</td>
<td>2.0</td>
</tr>
<tr>
<td>F 10,000–99,999</td>
<td>Screen + grit separator</td>
<td>Activated sludge/SBR</td>
<td>Yes</td>
<td>Biological + chemical</td>
<td>No</td>
<td>Anaerobic digestion</td>
<td>7.0</td>
<td>7.8</td>
</tr>
<tr>
<td>G 10,000–99,999</td>
<td>Screen + grit separator</td>
<td>Activated sludge</td>
<td>Yes</td>
<td>Biological + chemical</td>
<td>No</td>
<td>Anaerobic digestion</td>
<td>6.9</td>
<td>8.9</td>
</tr>
<tr>
<td>H &gt;100,000</td>
<td>Screen + grit separator + primary clarifier</td>
<td>Activated sludge</td>
<td>Yes</td>
<td>Biological + chemical</td>
<td>Drum filter</td>
<td>Anaerobic digestion</td>
<td>6.2</td>
<td>8.2</td>
</tr>
<tr>
<td>I &gt;100,000</td>
<td>Screen + grit separator + primary clarifier</td>
<td>Activated sludge</td>
<td>Yes</td>
<td>Chemical</td>
<td>Post-denitrification</td>
<td>Anaerobic digestion</td>
<td>5.5</td>
<td>8.4</td>
</tr>
</tbody>
</table>

**Method for assessment of the complexity of WWTPs and operators’ competence**

During the sampling event, an evaluation of operators’ competence and WWTP complexity was carried out according to the methodology described by Kõrgmaa et al. (2019). This evaluation was based on the following prerequisites: (a) the steps of the treatment processes (primary, secondary and tertiary treatment) are characteristic for all WWTPs; (b) different equipment and processes have the same function in the same treatment step (e.g. the bar screen and screw screen are both devices for removing particles from wastewater); and (c) all the processes and equipment having the same purpose at the same treatment step have to be comparable by setting specific critical control points (CCPs) for each treatment step. In this paper, CCPs are defined as factors that describe the complexity of the treatment step (e.g. screenings are pressed and washed). For each wastewater treatment step, a minimum of two CCPs were defined. To overcome the problem of assessment subjectivity, all the CCPs were formulated as questions containing a choice of answers, which was set between two to five variables, mainly in the form of ‘yes’ or ‘no’. In order to form an overall assessment each CCP was given a score (between 0 and 1) and a summary of evaluation (on the scale of 10 points) was formed from the weighted scores of the different treatment stages. The complexity of a WWTP was defined by Kõrgmaa et al. (2019) as the total evaluation of complexity (TEC) and it describes how many different treatment steps are involved in the wastewater treatment process and how sophisticated the technology is.

The assessment was performed in the presence of a local operator. During the plant visit, operator’s competence (on a
scale of 10 points) was assessed in the form of a hidden test similarly to the complexity assessment.

Table 1 summarizes the main properties of selected wastewater treatment plants.

**Sampling**

Seasonal spot samples of influent and effluent water were collected between June 2017 and April 2018 from all MWWTPs according to ISO 5667-10. Samples of sewage sludge were collected according to ISO 5667-13. The flow-proportional composite sampling strategy for both influent and effluent of each MWWTP was not realistic, but from six MWWTPs time-proportional composite samples were collected in parallel for certain analyses (PAHs, pesticides, alkylphenols, heavy metals and phthalates) in accordance with ISO 5667-3 in order to increase sampling reliability. In total, 72 spot samples, 48 composite samples and 32 sewage sludge samples were collected and analysed for 282 substances.

**Chemical analysis**

During the study, 282 hazardous substances were analyzed, including EU (n = 45) and Estonian (n = 31) priority substances. All analytical methods used in this study were accredited methods according to the standard ISO 17025.

Liquid chromatography (Agilent Technologies Infinity 1290) with tandem mass spectrometry and electrospray ionization (LC-ESI-MS/MS) (Agilent Technologies 6490 with JetStream ESI) was used for analysis of pesticides (including glyphosate), perfluorooctanesulfonate and its derivatives. Water samples were analyzed without any sample preparation, solid samples were analyzed after extraction procedures. Wastewater and sewage sludge pesticide samples were analyzed with the addition of OnlineSPE (Agilent Flexible Cube LC module).

Determination of selected organotin compounds was carried out with gas chromatograph and with tandem mass spectrometric analysis (Agilent Technologies 7890B/5977A MSD). Water samples were analyzed according to EN 24929 and solid samples according to CEN/TS 16182. GC/MS was used for determination of benzene and some derivatives with the headspace gas chromatographic method. Water samples were according to ISO 11423-1 and solid samples to ISO 22155.

Determination of individual isomers of nonylphenol extracted from the samples was carried out by gas chromatography/mass spectrometry (GC/MS) by Agilent Technologies (7890B/5977A MSD). Water samples were prepared according to EVS-EN ISO 9377-2 and solid samples according to EVS-EN ISO 16703. Extraction was carried out with n-hexane and in the case of solid samples with a mixture of acetone and n-hexane.

Mercury was analyzed according to EVS-EN ISO 12846 with an Hg Analyzer (RA-915, Lumex). Other metals were analyzed according to EVS-EN ISO 11885 with inductively coupled plasma optical emission spectrometry (Vista – MPX Varian).

**Statistical analyses**

Chemical analyses with measurements below the limit of quantification (LOQ) were substituted with LOQ/√2 prior to statistical evaluation. There is a possibility that this censoring will create some bias (Hesel 2005; Zeghnoun \textit{et al.} 2007), but according to Vriens \textit{et al.} (2019), in statistical approaches for multipollutant studies the use of more advanced techniques for handling undetectable levels is not supported. The Environmental Protection Agency (EPA 2000) guideline states also that if the rate of censoring is very high (greater than 50%) then focus should be put on the upper quantile of the contaminant distribution, or on the proportion of measurements above a certain critical level that is at or above the censoring limit. For studying the relationship between the MWWTP complexity, operators’ competence and removal of substances, tools of correlation and regression analysis were applied. Together with the Pearson coefficient, the Spearman correlation coefficient was also applied in those cases, where the dependence between study variables was of the monotonic type instead.
of linear. For categorical variables, analysis of variance (ANOVA) was used for comparing the population means in different groups. p-values of 0.05 or lower were considered to indicate statistical significance.

RESULTS AND DISCUSSION

Overview of detected hazardous substances

From 282 substances, only 45 (1,2,3,4,6,7,8-H7CDF, 1,2,3,6,7,8-H6CDF, 1,2,3,7,8,9-H6CDD, 1,2,3,7,8,9-H6CDF, 1,2,3,4,7,8-H6CDF, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, 2,3,4,6,7,8-H6CDF, 2,3,4,7,8-P5CDF, 2,3,4,7,8-P5CDF, 2,3,7,8-T4CDD, 2,3,7,8-T4CDF, aclonifen, alachlor, aldine, alpha-endosulfan, atrazine, bifenox, delta-hexachlorocyclohexane, dieldrin, dichlorophen, dimethoate, endrin, epsilon-hexachlorocyclohexane, hexachlorobutadiene, isodrine, chlorofenvinphos, chlorpyrifos, metazachlor, PCB-114, PCB-123, PCB-126, PCB-156, PCB-157, PCB-169, PCB-189, PCB-77, PCB-81, pentachlorobenzene, simazine, trifluralin, cybutrine) were not detected above the LOQ from any of the analysed samples. Di-2-ethylhexylphthalate (DEHP), toluene and heavy metals (As, Ba, Ni, Pb, Zn) were detected above LOQ from all samples. One hundred and twenty substances were found below LOQ in the influent. Table 2 shows the ten most frequently found substances in the influent samples. For some of the substances, seasonal patterns (e.g. diuron, glyphosate, trichloromethane were found in the summer and autumn samples) or connections to population density (e.g. tetrachloroethene was detected only from MWWTPs with capacity more than 10,000 PEs or median concentrations of trichloromethane increased linearly according to the plant size) could be detected.

One hundred and fifty-seven substances were found below the LOQ in effluent. Fluoride and diclofenac were the most frequently detected substances (Table 3).

Sewage sludge contained most of the substances above LOQ. In total, 16 substances (see Table 4) were found from all samples. Only 65 substances were not detected from any of the samples.

Removal efficiency of hazardous substances in municipal wastewater treatment plants

Municipal wastewater treatment plants are designed to reduce the pollution load to the environment. While nutrients and many other substances could be efficiently and consistently eliminated, the removal of hazardous substances is often insufficient (Luo et al. 2015). In order to understand whether the control of emissions of hazardous substances might be reduced by better process control, limiting the industrial discharges to the public sewer system or upgrading the existing technology, it is crucial to understand the fate and removal efficiency of said substances during the wastewater treatment process. Still, it has to be underlined that while discussing the removal of hazardous substances during the wastewater treatment process, the discussion generally refers to the removal of parent compounds from the aqueous phase (Luo et al. 2015). Sewage sludge analyses strongly indicate that for most substances an accumulation to the biomass has taken place. For example, during this study DEHP was detected from all influent samples above

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Substances found most frequently in the influent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>Unit</td>
</tr>
<tr>
<td>Di-2-ethylhexylphthalate (DEHP)</td>
<td>μg/l</td>
</tr>
<tr>
<td>Fluoride (F')</td>
<td>mg/l</td>
</tr>
<tr>
<td>Toluene</td>
<td>μg/l</td>
</tr>
<tr>
<td>Diisobutyl-phthalate (DIBP)</td>
<td>μg/l</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>μg/l</td>
</tr>
<tr>
<td>p/m-cresole</td>
<td>μg/l</td>
</tr>
<tr>
<td>Phenol</td>
<td>μg/l</td>
</tr>
<tr>
<td>Diethylphthalate (DET)</td>
<td>μg/l</td>
</tr>
<tr>
<td>PBDE 47</td>
<td>μg/l</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>μg/l</td>
</tr>
</tbody>
</table>
LOQ and only 25 per cent of effluent results exceeded LOQ, but all sewage sludge samples contained high levels of DEHP. Average removal efficiency was 69.1% for DEHP. This means that while DEHP is quite successfully removed from the aqueous phase, it is merely transferred to the sewage sludge.

Table 5 shows removal efficiencies calculated based on grab and composite samples respectively. Although Prasse et al. (2015) stated that grab sampling of influent and effluent wastewater is inappropriate to determine elimination efficiencies of MWWTPs as concentrations of hazardous substances might vary significantly over time, it was not possible to avoid grab sampling in order to satisfy the sampling conditions set in ISO 5667-3 for certain substances. Removal efficiencies expressed in Table 5 should therefore be regarded with certain reservations, as grab sampling can be considered random. As a result, for some of the substances (e.g. boscalid, diclofenac), the removal efficiency was negative. Negative removal efficiency (−85.5%) of aminomethylphosphonic acid (AMPA) indicates that...
Table 5 | Removal efficiencies of selected hazardous substances in municipal wastewater treatment plants

<table>
<thead>
<tr>
<th>Substance</th>
<th>Min (%)</th>
<th>25-Percentile (%)</th>
<th>Median (%)</th>
<th>75-Percentile (%)</th>
<th>Max (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heavy metals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>14.0</td>
<td>40.7</td>
<td>54.5</td>
<td>73.0</td>
<td>84.5</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>−85.0</td>
<td>65.2</td>
<td>85.3</td>
<td>90.1</td>
<td>97.5</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>1.0</td>
<td>63.6</td>
<td>74.5</td>
<td>86.7</td>
<td>92.9</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>84.4</td>
<td>97.0</td>
<td>98.4</td>
<td>99.5</td>
<td>99.6</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>−720.2</td>
<td>57.9</td>
<td>67.8</td>
<td>81.0</td>
<td>94.8</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>−34.4</td>
<td>60.2</td>
<td>70.7</td>
<td>82.9</td>
<td>95.1</td>
</tr>
<tr>
<td><strong>Organotin compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monobutyltin (MBT)*</td>
<td>30.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Monooctyltin (MOT)*</td>
<td>−130.0</td>
<td>80.2</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td><strong>Pesticides</strong></td>
<td></td>
<td></td>
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<tr>
<td>AMPA*</td>
<td>−288.9</td>
<td>−114.3</td>
<td>−66.9</td>
<td>0.7</td>
<td>40.9</td>
</tr>
<tr>
<td>Boscalid*</td>
<td>−800.0</td>
<td>−425.0</td>
<td>−180.4</td>
<td>−45.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Glyphosate*</td>
<td>−178.3</td>
<td>−51.3</td>
<td>30.7</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Propiconazole</td>
<td>−517.6</td>
<td>0.0</td>
<td>13.4</td>
<td>34.8</td>
<td>100.0</td>
</tr>
<tr>
<td>Tebuconazole</td>
<td>−182.4</td>
<td>−32.5</td>
<td>0.9</td>
<td>64.9</td>
<td>100.0</td>
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<tr>
<td>Terbutryn</td>
<td>−100.0</td>
<td>−47.9</td>
<td>−27.3</td>
<td>6.9</td>
<td>100.0</td>
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<tr>
<td>Phenols</td>
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<tr>
<td>o-Cresol*</td>
<td>−72.7</td>
<td>100.0</td>
<td>100.0</td>
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<td>100.0</td>
</tr>
<tr>
<td>p,m-Cresol*</td>
<td>−110.0</td>
<td>99.4</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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<tr>
<td>Phenol*</td>
<td>−18.5</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Resorcinol*</td>
<td>52.3</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
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<td><strong>Phthalates</strong></td>
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<tr>
<td>Di(2-ethylhexyl)phthalate (DEHP)</td>
<td>−84.8</td>
<td>63.2</td>
<td>84.8</td>
<td>94.7</td>
<td>98.6</td>
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<tr>
<td>Dibutyl phthalate (DBP)</td>
<td>−201.7</td>
<td>45.6</td>
<td>51.8</td>
<td>65.8</td>
<td>83.7</td>
</tr>
<tr>
<td>Diethyl phthalate (DET)</td>
<td>44.4</td>
<td>82.3</td>
<td>83.7</td>
<td>87.0</td>
<td>93.4</td>
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<tr>
<td>Diisobutyl phthalate (DIBP)</td>
<td>12.0</td>
<td>67.2</td>
<td>76.4</td>
<td>79.8</td>
<td>92.1</td>
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<td><strong>Polycyclic aromatic hydrocarbons</strong></td>
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<tr>
<td>Acenaphthene</td>
<td>55.8</td>
<td>61.7</td>
<td>79.0</td>
<td>89.3</td>
<td>92.5</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>−296.0</td>
<td>41.5</td>
<td>48.1</td>
<td>79.4</td>
<td>99.6</td>
</tr>
<tr>
<td>Anthracene</td>
<td>49.5</td>
<td>64.3</td>
<td>70.5</td>
<td>85.7</td>
<td>96.0</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>−578.8</td>
<td>70.5</td>
<td>80.4</td>
<td>85.9</td>
<td>95.6</td>
</tr>
<tr>
<td>Fluorene</td>
<td>72.8</td>
<td>84.5</td>
<td>90.8</td>
<td>92.9</td>
<td>98.1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>49.5</td>
<td>90.9</td>
<td>96.5</td>
<td>98.7</td>
<td>99.9</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>−324.3</td>
<td>91.2</td>
<td>94.8</td>
<td>96.6</td>
<td>98.8</td>
</tr>
<tr>
<td>Pyrene</td>
<td>−861.7</td>
<td>80.4</td>
<td>88.6</td>
<td>93.3</td>
<td>98.1</td>
</tr>
<tr>
<td><strong>Volatile organic compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene*</td>
<td>−70.0</td>
<td>68.1</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Tetrachloroethene (PER)*</td>
<td>17.1</td>
<td>79.5</td>
<td>92.7</td>
<td>99.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Toluene*</td>
<td>−262.5</td>
<td>96.3</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Trichloromethane*</td>
<td>−100.0</td>
<td>28.0</td>
<td>55.6</td>
<td>73.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
(continued)
This substance is formed during the biological wastewater treatment process. AMPA is a metabolite of microbial degradation of widely used herbicide glyphosate (Struger et al. 2018). Some of the negative removal efficiencies in Table 5 present the situation when MWWTP A was hydraulically overloaded during the snow melting period, resulting in wash-out of filter solids. During this event, it was noticed that MWWTP A was still able to remove 91.8% of BOD7, but chemical oxygen demand (COD) removal had reduced to 53.3%. Total suspended solids (TSS) and PAH removal efficiencies were negative. During the event, two-ring compound naphthalene was still degraded (49.5% was removed from wastewater), but removal efficiencies for four-ring compounds fluoranthene and pyrene, which need longer degradation time (Bouchez et al. 1996; Moscoso et al. 2018), were negative and wash-out of these compounds was observed.

Statistical analyses showed that removal efficiency of 238 organic hazardous substances had significant (p-value < 0.05) linear correlation with removal efficiencies of COD (Pearson’s r = 0.663) and TSS (Pearson’s r = 0.869), but a monotonic relationship with operators’ competency (Spearman’s P = 0.339).

One-way ANOVA showed that there was significant difference in COD, BOD7, TSS and organic hazardous substances removal efficiencies between less complex (TEC < 5) and more advanced treatment technologies (Table 6). MWWTPs with greater complexity (TEC > 5) had higher removal efficiency for said substances. This indicates that activated sludge systems could be more successful in removing pollutants from the water phase.

**Estimation of yearly emissions to the environment**

For Estonia, an estimation of loads of hazardous substances that end up in the different environmental compartments (mainly water and soil) was made based on the study results. The annual flow rates for each MWWTP were retrieved from the national water usage database (estimation based on 2017 flow rates). To estimate emissions of hazardous substances for all the country, all Estonian municipal WWTPs were divided into three groups according to their loadings (group I < 10,000 PEs, group II = 10,001 to 99,999 PEs, group III – more than 100,000 PEs). To calculate emissions for individual MWWTPs not having measured results,

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**Table 5** | continued

<table>
<thead>
<tr>
<th>Substance</th>
<th>Min (%)</th>
<th>25-Percentile (%)</th>
<th>Median (%)</th>
<th>75-Percentile (%)</th>
<th>Max (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon oil index (hydrocarbons C10-C40)*</td>
<td>68.4</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Perfluorobutanoic acid (PFBA)*</td>
<td>-17.4</td>
<td>27.3</td>
<td>46.4</td>
<td>89.2</td>
<td>100.0</td>
</tr>
<tr>
<td>Diclofenac*</td>
<td>-1285.0</td>
<td>-26.0</td>
<td>4.3</td>
<td>30.9</td>
<td>100.0</td>
</tr>
<tr>
<td>4-tert-octylphenol</td>
<td>22.8</td>
<td>45.3</td>
<td>61.4</td>
<td>79.5</td>
<td>89.2</td>
</tr>
<tr>
<td>4-nonylphenol</td>
<td>23.1</td>
<td>54.1</td>
<td>79.0</td>
<td>90.9</td>
<td>95.0</td>
</tr>
<tr>
<td>Fluoride (F-)</td>
<td>-233.3</td>
<td>-4.1</td>
<td>10.7</td>
<td>26.0</td>
<td>74.7</td>
</tr>
<tr>
<td>COD</td>
<td>53.3</td>
<td>87.3</td>
<td>92.9</td>
<td>96.4</td>
<td>99.5</td>
</tr>
<tr>
<td>BOD7</td>
<td>90.0</td>
<td>97.4</td>
<td>98.6</td>
<td>99.4</td>
<td>99.8</td>
</tr>
<tr>
<td>TSS</td>
<td>-160.0</td>
<td>93.8</td>
<td>97.7</td>
<td>98.6</td>
<td>99.7</td>
</tr>
</tbody>
</table>

*Calculated from grab samples.

**Table 6** | One-way ANOVA showed that higher complexity increases removal efficiencies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TEC &lt; 5</th>
<th>TEC &gt; 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Variance</td>
</tr>
<tr>
<td>∑(238 substances)</td>
<td>76.8</td>
<td>1028.5</td>
</tr>
<tr>
<td>COD</td>
<td>72.6</td>
<td>679.7</td>
</tr>
<tr>
<td>BOD</td>
<td>90.1</td>
<td>156.7</td>
</tr>
<tr>
<td>TSS</td>
<td>62.0</td>
<td>5215.4</td>
</tr>
</tbody>
</table>

The annual flow rates for each MWWTP were retrieved from the national water usage database (estimation based on 2017 flow rates). To estimate emissions of hazardous substances for all the country, all Estonian municipal WWTPs were divided into three groups according to their loadings (group I < 10,000 PEs, group II = 10,001 to 99,999 PEs, group III – more than 100,000 PEs). To calculate emissions for individual MWWTPs not having measured results,
median concentrations were calculated for each hazardous substance within the group (e.g. to calculate pyrene concentrations for group B, median concentrations from MWWTPs E, F and G were used) and multiplied by the annual flow rate of said MWWTP.

Table 7 shows an estimation of loadings of some hazardous substances. The determination of hazardous substances depends on their properties and their behaviour in analytical matrices. There are a number of compounds which, for example, do not dissolve well in water and therefore may even be adsorbed to particulate matter. This in turn might result in a situation where these compounds are determined, for example, in sewage sludge but not from the influent. Table 7 shows in italics the loads of hazardous substances entering the wastewater treatment plant that were below the LOQ in all influent samples, but were present in the effluent and/or sewage sludge. These loads were recalculated based on the total load of said substance in the effluent and in the sewage sludge.

Due to the randomness of spot sampling and the behaviour of substances in the wastewater treatment plant (depending on the properties of the substance it accumulates, volatilizes or decomposes during the treatment process), the loss of substances (see Table 7 column ‘Influent – effluent’) during the treatment process was also assessed when compiling the mass balance of hazardous substances.

The term ‘loss’ herein does not describe so much the loss of material in the process as it was used to evaluate the difference between the efficiency of the purification process and the accumulation in the sediment. For some substances, this allows an assessment of their fate in the wastewater treatment plant. For example, a total of 4.58 kg/year of prothioconazole is conveyed to Estonian WWTP through the influent and 2.71 kg/year is discharged into the environment with effluent. 1.67 kg/year of prothioconazole should be accumulated to the sewage sludge based on the difference between influent and effluent loads, but 0.74 kg/year of prothioconazole was estimated based on analytical results. However, further analysis of the results revealed that degradation of prothioconazole had taken place and 0.63 kg/year of the prothioconazole-destio was present in the sewage sludge. Similarly, influent contained 1,433 kg/year of phenol, 114 kg/year was emitted with effluent and 92 kg/year was found from sewage sludge. The 1,227 kg/year that was missing from the balance was most likely degraded during the treatment process.

**Effect of operators’ competency**

The importance of the human factor in the wastewater treatment process has been described very briefly in literature (Hegg et al. 1979; Olsson 2012) and in many cases it is considered to be the main reason for poor process performance (Hegg et al. 1979). Hegg et al. (1979) listed improper operator application of concepts and testing to process control as well as inadequate understanding of sewage treatment as the two highest ranking factors contributing to poor plant performance. The competence of the operator has been outlined as one of the key factors for successful plant control (Hegg et al. 1979; Muga & Michelic 2008; Olsson 2012). The competence of the operators was evaluated during the data collection in the form of a hidden test on the scale of 10 points according to the methodology described in Kõrgmaa et al. (2019). The operators’ competence was in the range between 0.6 and 8.9 with an average result of 5.7 points.

Statistical analyses showed that operators’ competency had moderate, but significant (p-value < 0.05) correlation with removal efficiencies of COD (Pearson’s $r = 0.474$), arsenic ($r = 0.485$), BOD$_5$ ($r = 0.526$), and naphthalene ($r = 0.530$). Strong correlation was observed for removal efficiencies of lead (Pearson’s $r = 0.603$), fluoranthene ($r = 0.617$), pyrene ($r = 0.660$) and chrysene ($r = 0.696$). Significant (p-value < 0.05) monotonic relationship was observed between operators’ competency and removal efficiencies of...
nickel (Spearman’s $\rho = -0.504$), COD ($\rho = 0.472$), 4-tetra-
octylphenol ($\rho = -0.658$), phentanthrene ($\rho = 0.569$), fluo-
rene ($\rho = 0.603$), fluoranthene ($\rho = 0.641$), and anthracene ($\rho = 0.731$).

Operators’ competence had a strong influence on the stability of the wastewater treatment efficiency. A com-
petent operator is more successful in ensuring stable COD removal and in avoiding decrease in process performance. While taking into consideration that there was significant ($p$-value $3.54\times 10^{-5}$) moderate correlation (Pearson’s $r = 0.663$) between COD and removal of organic hazardous sub-
stances, it can be concluded that operators’ competency plays the crucial role in successful removal of hazardous substances.

CONCLUSIONS

This study showed that many substances that are subject to international restrictions (e.g. di-2-ethylhexylphthalate, hex-
abromocyclododecane) are still present in raw sewage and treated effluent. For most of the substances, removal from the water phase in MWWTPs was observed but the chemical analyses of sewage sludge indicate that pollutants are often transmitted from water to the biomass. In order to under-
stand whether the control of emissions of hazardous substances might be reduced by better process control, limit-
ing industrial discharges to the public sewer system or upgrading the existing technology, it is crucial to understand the removal efficiency of said substances during the wastewater treatment process.

Wastewater treatment systems that had a greater level of complexity (TEC $>5$) were more successful in removing hazardous substances. Statistical analyses showed that removal efficiency of organic hazardous substances had sig-
nificant ($p$-value $<0.05$) linear correlation with removal efficiencies of COD and TSS, but a monotonic relationship with operators’ competency. Increasing operators’ competency will help to reduce emissions of hazardous substances to the environment. This study showed that operators’ competency had a strong influence on the stability of the wastewater treatment efficiency and removal of organic hazardous substances.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/wst.2020.264.

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