Proceedings of the Estonian Academy of Sciences,
2018, **67**, 4, 305–314
https://doi.org/10.3176/proc.2018.4.02
Available online at www.eap.ee/proceedings

ENVIRONMENTAL
ENGINEERING

Combined effect of heavy metals on the activated sludge process

Erki Lember[a*], Vitali Retšnoi[b], Karin Pachel[a], and Enn Loigu[a]

[a] Department of Environmental Engineering, Tallinn University of Technology, 19086 Tallinn, Estonia;
{karin.pachel, enn.loigu} @ttu.ee
[b] Tallinn University of Applied Sciences, Tallinn, Estonia; vitali.retsnoi@tktk.ee

Received 29 March 2018, accepted 16 April 2018, available online 30 August 2018

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.

---

[*] Corresponding author, erkilember@gmail.com

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.

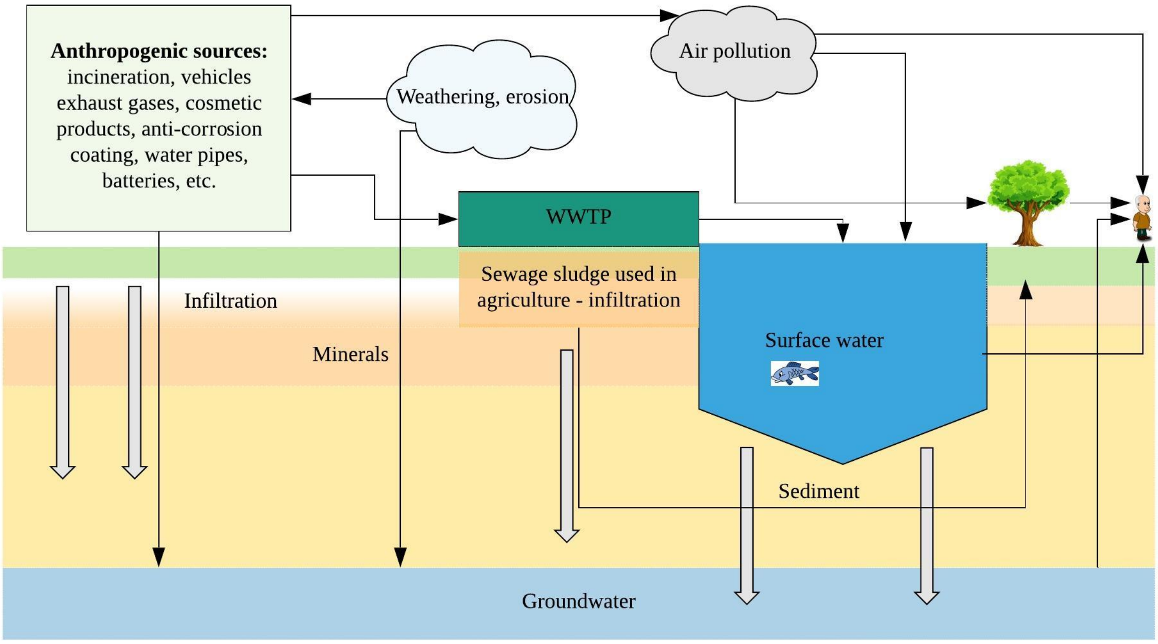

Fig. 1. Migration of heavy metals in/to the environment.

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).

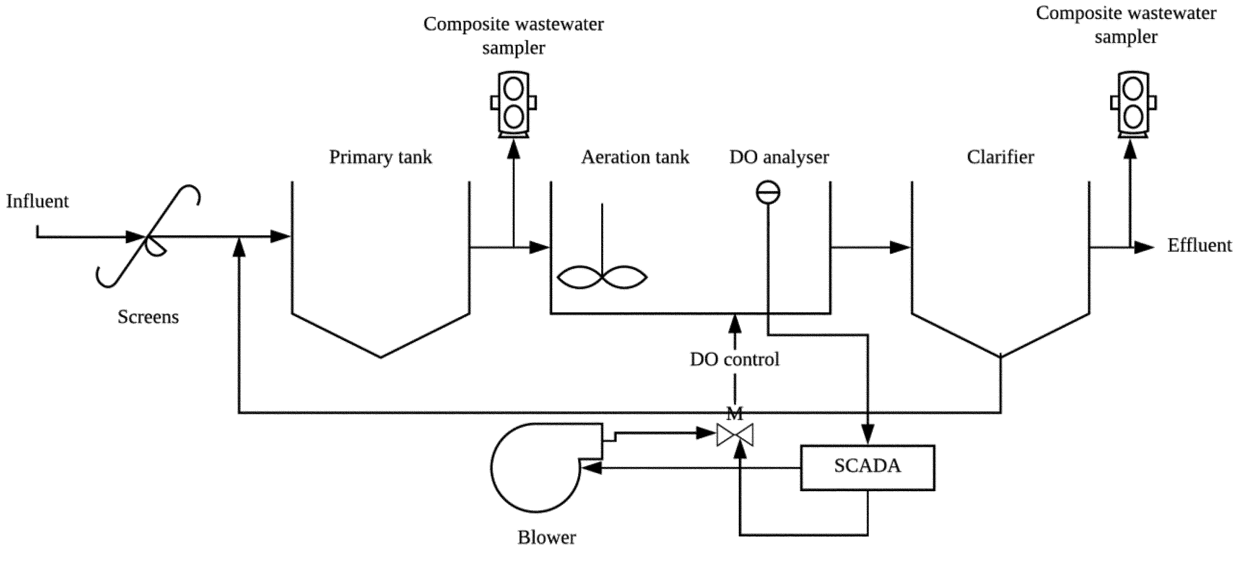

Fig. 2. Flow diagram of the WWTP and sampling points. DO – dissolved oxygen, SCADA – Supervisory Control and Data Acquisition.

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:

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

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:

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

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

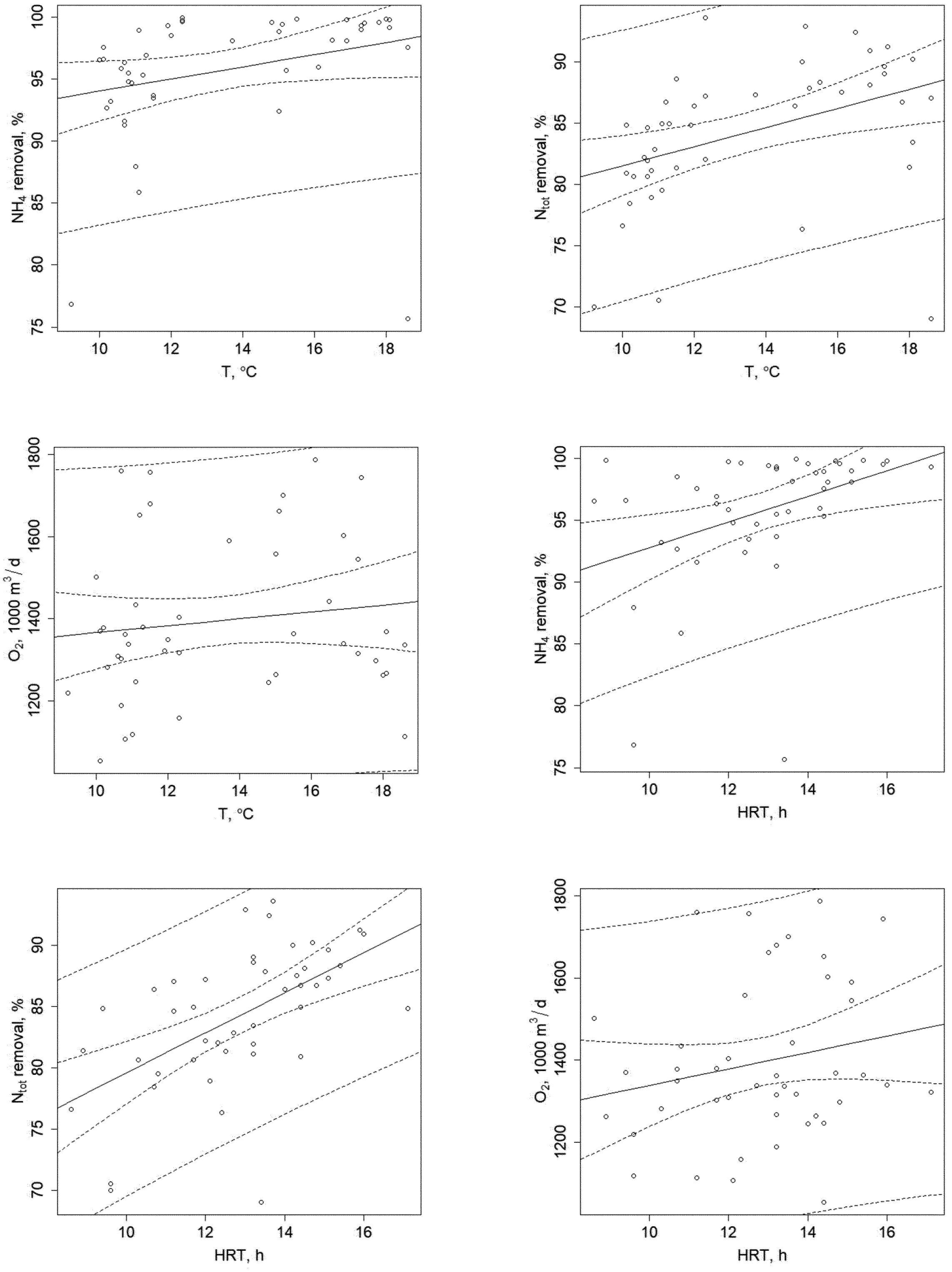

Fig. 3. Scatter plots with regression lines and the lines showing 95% tolerance and the width of confidence intervals. The straight dotted lines mark the area where 95% of the measurement results should remain, and the curved dotted lines show where the real regression line with a 95% probability is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

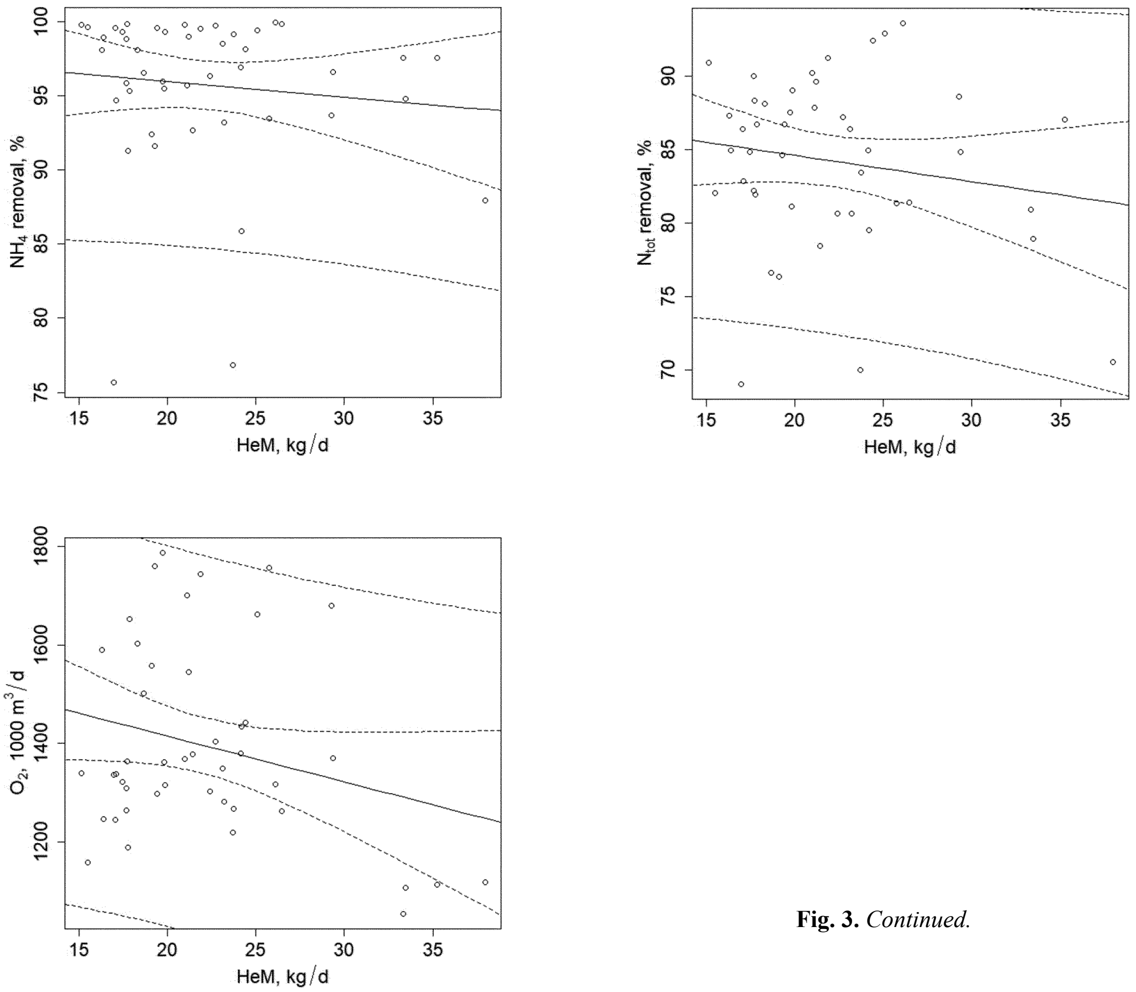

Fig. 3. *Continued.*

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.

REFERENCES

1. Men, C., Liu, R., Xu, F. Wang, Q., Guo, L., and Shen, Z. Pollution characteristics, risk assessment, and source apportionment of heavy metals in road dust in Beijing, China. *Sci. Total Environ.*, 2018, **612**, 138–147.
2. Zhang, Q-Q., Ying, G-G., Pan, C-G., Liu, Y-S., and Zhao, J-L. Comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modeling, and linkage to bacterial resistance. *Environ. Sci. Technol.*, 2015, **49**, 6772–6782.
3. Chowdhury, S., Mazumder, M. A. J., Al-Attas, O., and Husain, T. Heavy metals in drinking water: occurrences,

implications, and future needs in developing countries. *Sci. Total Environ.*, 2016, **569–570**, 476–488.

4. Egodawatta, Y., Ma, P., McGree, J., Liu, A., and Goonetilleke, A. Human health risk assessment of heavy metals in urban stormwater. *Sci. Total Environ.*, 2016, **557–558**, 764–772.
5. Bernard, E., Jimoh, A., and Odigure, J. O. Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. *Res. J. Chem. Sci.*, 2013, **3**, 3–9.
6. Fang, L., Li, L., Qu, Z., Xu, H., Xu, J., and Yan, N. A novel method for the sequential removal and separation of multiple heavy metals from wastewater. *J. Hazard. Mater.*, 2018, **342**, 617–624.
7. Goonetilleke, A., Liu, A., Managi, S., Wilson, C., Gardner, T., Bandala, R., et al. Stormwater reuse, a viable option: fact or fiction? *Econ. Anal. Policy*, 2017, **56**, 14–17.
8. Wu, C., Zhou, Y., Zhang, S., Xu, M., and Song, J. The effect of toxic carbon source on the reaction of activated sludge in the batch reactor. *Chemosphere*, 2018, **194**, 784–792.
9. Kobielska, P. A., Howarth, A. J., Farha, O. K., and Nayak, S. Metal–organic frameworks for heavy metal removal from water. *Coord. Chem. Rev.*, 2018, **358**, 92–107.
10. Napa, Ü. *Heavy Metals in Estonian Coniferous Forests*. Dissertationes Geographicae Universitatis Tartuensis, **65**. University of Tartu Press, 2017.
11. Gunawardana, C., Goonetilleke, A., Egodawatta, P., Dawes, L., and Kokot, S. Source characterisation of road dust based on chemical and mineralogical composition. *Chemosphere*, 2012, **87**, 163–170.
12. Charters, F. J., Cochrane, T. A., and O'Sullivan, A. D. Untreated runoff quality from roof and road surfaces in a low intensity rainfall climate. *Sci. Total Environ.*, 2016, **550**, 265–272.
13. Pan, H., Lu, X., and Lei, K. A comprehensive analysis of heavy metals in urban road dust of Xi'an, China: contamination, source apportionment and spatial distribution. *Sci. Total Environ.*, 2017, **609**, 1361–1369.
14. Bauhaus–Universität Weimar. *Abwasserbehandlung: Gewässerbelastung, Bemessungsgrundlagen, Mechanische Verfahren und Biologische Verfahren, Reststoffe aus der Abwasserbehandlung, Kleinkläranlagen*. VDG, Weimar, 2014.
15. Ullah, H., Noreen, S., Fozia, A. R., Waseem, A., Zubair, S., Adnan, M., and Ahmad, I. Comparative study of heavy metals content in cosmetic products of different countries marketed in Khyber Pakhtunkhwa, Pakistan. *Arab. J. Chem.*, 2017, **10**, 10–18.
16. Sani, M., Gaya, B., and Abubakar, F. A. Determination of some heavy metals in selected cosmetic products sold in Kano metropolis, Nigeria. *Toxicol. Reports*, 2016, **3**, 866–869.
17. Vabariigi Valitsus. Reovee puhastamise ning heit- ja sademevee suublasse juhtimise kohta esitatavad nõuded, heit- ja sademevee reostusnäitajate piirmäärad ning nende nõuete täitmise kontrollimise meetmed. *RT I*, 16.12.2016, 6. https://www.riigiteataja.ee/akt/116122016006 (accessed 2017-02-10).
18. González-Acevedo, Z. I., García-Zarate, M. A., Núñez-Zarco, E. A., and Anda-Martín, B. I. Heavy metal sources and anthropogenic enrichment in the environment around the Cerro Prieto Geothermal Field, Mexico. *Geothermics*, 2018, **72**, 170–181.
19. Tahri, M., Larif, M., Bachiri, B., Kitanou, S., Rajib, B., Benazouz, K., et al. Characterization of heavy metals and toxic elements in raw sewage and their impact on the secondary treatment of the Marrakech wastewater treatment plant. *J. Mater. Environ. Sci.*, 2017, **8**, 2311–2321.
20. Henze, M., Loosdrecht, C. M., Ekama, A. G., and Brdjanovic, D. *Biological Wastewater Treatment*. IWA Publishing, London, 2011.
21. Hartmann, S., Skrobankova, H., and Drozdova, J. Inhibition of activated sludge respiration by heavy metals. In *Proceedings of the 2013 International Conference on Environment, Energy, Ecosystems and Development*, 2013, 231–235.
22. Antoniou, P., Hamilton, J., Koopman, B., Jain, R., Holloway, B., Lyberatos, G., and Svoronos, S. A. Effect of temperature and pH on the effective maximum specific growth rate of nitrifying bacteria. *Water Res.*, 1990, **24**, 97–101.
23. United States Environmental Protection Agency. *Process Design Manual for Nitrogen Control*. Office of Technology Transfer, Washington D.C., 1973.
24. Raud, M., Lember, E., Jõgi, E., and Kikas, T. *Nitrosomonas* sp. based biosensor for ammonium nitrogen measurement in wastewater. *Biotechnol. Bioprocess Eng.*, 2013, **18**, 1016–1021.
25. Rittmann, B. E. and McCarty, P. L. *Environmental Biotechnology: Principles and Applications*. Tata McGraw Hill Education Private Limited, New Delhi, 2012.
26. Donnachie, R. L., Johnson, A. C., Moeckel, C., Pereira, M. G., and Sumpter, J. P. Using risk-ranking of metals to identify which poses the greatest threat to freshwater organisms in the UK. *Environ. Pollut.*, 2014, **194**, 17–23.
27. Quintana, V., Olalla-Herrera, M., Ruiz-López, M. D., Moreno-Montoro, M., and Navarro-Alarcón, M. Study of the effect of different fermenting microorganisms on the Se, Cu, Cr, and Mn contents in fermented goat and cow milks. *Food Chem.*, 2015, **188**, 234–239.
28. Cai, X., Zhang, B., Liang, Y., Zhang, J., Yan, Y., Chen, X., et al. Study on the antibacterial mechanism of copper ion- and neodymium ion-modified α-zirconium phosphate with better antibacterial activity and lower cytotoxicity. *Colloids Surfaces B*, 2015, **132**, 281–289.
29. Oviedo, M. D. C., Márquez, D. S., and Alonso, J. M. Q. Toxic effects of metals on microbial activity in the activated sludge process. *Chem. Biochem. Eng. Q.*, 2002, **16**, 139–144.
30. Huang, J., Yuan, F., Zeng, G., Li, X., Gu, Y., Shi, L., et al. Influence of pH on heavy metal speciation and removal from wastewater using micellar enhanced ultrafiltration. *Chemosphere*, 2016, **173**, 199–206.
31. Ong, S. A., Toorisaka, E., Hirata, M., and Hano, T. Adsorption and toxicity of heavy metals on activated sludge. *ScienceAsia*, 2010, **36**, 204–209.
32. Hammaini, A., González, F., Ballester, A., Blázquez, M. L., and Muñoz, J. A. Biosorption of heavy metals by

activated sludge and their desorption characteristics. *J. Environ. Manage.*, 2007, **84**, 419–426.

33. Montgomery, D. C. and Runger, G. C. *Applied Statistics and Probability for Engineers*. John Wiley & Sons, New York, 2003.
34. Özbelge, T. A., Özbelge, H. O., and Altinten, P. Effect of acclimatization of microorganisms to heavy metals on the performance of activated sludge process. *J. Hazard. Mater.*, 2007, **142**, 332–339.
35. You, S. J., Tsai, Y. P., and Huang, R. Y. Effect of heavy metals on nitrification performance in different activated sludge processes. *J. Hazard. Mater.*, 2009, **165**, 987–994.

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.