Occurence of Metals in Total Suspended Solids in Urban Waters Determined by Sequential Extraction

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Summary

The binding of metals to total suspended solids (TSS) and their speciation in urban wastewater drastically influences the efficiency of capturing metals in sewage sludge in the framework of wastewater treatment plant technology. In this article, a modified sequential extraction procedure of the Bureau Communautaire de reference (BCR) was applied to TSS from urban wastewater and digested sludge samples. Samples were collected from combined sewer system and the Central Wastewater Treatment Plant in Ostrava, Czech Republic. The collection of wastewater samples and digested sludge was performed April to June 2013. Altogether, 42 samples of urban wastewater and 3 samples of digested sludge were obtained. The sequential extraction of TSS has proven that the highest proportions of As, Cr, Cu, Ni and Fe are associated with the residual fraction (61-75%). Zn and Mn are bound to the reducible fraction (64-65%). Finally, Pb and Cd are bound predominantly to the oxidizable fraction (56%). The results show that general trend proportions of metals from TSS in the oxidizable fraction is Cd ~ Pb > Cu > Zn > Fe > Ni > Cr > As > Mn. The distribution of metals between fractions was highly variable in digested sludge. The smallest amounts of all metals in digested sludge are associated with the exchangeable fraction (Ni 5.8%; other metals < 3.7%). Cadmium, Zn and Mn are predominantly bound within the reducible fraction (68%, 37% and 35%). In the case of the oxidizable fraction, the contents of all metals are relatively low (max 20.3% of Fe). Except Cd, the predominant portions of all metals in digested sludge are bound to residual fraction (45.8-99.7%). The comparison of distribution metals in the individual fractions from TSS and digested sludge shows that the portions of Cd, Cu, Cr, Mn, Pb, Zn and Fe are significantly different. The results indicated that Cu, Cd, Pb, Zn and Mn in digested sludge are bound in silicates well as to the phosphates.

Keywords: digested sludge, metals, sequential extraction, total suspended solids, urban wastewater

Introduction

The manner in which metals are bound to the TSS in urban wastewater significantly influences the efficiency of capturing metals in the framework of wastewater treatment plant technology. The binding of metals in TSS and digested sludge in different fractions has been determined by sequential extraction procedure. Presently, the sequential extraction procedure is considered to be the best available method for obtaining information on the origin, manner of occurrence, mobility, eco-toxicity, and bioavailability of metals [1, 2, 3, 4]. The principle of sequential extraction procedure is the application of progressively stronger extraction agents to the same sample, with decreasing mobility of the metals from each following fraction. The result of sequential extraction is concentration of metals: in the soluble and exchangeable form and bound to carbonates (exchangeable fraction), bound to Fe-Mn oxides (reducible fraction), bound to organic matter and sulphides (oxidizable fraction), bound in the crystal structure of minerals, primarily to silicates (residual fraction). Chen et al. [5] and Liu and Sun [6] divided chemical fractions of metals based on their eco-toxicity and bioavailability into three classes: direct effect fraction (exchangeable and reducible fraction), potential effect fraction (oxidizable fraction), and stable fraction (residual fraction).

Currently, the Tessier procedure and BCR procedure (Community Bureau of Reference) are amongst the most widely used [7, 8]. The main difference between them is in the first fraction of the procedure. Instead of evaluating exchangeable and carbonate bound separately, the BCR procedure connects both only to the first fraction (7, 9, 10]. The disadvantage of sequential extraction is that it is the very time consuming [11, 12].

The aim of this article was to study the bindings of metals in total suspended solids from urban wastewater, and their changes during the wastewater treatment process by comparing with bindings of metals in digested sludge.

Materials and methods

Study area and materials

As the third largest town in the Czech Republic, Ostrava has an area of 214.2 km^2 (Figure 1). Currently, Ostrava has approximately 294,300 inhabitants with an average population density of 1500 inhabitants/km^2. It differs from other towns in having a high concentration of chemical and heavy industries. In Ostrava, the combined sewer system carries wastewater from both inhabitants and industry. Overall, 290,300 inhabitants are connected to the sewer system. Approximately 32 million m^3 of wastewater flows through the combined sewer system to the Central Wastewater Treatment Plant (CWWTP) annually. The Central Wastewater Treatment Plant treats 98.7% of urban wastewater from Ostrava. The treatment technology is based on the mechanical-biological treatment of wastewater using principle of low-load activation with nitrification and pre-denitrification. Treated wastewater is discharged to the Cerny potok stream that joints the Odra River.

In the town of Ostrava, 14 sampling points of wastewater were selected. The collection of samples was performed from the combined sewer system from April to June 2013. The samples were taken once a month for 24 hours using a portable sampling device (SIGMA 900 autosampler). Figure 1 illustrates location of study area and sampling points with corresponding drainage areas. Furthermore, 3 samples of digested sludge were taken from CWWTP during the sampling periods of wastewater. The samples of digested sludge were taken for identification changes in the bindings of metals during the wastewater treatment process.

Sequential extraction

The purpose of sequential extraction is to define the speciation of individual metals in TSS. Using sequential extractions, Tessier et al. [13] categorised metals as exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, or residual. In our case we used the modified sequential extraction procedure of the Bureau Communautaire de reference (BCR), as described by Pueyo et al. [10] and Mossop and Davidson [14]. The first step includes exchangeable and weak acid soluble fraction (leaching agent = acetic acid); the second step includes reducible fraction (leaching agent = hydroxylammonium chloride); the third step includes oxidizable fraction (leaching agent = hydrogen peroxide); and residue from the third step is residual fraction (extraction with Aqua Regia). For the analysis, a 10-g sample of TSS was prepared. The resultant solutions were subsequently used to determine the individual metals.

The concentration of metals in different fractions were determined according to "ISO 15587-2 Water quality – Digestion for the determination of selected elements in water – Part 2: Nitric acid digestion" and "ISO 8288 Water quality – Determination of cobalt, nickel, copper, zinc, cadmium and lead – Flame atomic absorption".

Statistical methods

The exploratory data analysis (EDA) and the statistical analysis for descriptive statistics were performed using Statgraphics Plus 5.0 software. In the case of a non-normally (asymmetric) distributed data set, a Box-Cox transformation of the data set was performed.

Results and discussion

The proportions of metals from TSS and digested sludge estimated by sequential extraction procedure are shown in Figure 2a and 2b. The results are represented as mean percentages of their total concentrations of all samples.

As can be seen, the distribution of metals between fractions from TSS varied widely (Fig. 2a). The smallest amount of metals was associated with the exchangeable fraction. Only less than 6% of all metals were found to be present in this fraction. The predominant portions of Zn and Mn (64-65%) were in TSS bound to Fe-Mn oxides. This indicates the high bioavailability and potential eco-toxicity of those metals.

The bonds of metals to organic components are, from the point of view of WWTP technology, the most significant. The possibility of releasing metals over the course of decomposing the organic component during the process of anaerobic digestion or aerobic processes exists. When organic matter decomposes, some researchers have claimed, the metals previously bound to organic matter will be remobilised into the environment; others have predicted that such metals will be further immobilised due to the formation of less soluble complexes with strong, humified material and incorporated into crystal structures of the residual phase [15].

In our study, the highest contents of Pb and Cd in TSS (approximately 56%) were principally associated with the oxidizable fraction (organic matter/sulphides). In addition, approximately 23 29% of Cu and Zn and 16-19% of Cr, Ni and Fe are bound to that fraction. The metals bound to the organic component should be largely excreted during metabolic processes. The results show that general trend propor-

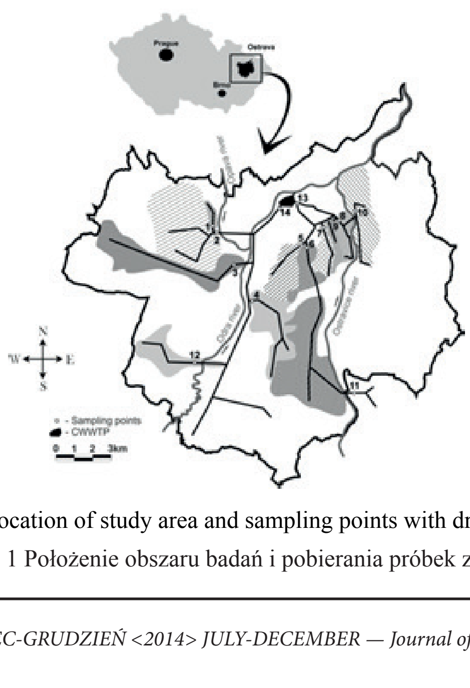

Fig. 1 Location of study area and sampling points with drainage areas

Rys. 1 Położenie obszaru badań i pobierania próbek ze zlewni

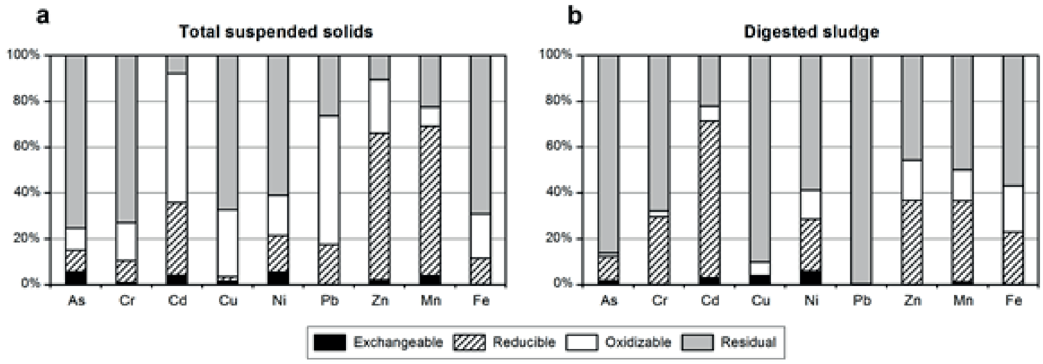

Fig. 2 Distribution of fractions for metals from TSS in urban wastewater (a) and digested sludge (b)

Rys. 2 Rozkład frakcji metali z TSS w miejskich ściekach (a) i osadach przefermentowanych (b)

tions of metals from TSS in the oxidizable fraction is Cd ~ Pb > Cu > Zn > Fe > Ni > Cr > As > Mn. In TSS, Cr and As (73-75%) and Fe, Cu and Ni (61-69%) were predominantly distributed in the residual fraction, thus reducing their mobility and toxicity potential.

As shown in Fig. 2b, the distribution of metals between fractions was highly variable in digested sludge. Exchangeable fraction was found to contain much less metals in comparison to other fractions (Ni 5.8%; other metals < 3.7%). Cadmium, Zn and Mn were predominant metals in reducible fraction (approximately 68%, 37% and 35%). The behavior of these metals in sewage sludge from WWTPs was in accordance with published results [16, 17, 18]. The high content of Mn associated with Fe oxides also corresponded to other studies, which have connected the behavior of Mn to a low redox potential [15, 17]. In the case of the oxidizable fraction, the contents of all metals were relatively low (max 20.3% of Fe). Except Cd, the predominant portions of all metals were in digested sludge bound to residual fraction (approximately 45.8-99.7%). This finding is in accordance with results published by Wang et al. [19] and Alonso et al. [16]. Metals bound to residual fraction show low mobility and potential eco-toxicity to the environment [5, 3].

The comparison of distribution metals in the individual fractions from TSS and digested sludge shows that the portions of As and Ni are about the same. The portions of Cd, Cu, Cr, Mn, Pb, Zn and Fe were significantly different. The results show an obvious increase of portions Fe and Cr from digested sludge in reducible fraction (11-20%). The increase of portions Fe and Cr was due to the addition of flocculating agent based on ferric sulphate and ferric chloride during the wastewater treatment process. The portion of Cu, Cd and Pb bound to organic matter (oxidizable fraction) in TSS decreased in favor of the portion bound to residual fraction in digested sludge. These results show that Cu, Cd and Pb in digested sludge are bound in silicates well as to the phosphates. The basic structure of minerals with phosphorous is tetrahedral group $[PO_4]^{3-}$, which is analogous to the spatial structure formed by tetrahedral group of silicates $[SiO_4]^{4-}$. It is apparent, that for the structure of phosphates and silicates, can be found exactly the same crystal structures. This is also reflected in their isomorphic substitution. Raclavská et al. [20] state that major phase in sewage sludge from CWWTP in Ostrava is hydrated ferrous phosphate - vivianite ($Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$). Furthermore the significant changes of portion Zn and Mn between the fractions from TSS and digested sludge were identified during the wastewater treatment process. Zn and Mn were in TSS primarily associated with the reducible fraction (Zn 64%, Mn 65%), but in sewage sludge they were primarily associated with residual fraction (Zn 46%, Mn 50%). Even in this case, the binding of Zn and Mn in residual fraction apparently influenced by the occurrence of phosphates.

Conclusions

The results of the present study indicate that in total suspended solids from urban wastewater were predominantly bound: As, Cr, Cu, Ni and Fe in residual fraction (61-75%), Cd and Pb in oxidizable fraction (56%), Zn and Mn in reducible fraction (64-65¬%). The distribution of As, Cr, Ni and Fe between fractions in digested sludge was comparable with distribution in TSS. Concerning all metals, except Cd, they were in digested sludge mainly in the residual bound fraction (45.8-99.7%). The results showed that Cu, Cd, Pb, Zn and Mn in residual fraction from digested sludge are not only incorporated into the silicates but apparently also into the phosphates.

Acknowledgments

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Literatura - References

1. *Ma, L. Q. and Rao G. N.. Chemical Fractionation of Cadmium, Copper, Nickel, and Zinc in Contaminated Soils. Journal of Environment Quality. 1997, vol. 26, no 1, p. 259-264. DOI: 10.2134/jeq1997.00472425002600010036x*
2. *Nemati, K., Nor Kartini Abu Bakar, Mhd. Radzi Abas, Elham Sobhanzadeh. Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. Journal of Hazardous Materials. 2011, vol. 192, issue 1, p. 402-410. DOI: 10.1016/j.jhazmat.2011.05.039*
3. *Leleyter, L., Rousseau C., Biree L., Baraud F. Comparison of EDTA, HCl and sequential extraction procedures, for selected metals (Cu, Mn, Pb, Zn), in soils, riverine and marine sediments. Journal of Geochemical Exploration. 2012, vol. 116-117, p. 51-59. DOI: 10.1016/j.gexplo.2012.03.006*
4. *Dong, B., Liu X., Dai L., Dai X.. Changes of heavy metal speciation during high-solid anaerobic digestion of sewage sludge. Bioresource Technology. 2013, vol. 131, p. 152-158. DOI: 10.1016/j.biortech.2012.12.112*
5. *Chen, M., Li X., Yang Q., Zeng G., Zhang Y., Liao D., Liu J., Hu J., Guo L. Total concentrations and speciation of heavy metals in municipal sludge from Changsha, Zhuzhou and Xiangtan in middle-south region of China. Journal of Hazardous Materials. 2008, vol. 160, issue 2-3, p. 324-329. DOI: 10.1016/j.jhazmat.2008.03.036*
6. *Liu, J., Sun S. Total concentrations and different fractions of heavy metals in sewage sludge from Guangzhou, China. Transactions of Nonferrous Metals Society of China. 2013, vol. 23, issue 8, p. 2397-2407. DOI: 10.1016/S1003-6326(13)62747-8*
7. *Ure, A. M., Quevauviller Ph., Muntau H., Griepink B. Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of Extraction Techniques Undertaken Under the Auspices of the BCR of the Commission of the European Communities. International Journal of Environmental Analytical Chemistry. 1993, vol. 51, issue 1-4, p. 135-151. DOI: 10.1080/03067319308027619*
8. *Abollino, O., Malandrino M., Giacomino A., Mentasti E. The role of chemometrics in single and sequential extraction assays: A review: Part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition. Analytica Chimica Acta. 2011, vol. 688, issue 2, p. 104-121. DOI: 10.1016/j.aca.2010.12.020*
9. *Bacon J. R., Davidson Ch. M. Is there a future for sequential chemical extraction? The Analyst. 2008, vol. 133, issue 1, p. 25-46. DOI: 10.1039/B711896A*
10. *Pueyo M., J. Mateu, Rigol A., Vidal M., López-Sánchez J. F., Rauret A. G. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environmental Pollution. 2008, vol. 152, issue 2, p. 330-341. DOI: 10.1016/j.envpol.2007.06.020*
11. *Jamali M. K., Tasneem G., Kazi, H I. Afridi, Arain M. B., Jalbani N., Memon A. R.. Speciation of heavy metals in untreated domestic wastewater sludge by time saving BCR sequential extraction method. Journal of Environmental Science and Health, Part A. 2007, vol. 42, issue 5, p. 649-659. DOI: 10.1080/10934520701244433*
12. *Sutherland, R. A. BCR®-701: A review of 10-years of sequential extraction analyses. Analytica Chimica Acta. 2010, vol. 680, issue 1-2, p. 10-20. DOI: 10.1016/j.aca.2010.09.016*
13. *Tessier A., Campbell P. G. C., Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry. 1979, vol. 51, issue 7, p. 844-851. DOI: 10.1021/ac50043a017*
14. *Mossop K. F. Davidson Ch. M. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Analytica Chimica Acta. 2003, vol. 478, issue 1, p. 111-118. DOI: 10.1016/S0003-2670(02)01485-X*

15. *Staelens, N., Parkpian P., Polprasert Ch. Assessment of metal speciation evolution in sewage sludge dewatered in vertical flow reed beds using a sequential extraction scheme. Chemical Speciation and Bioavailability. 2000, vol. 12, issue 3, p. 97-107. DOI: 10.3184/095422900782775517*
16. *Alonso, E., I. Aparicio, J.l. Santos, P. Villar, A. Santos. Sequential extraction of metals from mixed and digested sludge from aerobic WWTPs sited in the south of Spain. Waste Management. 2009, vol. 29, issue 1, p. 418-424. DOI: 10.1016/j.wasman.2008.01.009*
17. *Lasheen M.R., Ammar N. S. Assessment of metals speciation in sewage sludge and stabilized sludge from different Wastewater Treatment Plants, Greater Cairo, Egypt. Journal of Hazardous Materials. 2009, vol. 164, issue 2-3, p. 740-749. DOI: 10.1016/j.jhazmat.2008.08.068*
18. *Zhu N., Qiang-Li X., Guo, Hui-Zhang, Yu-Deng. Sequential extraction of anaerobic digestate sludge for the determination of partitioning of heavy metals. Ecotoxicology and Environmental Safety. 2014, vol. 102, p. 18-24. DOI: 10.1016/j.ecoenv.2013.12.033*
19. *Wang, C., Li X., Ma H., Qian J., Zhai J. Distribution of extractable fractions of heavy metals in sludge during the wastewater treatment process. Journal of Hazardous Materials. 2006, vol. 137, issue 3, p. 1277-1283. DOI: 10.1016/j.jhazmat.2006.04.026*
20. *Raclavská, H., Škrobánková H., Doškářová Š. Potential reduction in nutrient leachability from sewage sludge applied in land reclamation. Journal of the Polish Mineral Engineering Society. 2011, vol. 28, no. 2, p. 47-61*

Występowanie metali w całkowitej ilości cząstek zawieszonych w wodach miejskich określona za pomocą ekstrakcji sekwencyjnej

Wiązanie metali we frakcji ciał stałych zawieszonych w wodzie (TSS – Total Suspended Solids) oraz ich specjacji w miejskich ściekach drastycznie wpływa na efektywność wychwytywania metali w osadach ściekowych w ramach technologii oczyszczalni ścieków. W tym artykule, zmodyfikowana procedura ekstrakcji sekwencyjnej biura Bureau Communautaire de Reference (BCR) została zastosowana do zawiesiny ciał stałych ze ścieków komunalnych i przefermentowanych próbek osadu. Próbki pobrano z połączonego systemu kanalizacji i Centralnej Oczyszczalni Ścieków w Ostrawie, Czechy. Pobieranie próbek ścieków i przefermentowanego osadu przeprowadzano od kwietnia do czerwca 2013 roku. Łącznie uzyskano 42 próbki ścieków komunalnych oraz 3 próbki przefermentowanego osadu. Sekwencyjna ekstrakcja TSS dowiodła, że największy odsetek As, Cr, Cu, Ni i Fe jest związany we frakcji pozostałości (61-75%). Zn i Mn są związane we frakcji redukowalnej (64-65%). Wreszcie, Pb i Cd są związane głównie we frakcji utlenialnej (56%). Wyniki pokazują, że ogólny trendu proporcji metali pochodzących z TSS we frakcji utlenialnej przedstawia się następująco: Cd ~ Pb> Cu> Zn> Fe> Ni> Cr> W> Mn. Rozkład metali między frakcjami różnił się znacząco w przefermentowanym osadzie. Najmniejsze ilości wszystkich metali w przefermentowanym osadzie związane są z frakcją wymienną (Ni 5,8%; inne metale <3,7%). Kadm, Zn i Mn są głównie związane we frakcji redukowalnej (68%, 37% i 35%). W przypadku frakcji utlenialnej, zawartość wszystkich metali jest stosunkowo niska (maksymalnie 20,3% Fe). Z wyjątkiem Cd, dominujące porcje wszystkich metali w przefermentowanego osadu są związane z frakcji pozostałości (45.8-99.7%). Porównanie dystrybucji metali w poszczególnych frakcjach z TSS i przefermentowanego osadu wskazuje, że części Cd, Cu, Cr, Mn, Pb, Zn i Fe są znacząco różne. Wyniki wskazują, że Cu, Cd, Pb, Zn i Mn z przefermentowanego osadu związane są z krzemianami a także fosforanami.

Słowa kluczowe: osad przefermentowany, metale, wydobycie sekwencyjne, całkowita zawartość zawiesin, ścieki miejskie