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HEAVY METALS IN SLUDGE PRODUCED DURING PRODUCTION OF DRINKING WATER FROM SURFACE SOURCES

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Abstract: Samples of water and sludge were analysed from two different water treatment plants which produce drinking water from surface sources taken in two territories with different geology. In one territory, polymetalic deposits of Cu, Pb, Zn are located (primary rocks – Kulm). The second territory is located in the flysch range with no presence of heavy metals. Concentration of heavy metals (Cu, Cr, Ni, Pb, Cd, As, Hg, B) in water was below detection limits. Analyses of the sludge produced during coagulation filtering treatment have proved presence of heavy metals in the sludge. Following metals in the sludge: As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn. Most heavy metals are of anthropogenic origin. It is only Zn and As which originate in the geology of the catchment area. The heavy metal concentrations were low, the exception being As which was 30.6 mg/kg in dry mass of sludge for the Podhradí water treatment plant. This value is three times higher than the limit permitted for the sludge. Regular monitoring of heavy metal concentration in the water treatment sludge will improve assessment of presence of the heavy metals in the treated water.

Keywords: water treatment sludge, heavy metals, treatment of surface water

1. INTRODUCTION

Water treatment sludge is produced during production of drinking water. Physical properties and chemical composition of the water treatment sludge depends on quality of the treated water, treatment methods and on the quantity and quality of chemicals dosed during the water treatment process.

Drinking water is produced from sources which comply with strict requirements applicable to the quality of treated water. In spite of this, some heavy metals are present there in addition to organic and suspended substances (Salem et al., 2000). During the water treatment, most of such substances appear in the water treatment sludge. The water treatment sludge contains the used coagulant which is typically in a form of aluminium hydroxide or iron hydroxide. The sludge also contains other organic or inorganic substances removed from the treated water such as clay, plant residues or microorganisms. It contains also heavy metals such as Cd, Cu, Cr, Ni, Pb or other elements (Kriš et al., 2013).

This paper discusses and evaluates presence of the heavy metals in sludge produced in two water treatment plants which treat the surface water. The source of water for each water treatment plant is different: these are the Ostravice River and Moravice River, both in the Czech Republic. The rivers are located in territories with very different geology.

The purpose was to find out how much the geology of the river catchment area influences the presence of heavy metals in water. Another goal was to check whether this might indicate presence of heavy metals in raw water. This should be also checked for cases when the heavy metals were present in the water below limits of detection which can be determined by standard analytical methods. The purpose was also to decide whether the heavy metal in the coagulant (this means, in aluminium sulphate) could influence the concentration of heavy metals in the water treatment sludge. The concentration of heavy metals in the water treatment sludge may provide information whether such sludge can be placed on allotments or agricultural land.

The research focused on the water treatment sludge and surface waters used for production of drinking water. One water treatment plant takes water from the Ostravice River, while the other plant uses the water from the Moravice River (both rivers are located in the Moravian-Silesian Region in the Czech Republic).

2. MATERIALS AND METHODS

From the point of view of geology the Moravian-Silesian Region is located in the eastern part of the Bohemian Massif. To the east, there is a boundary region of the Western Carpathians Mountains. This part of the Bohemian Massif is formed by Silesicum (crystalline forms of the Hrubý Jeseník Mountains), Žulová Massif (Variscian solid mass) and by Moravian-Silesian primary rocks. Prevailing types of rock are gneiss, mica slate and culm shalestone. In the Kulm rock of the Nízký Jeseník Mountains there are many deposits of ore. There are also deposits of polymetallic ore (Cu, Pb, Zn, Ag) with an increased contents of As (Mísař et al., 1983). Water from this territory flows into the Moravice River.

The boundary part of the Western Carpathian Mountains is formed by a range of flysch. Prevailing materials are claystone, sandstone and conglomerates from the Mesolithic and Tertiary Eras (Holubec, 1990). This area is located in the Beskydy Mountains and water from that territory flows into the Ostravice River.

The catchment area of the Moravice River is 566 km^2. About 50 % of the territory is covered with woods. An average flow rate in the place of water takeoff is 6.46 m^3/s, Q_{355} being 0.36 m^3/s.

Water from the Moravice River is collected in the Kružberk Dam. Then, it is treated in the water treatment plant in Podhradí. The population is 28,000 and no major industries are located there. The catchment area of the Ostravice River is 146 km^2. About 86 % of the territory is covered with woods.

The average flow is 3.25 m^3/s, Q_{355} being 0.28 m^3/s. The population is 860 and no local sources of pollution are located there.

Not only the raw water and treated water, but also the water treatment sludge from the both water treatment plants were analysed. This was the sludge produced from washing water from gravity rapid sand filters. The washing water settled and thickened in settling ponds. Samples taken in the settling ponds were analysed and checked for concentration of heavy metals in the water treatment sludge. One filtering cycle was chosen in order to monitor the metals in sludge produced in the both water treatment plants. Table 1 gives basic data from the washing cycle.

The thickened sludge from one washing cycle in the water treatment plant was checked for presence of metals using atomic adsorption spectroscopy after mineralisation. The reason for this monitoring was the fact suggested by many studies: most metals is cumulated during the water treatment on sludge particles (Zhou & Haynes, 2011). Coagulation results in fast formation of hydrated aluminium oxides. The capacity of the freshly precipitated hydrated aluminium oxides or hydroxides is so large that it is possible to precipitate and sorb metal ions from the aqueous environment (Elliott et al., 1990). It was also found out (Kinniburgh et al., 1976) that heavy metals are adsorbed in gels of hydrated Al and Fe metals, these being, in fact, the same compounds as those which are produced when using coagulation for water treatment.

Heavy metal cations are absorbed on the Al and Fe gels very intensively even if the environment is slightly acid. Where pH was almost neutral, the adsorption was close to 100 %. In addition to standard analytical methods which include the atomic adsorption spectroscopy, an x-ray fluorescent analysis was used to detect presence of metals and other elements in the water treatment sludge.

Before the X-ray fluorescent analysis, the sample was dried up at 105^{o}C. Once a constant weight was reached, majority elements were determined. 4 g of the sample were mixed with 0.9 g of binding agent (Hoechs wax C for XRF analysis). Using a manual hydraulic press (Maasen 54MP250) and 100 kN pressure, a pellet was created (dia. 32 mm). Then, the pellet was introduced into a measuring cell. The sample was measured using a calibration method and a wave dispersion x-ray spectrometer Spectroscan MAK-GV.

The measurements were compliant with GBW 07309, 07101, 07310, 07311, 07312, GBW 3102. Table 1 lists the scanning parameters for the qualitative analysis. Some heavy metals are present in small quantities as undesirable impurities in coagulants. Keeping this in mind, the aluminium sulphate was also analysed for presence of heavy metals.

Table 1. Scanning parameters for the qualitative analysis in FPM software

Crystalline	Scope (mgÅ)	Step (mgÅ)	Exposure (s)	Current (mpÅ)	Voltage (kV)
LiF(200	800-3200	5	10	0,5	40
COO2	3000-5600	10	10	1	40
PET	6000-7300	15	10	2	40
KAP	7600-13000	50	10	4	40

The water treatment sludge with trace elements is regarded as a chemical waste (Aktor, 1994) which should be managed in line with legal regulations. Therefore, attention has been also paid to concentration of the heavy metals in the sludge in terms of compliance with laws of the Czech Republic. Following indicators should be monitored for wastes placed in the field: Hg, As, Cd, Cr, Ni and Pb. Following indicators should be considered in connection with the duty to inform and to provide data into the Integrated Registry of Environment Contamination: Hg, Cd, Cr, Cu, Ni, P, Pb and Zn.

3. RESULTS AND DISCUSSIONS

The quality of water taken for treatment from the both rivers is very good, the exception being minor seasonal deviations. A one-stage water treatment is sufficient for water of such quality. The produced drinking water fulfills entirely all requirements stipulated in regulations for the quality of water. Table 2 lists the basis indicators for quality of raw water and processed water. The heavy metal concentration was measured in both the raw and treated water. The results prove that the concentration of heavy metals is below the detection limit for any indicator. On one hand, this suggests that the heavy metals do not rank among risk elements in those sites. On the other hand, the standard analytical methods are not able to detect low concentration of heavy metals in water. Table 3 shows the concentration of heavy metals in the studied waters.

Table 2. Basis indicators for quality of raw water and processed water

		Water treatment plant in Podhradí		Water treatment plant in Nová Ves	
		Raw water	Processed water	Raw water	Processed water
Conductivity	mS/m	17	20	10	13
pH		7.19	7.84	7.03	8.27
Acid neutralising capacity (ANC) -4.5	mmol/l	1.0	1.0	0.7	0.8
Base neutralising capacity (BNC) -8.3		0.20	0.08	0.18	0.03
Absorbance		0.093	0.037	0.039	<0.010
COD-Mn	mg/l	2.9	1.5	2.2	0.9
Calcium	mg/l	18.04	23.25	12.02	18.44
Magnesium	mg/l	5.10	5.34	2.92	2.43
Iron	mg/l	<0.10	<0.10	<0.10	<0.10
Manganese	mg/l	<0.025	<0.025	<0.025	<0.025
Aluminium	mg/l	<0.02	<0.03	<0.02	<0.05
Chlorides	mg/l	11.3	11.5	<4.0	<4.0
Sulphates	mg/l	20.4	24.8	14.4	18.8
Fluorides	mg/l	0.10	0.10	0.07	0.07
Nitrates	mg/l	6.1	5.7	3.1	2.8
Nitrites	mg/l	<0.01	<0.01	<0.01	<0.01
Amonnia ions	mg/l	<0.05	<0.05	<0.05	<0.05

Table 3. Metals in raw water and processed water from the both water treatment plants

		Water treatment plant in Podhradí		Water treatment plant in Nová Ves	
		Raw water	Processed water	Raw water	Processed water
Copper	mg/l	<0.005	<0.005	<0.005	<0.005
Chromium	mg/l	<0.025	<0.025	<0.025	<0.025
Nickel	mg/l	<0.015	<0.015	<0.015	<0.015
Lead	mg/l	<0.005	<0.005	<0.005	<0.005
Cadmium	mg/l	<0.0010	<0.0010	<0.0010	<0.0010
Arsenic	mg/l	<0.0025	<0.0025	<0.0025	<0.0025
Mercury	mg/l	<0.0002	<0.0002	<0.0002	<0.0002
Borium	mg/l	<0.1	<0.1	<0.1	<0.1

The analysis of one washing cycle has proved that 99% of aluminium from the supplied aluminium sulphate is transferred into the water treatment sludge. The concentration of aluminium in the thickened sludge has indicated that the sludge thickening rate is ca. 1,600 and ca. 2,400 for the water treatment plants in Podhradí and Nová Ves, respectively. Because this is an operational measurement only, the measurement accuracy is ± 25 %. The heavy metals are trapped often much in aluminium hydroxides and sludge thickening (Ippolito; 2009, Markis et al., 2009).

The concentration of the heavy metals in the sludge is then easy to measure. Table 4 shows the concentration of heavy metals in the water treatment sludge. Table 5 shows the concentration of some elements and heavy metals in the sludge measured by means of the x-ray fluorescent analysis. Attached are also results obtained by the atomic adsorption spectroscopy.

Table 4. Concentration of heavy metals in the water treatment sludge

	Unit	Water treatment plant in Podhradí	Water treatment plant in Nová Ves
Mercury	mg/kg in dry matter	0.137	0.194
Aluminium	mg/kg in dry matter	154000	136000
Arsenic	mg/kg in dry matter	30.6	20.5
Boron	mg/kg in dry matter	7.06	19.5
Barium	mg/kg in dry matter	75.0	153
Calcium	mg/kg in dry matter	46900	35100
Cadmium	mg/kg in dry matter	0.213	0.659
Chromium	mg/kg in dry matter	10.3	23.6
Copper	mg/kg in dry matter	54.1	50.9
Iron	mg/kg in dry matter	19700	35100
Magnesium	mg/kg in dry matter	6390	6130
Manganese	mg/kg in dry matter	4730	3380
Molybdene	mg/kg in dry matter	1.36	<1.00
Nickel	mg/kg in dry matter	21.4	32.00
Phoshorus	mg/kg in dry matter	936	670
Lead	mg/kg in dry matter	30.0	41.1
Antimony	mg/kg in dry matter	<2.00	<2.00
Selenium	mg/kg in dry matter	3.11	<2.00
Zinc	mg/kg in dry matter	62.2	43.7

Table 5. Weight concentration of elements in the dry matter of the sludge determined by the x-ray fluorescence method

	Water treatment plant in Podhradí, weight %		Water treatment plant in Nová Ves, weight %	
Analyte	Value	Deviation	Value	Deviation
Na_2O	1.32	0.66	0.22	0.13
MgO	0.54	0.27	0.93	0.28
Al_2O_3	23.5	0.4	22.3	0.4
SiO_2	9.04	0.15	15.4	0.18
P_2O_5	0.22	0.01	0.15	0.01
SO_3	0.65	0.01	0.61	0.01
Cl	0.13	0.01	0.05	0.01
K_2O	0.17	0.01	0.78	0.01
CaO	9.09	0.04	6.66	0.03
TiO_2	0.07	0.01	0.21	0.01
MnO	0.84	0.01	0.56	0.01
Fe_2O_3	4.36	0.01	7.15	0.02
	mg/kg	mg/kg	mg/kg	mg/kg
Ni	31	4	39	4
Cu	27	13	23	12
Zn	229	2	113	2
As	41	1	42	1
Sr	84	9	100	9
Ba	113	26	211	28

Table 6 shows the average concentration of the heavy metals in the sludge from each water treatment plant. This indicates how much the results of the one-off monitoring of the heavy metals correspond to long-termed trends. These are average values for a six-year period.

It follows from the analysis of the aluminium sulphate which is used as a coagulant and from the checks for presence of some heavy metals that the concentration of heavy metals can, in no case, influence the concentration of heavy metals in the sludge, this being even the case of arsenic which is contained regularly in the coagulant. Results are listed in table 7.

Heavy metals in the sludge originate in the geology of the catchment areas of each river. Another source of the heavy metals is wastewater from people and deposits in air pollution. It is the air pollution which plays a key role in the territories under investigation because the nearby industrial conurbation – the Great Ostrava – is a big source of air pollution (coal power plants, steelworks) (Jančík, 2013).

Attention was paid to the concentration of heavy metals in terms of geology of the catchment area. In the catchment area of the Moravice River where the polymetallic ore deposits (Cu, Pb, Zn) are located these were only Zn and As which were found in increased concentrations. Rather much zinc gets into the water upon oxidative disintegration of sulphide ore (Pitter, 2009). This, however, does not play an important role in terms of health safety.

An element which is relevant for health is arsenic. Its concentration in the sludge ranges between 20 and 30 mg/kg dry matter. The x-ray fluorescence method has revealed even higher values. The concentration of As is three times higher than the health limit for As in the sludge. An important source of As can be disintegration of insoluble As - minerals, arsenides and sulphides (Morin & Calas, 2006). Arsenopyrit is stable, if present under the groundwater table.

If it occurs in the zone which is not saturated with water, it starts oxidising and releasing into ground water and surface water (Craw et al., 2003). This may explain higher concentration of As in the sludge produced in the water treatment plant in Podhradí. The catchment area of the Ostravice Region is located in the range of flysch. There are not any geological reasons which could explain occurrence of the heavy metals in water in that territory.

The sludge produced there contains increased concentrations of most elements under investigation, the exception being Zn and As. Those heavy metals are of anthropogenic origin.

The mercury is the most abundant heavy metal which occurred in health relevant concentrations. The mercury is easy to trap in the sludge (Hovsepyan & Bonzongo, 2009). The mercury concentration is lower than limits set forth in health regulations.

Table 6. Concentration of heavy metals in aluminium sulphate

	Unit	Water treatment plant in Podhradí	Water treatment plant in Nová Ves
Arsenic	mg/kg in dry matter	29.8	11.3
Cadmium	mg/kg in dry matter	0,352	0.387
Chromium	mg/kg in dry matter	12.2	19.6
Mercury	mg/kg in dry matter	0.121	0.265
Nickel	mg/kg in dry matter	28.1	19.8
Lead	mg/kg in dry matter	29.1	29

Table 7. Concentration of heavy metals in aluminium sulphate

	mg/kg of dry matter of $Al_2(SO_4)_3.18H_2O$	mg/kg Al
Arsenic	<1.3	13.5
Iron	40.2	419
Cadmium	<0.15	1.6
Chromium	1.88	19.6
Nickel	<0.7	7.3
Lead	<1.4	14.6
Antimony	<1.1	11.5
Selenium	<1.4	14.6
Mercury	<0.02	0.2
Aluminium	96000	

As the mercury concentration is higher for Nová Ves, this might suggest that the origin of the mercury is rain which passes through air pollution. The catchment area of the Ostravice River is located 30 km only from air pollution sources.

Boron has been also found in the water treatment sludge: 19.5 mg/kg dry matter for Nová Ves and 7.6 mg/kg dry matter for Podhradí.

Typically, no checks for boron are performed in water analyses. Boron is regarded as a micronutrient and its toxicity is very low (Pitter, 2009). Barium is not analysed regularly in water either and no standards exist for barium concentration in drinking water.

The barium concentration was rather high: 153 mg/kg dry matter for Nová Ves and 75 mg/kg dry matter in Podhradí.

Cadmium is the second most toxic metal (mercury being the most toxic one). Cadmium concentration in the sludge is very low. The fact that the cadmium concentration in Nová Ves is three times higher than that in Podhradí proves that the primary source of cadmium is air pollution. Cr and Cu rank among essential microelements. Their concentration in the sludge is rather low and play not role in terms of health. The same situation is with Ni.

The concentration of molybdenum is negligible and is not limited for the drinking water.

Lead is toxic and regarded as very harmful. The concentration of lead in the sludge ranged between 40 and 30 mg/kg dry matter, this posing, however, no risk for health. The bond between lead and sludge is strong (Putra & Tanaka, 2011; Chu, 1999).

The concentration of antimony and selenium is minimum and it is not necessary to pay attention to them.

A possibility to spread the water treatment sludge in the landscape or on agricultural land depends on laws and regulations. Legislative of the Czech Republic sets forth limits for concentration of Hg, As, Cd, Cr, Ni and Pb. All metals except for As were below the limits for the water treatment sludge which was tested and analysed. In case of As the limit for placing the sludge on the land is 10 mg/kg. The concentration in the treatment sludge was, however, 20.5 mg/kg for Nová Ves and 30.6 mg/kg for Podhradí. This means, that the water treatment sludge should be placed at protected waste landfills.

4. CONCLUSIONS

It follows from the analyses that most heavy metals which occur in the sludge are of the anthropogenic origin. In the catchment area where polymetallic deposits (Cu, Pb, Zn) are located, it is only Zn which is released into aqueous environment. Cu and As are released partly only and are also bound in the rock there. Other metals are present in increased quantities in the catchment areas without any geological reason for their occurrence.

The analyses of heavy metals in the sludge can help reveal heavy metals in the water processed by means of coagulation. The heavy metals are mainly removed from the processed water along with the coagulants. The heavy metals should be monitored if standard analyses of water suggest that the heavy metals in the water are below detection limits. It should be, however, kept in mind that the concentration of heavy metals in water measured on the basis of the sludge analysis is approximate only because few quantity data are still available about adsorption and precipitation of heavy metals.

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