The main microelements and phosphorus content of sediments formed in a drinking water supply system

Marina Valentukeviciene[a], Ramune Zurauskiene[a] and Jonas Satkunas[b]

[a] Department of Water Management Faculty of Environmental Engineering, Vilnius Gediminas Technical University, Sauletekio al. 11, Vilnius, Lithuania, LT 10223; marina.valentukeviciene@vgtu.lt, ramune.zurauskiene@vgtu.lt
[b] Department of Environmental Research, Vilnius University, Lithuania, LT 10223; jonas.satkunas@lgt.lt

Abstract. Groundwater is the only source for drinking water supply in Lithuania. Twenty water intakes exploiting Quaternary aquifers are operating in Vilnius City. The main aim of this study was to characterize the heavy metal content of internal pipeline sediments in the water supply network. It also provides a new insight into the accumulation of phosphorus and its variation in pipeline sediments in the study area. The results of this research reflect the level of heavy metals that accumulated during the water supply process. The main microelements detected were lead, nickel, zinc and copper. The research results will be useful for conducting preliminary evaluations of possible microelement accumulation in other similar water supply systems. The evaluation of water supply sediments is considered as one of the most important activities associated with a water safety approach. The results of this research indicate the dependence between phosphorus accumulation and Pb, Cr, Zn, Ni and Cu quantities in the internal sediments of water supply pipelines.

Key words: groundwater, water supply, microelements, pipeline sediments, pipe materials.

INTRODUCTION

Groundwater in Lithuania is the only source for drinking water supply. In Vilnius City there are 20 operating water intakes exploiting Quaternary aquifers. The interaction of different metals in drinking water systems can cause adverse effects on water quality, such as changes in water colour, taste and smell, pipeline fouling and staining on surfaces, thus leading to complaints by water consumers (Lehtola et al. 2004; Cerrato et al. 2006; Agatemor & Okolo 2007). The European Council (EC 1998) has set limiting chemical parameter values and the World Health Organization (WHO 2004) provides guideline values for various heavy metals in drinking water (Table 1). The National Hygiene Norm for the Drinking Water Quality of Lithuania (LMH 2003) has established the same limits as those in the EC Directive (EC 1998).

Chromium, iron, manganese, nickel, copper, zinc and molybdenum are essential elements for human health and have recommended daily dietary intakes but their excessive amounts can be harmful. However, cadmium, lead, arsenic and mercury do not play any significant role in human physiology and are also highly toxic. It is stated by medical research that Cr sources from water supply can have a toxic impact on human health (Paustenbach et al. 2003). The WHO has established recommended daily allowances, a tolerable daily intake

Table 1. Guideline values for various heavy metals in drinking water

Element	EC (1998) chemical parameter values (µg/L)	WHO (2004) guideline values (µg/L)
Arsenic	10	10*
Cadmium	5	3
Chromium	50	50*
Copper	2000	2000
Lead	10	10
Manganese	50**	400
Mercury	1	1
Molybdenum	–	70
Nickel	20	20*
Zinc	–	3000

* Provisional guideline values; ** indicator parameter value; – not mentioned.

and a tolerable weekly intake for the elements listed below (Table 2).

According to WHO (2003), some nutrients in drinking water are known or suspected to be essential for human health, e.g. phosphorus as PO_4^{3-} and molybdenum as MoO_4^{2-} that function physiologically as anions or in anionic groupings in combined form affecting bone and membrane structure. Some metals, e.g. ferrous iron (Fe^{2+}), copper (Cu^{2+}), zinc (Zn^{2+}) and

Table 2. Recommended daily allowances (RDA), tolerable daily intake (TDI) and tolerable weekly intake (TWI) of the main microelements

Element	RDA	TDI or TWI
Arsenic	–	Equivalent to 15 µg/kg bw weekly
Cadmium	–	7 µg/kg bw TWI
Chromium	50–200 µg/d (USA)	0.15 mg/kg bw TDI (trivalent chromium)
Copper	2–4 mg/d	–
Lead	–	Equivalent to 50 µg/kg bw TWI
Manganese	2–5 mg/d	–
Mercury	–	Equivalent to 5 µg/kg bw TWI
Molybdenum	75 and 250 mg/d (USA)	–
Nickel	–	5 µg/kg of bw TDI
Zinc	8–11 mg	15 mg (60 kg person) TDI

bw, body weight; – not mentioned.

manganese (Mn^{2+}), are believed to function in their simple cationic forms. Metabolic catalysis is related to Zn, Cu, Se, Mg, Mn, Mo, and Cr is related to hormone functions (WHO 2003).

It has been stated by Zhang et al. (2009) that Cu, Pb and Zn levels tend to be higher in domestic water supplied via plastic pipelines than in water delivered via copper pipelines.

Dissolved manganese, Mn(II), and iron, Fe(II), also occur naturally in groundwater sources due to electron exchange reactions (anaerobic respiration) that take place in the presence of metal-reducing bacteria under anoxic conditions at the water/sediment interface (Agatemor & Okolo 2007). Manganese compounds from a water treatment plant can accumulate in distribution pipelines where Mn is oxidized to its insoluble form and these oxidized solids become deposited on the pipe surfaces (Valentukevičienė et al. 2013). Filtration has been the conventional way of separating Mn and Fe compounds from groundwater in Lithuanian water treatment plants. This technique was adopted at the largest water treatment plant at Antaviliai (Diliūnas et al. 2006; Valentukevičienė et al. 2013). Relatively high concentrations of Mn were detected in the water supply system of Vilnius (capital of Lithuania) and have continued to cause occasional severe 'black water' issues for water consumers (Valentukevičienė et al. 2011, 2013; Valentukevičienė & Ignatavičius 2012). 'Black water' formation was more often noticeable where ductile iron or steel pipes were used for water supply system mains and internal plumbing while few cases were reported in areas with plastic pipes. To eliminate these problems, preference

has lately been given to plastic (PVC) pipes for new or renovated water supplies. However, the dominant pipeline material is still cast iron which constitutes approximately 56.6% of all pipelines material, i.e. using two times less steel – 22.5% and plastic – 20.7% in all Lithuanian water supply systems (Valentukevičienė et al. 2011).

The other metals have not been investigated previously for Lithuanian water supplies. Also, the existing drinking water monitoring results obtained by standard methods were below detection limits, with the exception of mercury. In one specific section of the Vilnius water networks the concentration of mercury was eight times lower than the EC and WHO limit values. Phosphorus compound concentrations are not regulated by the EC Directive and had not been measured in drinking water.

Our working hypothesis is based on the suggestion that the accumulation of some microelements in sediments in water supply pipelines depends on the phosphorus content in the solid phase. Therefore, the aim of this study was to investigate the effect of pipe materials, such as cast iron and steel, on microelement accumulation in the water supply system by analysing (1) the content of phosphorus of internal sediments in different pipes and (2) the quantities of heavy metals in these sediments. Quantitative results were obtained for Cr, Ni, Cu, Zn, Mo, Cd, Pb, As and Hg. These were examined in relation to the phosphorus content of the sediments in the water supply pipelines.

MATERIALS AND METHODS

All selected sampling locations were on pathways from different groundwater sources at Paneriai and the water treatment plant at the Antaviliai Reservoir (Vilnius, Lithuania). The water supply can use an admixture of both of these sources of water in various pipelines.

A previous study on the Vilnius water supply system provided a database of relevant water quality parameters and the types of pipe materials installed in the studied sections of the distribution system (Valentukevičienė et al. 2011). This allowed the identification of locations where steel and iron pipes had been used, in order to evaluate both materials independently. Steel and cast iron pipes were installed more than 35 years ago in the water supply system mains.

The sampled points of the water supply system are shown in Fig. 1. The storage tank and water distribution system pipe mains were located in the same region approximately 6 km away from the water supply field. The sampling point for the cast iron pipes was approximately 9 km away from the water supply field.
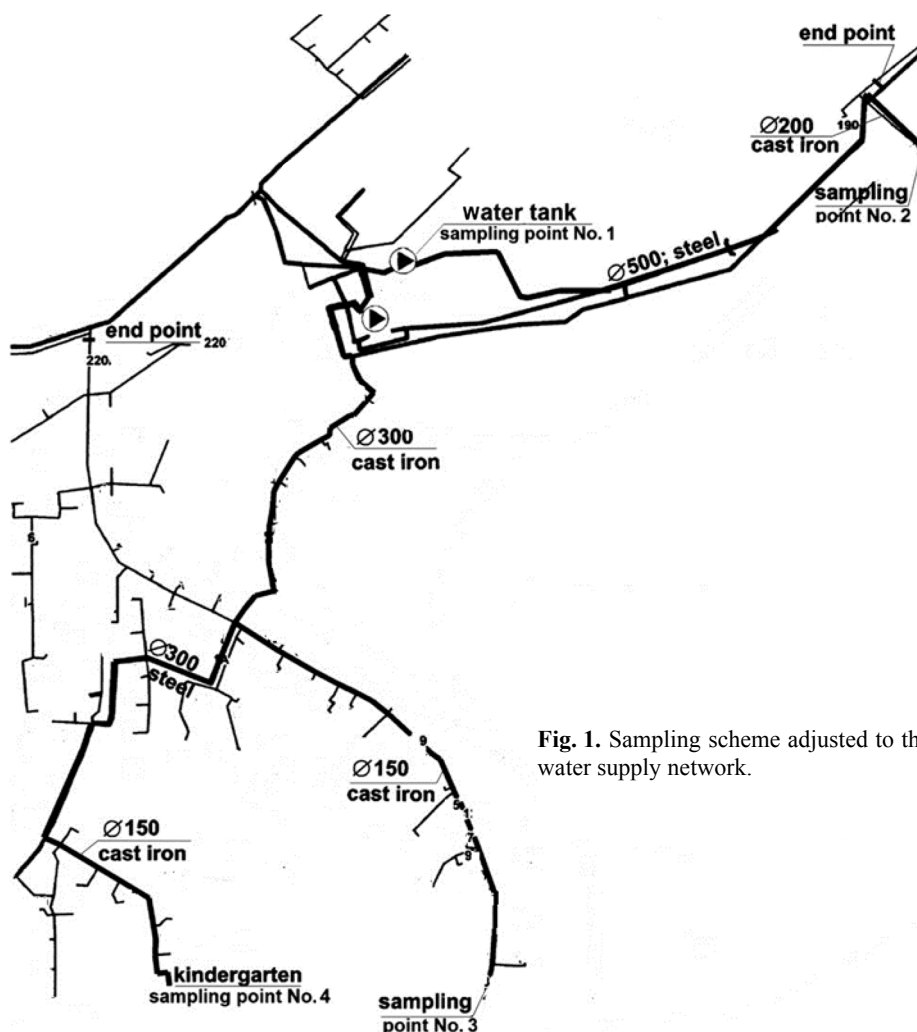
Fig. 1. Sampling scheme adjusted to the water supply network.

These regions received water 24 h per day, with short exceptions in emergency cases (e.g. broken pipelines or during renovation) and water flow stagnation for 6 h, from 11 PM to 5 AM. All locations were sampled five times for internal sediment scrapings during stagnation when the water supply was interrupted by renovation works.

All sediment samples from each sampling point were collected in 1 L acid washed polyethylene reservoirs for laboratory research and microelement analyses. Total contents of 17 predominant elements, Mn, Si, P, S, Ca, Fe, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Zn and Hg, were obtained. These were determined by the energy-dispersive X-ray fluorescence (EDXRF) method. Samples were prepared by following the procedures of milling with MM 400 (the mixer mill is a compact versatile bench-top unit which has been developed specially for dry and wet small amounts of the sample), homogeni-zation with Licowax (4 g of sample and 0.9 g of poly-ethylene wax) and pressing with a PP15 press into 32 mm pellets. Two pellets were prepared for each sample. The primary content of the 17 chemical elements was determined by EDXRF by using the SPECTRO XEPOS equipment and the TURBOQUANT calibration method for pressed pellets. The results showed that the contents of two heavy metals, Cd and Hg, were below their detection limits in all samples. The following conditional values were used for these elements when the content was below the detection limit: As – 0.05 mg/kg, Mo – 0.1 mg/kg. A statistical median value of each element was calculated by using repeated measurements of each sample four times. The results were then recalibrated by using 44 ISE certified reference materials, CRM 2709 and CRM 2711. The element concentrations in collected sediments were reported as weight per cent (wt%) contents.

Sediment samples from steel and iron pipes were collected at the same points of the water supply system from which water samples were obtained (as shown above). The handling of groundwater samples followed

the ISO and EN standard procedures, with refrigerated storage at laboratory, according to *Water Quality – Sampling – Part* 1: *Guidance on the design of sampling programmes and sampling techniques* (ISO 5667-1:2006). All plastic sampling bottles were cleaned carefully before microelement determinations, by immersion in warm 5% (V/V) aqueous nitric acid solution for a minimum of 6 h, and by rinsing with deionized water before use. All water samples were collected in pre-washed hermetically closed plastic bottles. All sampling bottles and caps were rinsed three times with the water taken from the water supply system in the sampling sites. All samples were obtained directly from the tap after allowing the water to run for at least 10 min. The samples were then acidified to 1% with nitric acid and were stored in 1 L hermetically closed plastic bottles at 4 °C for as short time as possible before analysis. These samples were analysed by using an ICP emission instrument on a Perkin Elmer ICP-400 (The Perkin–Elmer Plasma 400 ICP Emission Spectrometer). All microelements evaluated in this research were within the method-specified acceptance criterion of ±10% of the known value. The typical deviation for most elements was less than 3%.

The data were analysed using MathCad statistical software with a type I error (a) of 0.05. Also, appropriate normal and nonparametric statistics were applied. The statistical values such as maximum, minimum, median, standard deviation and coefficient of determination were calculated.

RESULTS

The statistically evaluated results of microelement concentrations for treated water obtained annually from the Antaviliai reservoir and for raw groundwater obtained from the Paneriai reservoir annually are presented in Table 3. All concentrations were nearly the same from both water sources with the exception of mercury which was detected in higher concentrations (i.e. up to 0.12 µg/L) in raw groundwater.

Total phosphorus concentrations ranging from 0.01 to 0.13 mg/L had previously been measured in Lithuanian groundwater during investigations of hydrogeochemical indexes of typical Quaternary hydrogeological systems with extremes up to 0.25 mg/L occurring in water with centralized management (Diliūnas et al. 2006). These total phosphorus concentrations were significantly lower than 0.027 to 0.045 mg/L in the Jinpen Drinking Water Reservoir, China (Zhang et al. 2008).

In a comparative overview Friedman et al. (2011) mentioned that bacteria, fungus, plants and DNA aptamers accumulate metals (Cd, Cr, Zn, As, Fe, Ni) in cell cytoplasm, or stabilize them. Total heavy metal concentrations in the sediment samples from Friedman et al. (2011) followed the sequence: Fe > Cu > Mn > Zn > Pb > Ni > Co > Cr > As > Cd. These results were partly similar to those obtained in the Vilnius water supply study, for the following metals: Fe > Mn > Cr > Pb > Zn > Cu > Co > Ni > As > Mo. However, Cd and Hg were below detection limits and were not obtained from either water or sediment samples from any of the investigated pipelines and pipe segments. The highest concentration of molybdenum (0.00278%) was obtained from sediments of a cast iron pipeline and was 2.5 times higher than in samples from steel pipeline sediments and 4.5 times higher than in samples from the water treatment plant outlet. This observation confirms the suggestion that Mo accumulates in both investigated pipe materials but was found mostly in cast iron pipes.

All results obtained from the sediment analysis are presented in Table 4 with statistically evaluated highest concentrations.

The concentration of Cr was highest in cast iron pipeline sediment samples (sample point No. 4), i.e. 0.0246%, or 3.5 times higher than in samples from the water tank outlet (point No. 1) and twice as high as in

Table 3. Microelement concentrations for treated water obtained from the Antaviliai and Paneriai reservoirs

Heavy metals	Required concentration limit	Annual maximum value	Annual minimum value	Annual medium value
Manganese (µg/L)	50	26	<6	11
Arsenic (µg/L)	10	<1.0	<1.0	<1.0
Mercury (µg/L)	1.0	0.12	<0.05	<0.05
Cadmium (µg/L)	5.0	<0.1	<0.1	<0.1
Chromium (µg/L)	50	<2.0	<2.0	<2.0
Nickel (µg/L)	20	<2.0	<2.0	<2.0
Lead (µg/L)	10	<2.0	<2.0	<2.0
Copper (mg/L)	2.0	<0.03	<0.03	<0.03

Table 4. Concentrations of elements (%) in sediments obtained by the energy-dispersive X-ray fluorescence (EDXRF)

Element	Sample points				Abs. error (%)
	No. 1 Water tank	No. 2 End point	No. 3 New junction	No. 4 Kindergarten	
Manganese	0.4141	0.4853	0.5130	5.786	0.0014–0.007
Silicon	3.214	2.322	2.309	3.266	0.003–0.006
Phosphorus	2.176	0.09570	0.1192	0.5762	0.0004–0.002
Sulphur	0.3384	0.8984	0.9184	0.5540	0.0004–0.001
Calcium	4.508	1.366	1.298	2.083	0.003–0.006
Iron	33.08	55.11	54.90	43.28	0.01–0.04
Arsenic	0.00099	bdl	bdl	0.00483	0.0001–0.00019
Cadmium	bdl	bdl	bdl	bdl	bdl
Cobalt	0.00147	bdl	0.00184	0.00371	0.00027–0.00075
Chromium	0.00801	0.0133	0.0142	0.0246	0.00064–0.0015
Copper	0.00246	0.00593	0.00508	0.00949	0.00013–0.00035
Molybdenum	0.00058	0.00184	0.00111	0.00278	0.00008–0.00015
Nickel	0.00167	bdl	0.00081	0.01266	0.00013–0.00047
Lead	0.00322	0.00619	0.00450	0.00510	0.00019–0.00039
Zinc	0.00308	0.00505	0.00504	0.00667	0.0001–0.00023
Mercury	bdl	bdl	bdl	bdl	bdl

bdl, below detection limit.

samples from a new junction pipeline (point No. 3) (Table 4). This finding is in agreement with previous research summarized by Friedman et al. (2011), which demonstrated that the reductive precipitation of Cr(VI) as $Cr(OH)_3$ or as solid $Fe \times Cr_2 \times (OH)_3$ can be found on internal surfaces of metallic pipes.

The highest amount of Ni (0.01266%) was obtained from cast iron pipe (point No. 4) samples. This value was approximately nine times higher than the lowest amount from the water treatment plant outlet (point No. 1) and steel pipe samples. The only reference provided by WHO (2007) mentions in Table 2 a tolerable daily intake of 5 µg/kg of body weight.

The lowest concentration of Zn, 0.00308%, was obtained from samples collected at the outlet of water treatment plants (point No. 1), followed by approximately a two times higher level from cast iron and steel water supply pipelines (points Nos 2 and 3). This observation confirms the suggestion that sources of Zn accumulation are integrated in both of the investigated pipe materials. An opposite situation was observed in the zinc concentration in biofilm from a groundwater plant at Riga (Latvia), where the highest concentration was 19.05 µg/cm^2 and a six times smaller concentration of only 3.13 µg/cm^2 was obtained in biofilm from a water supply network (Lehtola et al. 2004).

Conversely, the highest amount of Cu was obtained from cast iron pipeline (point No. 4) sediment samples (0.00949%). It was approximately five times higher than in samples from the water tank outlet (point No. 1) and twice as high as samples from the steel pipeline.

The amounts of Cd were lower than detection limits in all pipeline segments.

All obtained results were compared with data in previous relevant papers and finally phosphorus contents were compared with concentrations of different metals. The results are presented in Figs 2–6. The coefficient of determination for phosphorus content and Pb, Cr, Zn, Ni and Cu indicates strong correlations and a common chemical behaviour.

Following the results obtained by Friedman et al. (2011), low-solubility compounds of Pb are formed by complexing with inorganic ligands (chlorides, carbonates, sulphates, phosphates) in accordance with the previous statement. It can be seen from the quantitative evaluation of Pb concentrations that these are related to phosphorus accumulation in sediments in water supply pipelines as shown in Fig. 2.

The highest percentage of lead was found in association with the lowest phosphorus percentage (Fig. 2). This can be explained by the formation of complexes in the water supply pipelines.

A similar behaviour of Cr was established showing the dependence presented in Fig. 3. Chromium is applied to pipeline surface refining and in alloys. Stainless steel consists of 12–15% chromium.

The highest Zn and Ni percentages in water supply sediments were obtained from all samples that contained
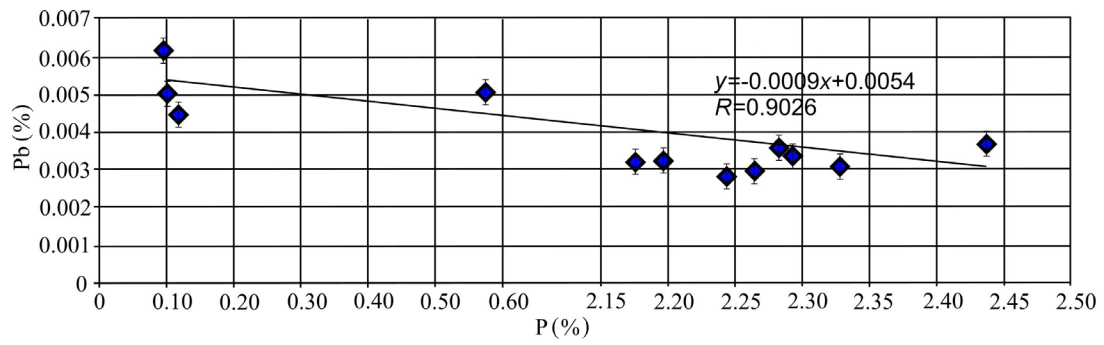
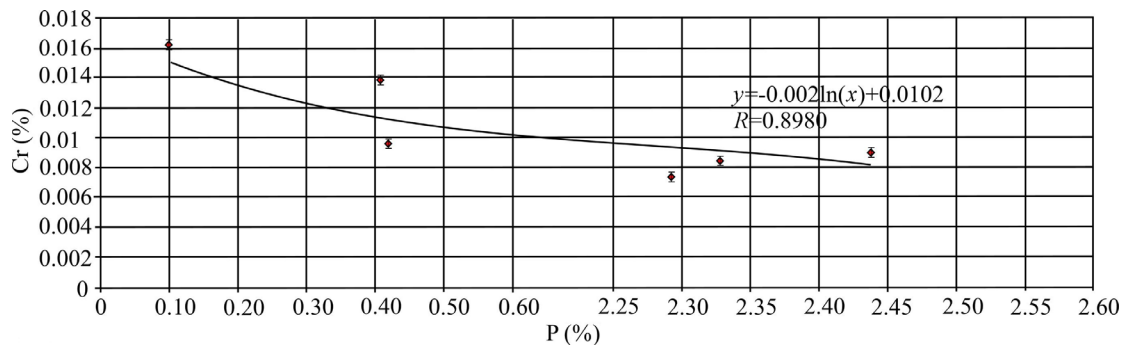**Fig. 2.** Lead and phosphorus contents in sediments from drinking water supply (standard error 0.000307).

Fig. 3. Chromium and phosphorus contents in sediments from drinking water supply (standard error 0.001409).
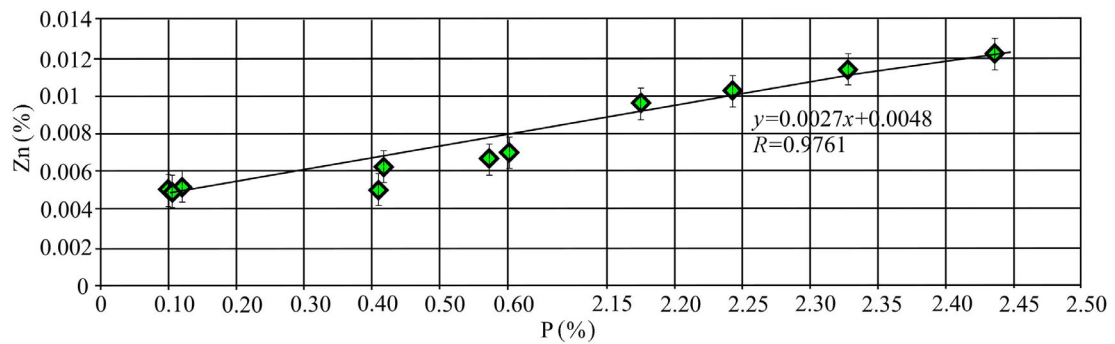

Fig. 4. Zinc and phosphorus contents in sediments from drinking water supply (standard error 0.000837).
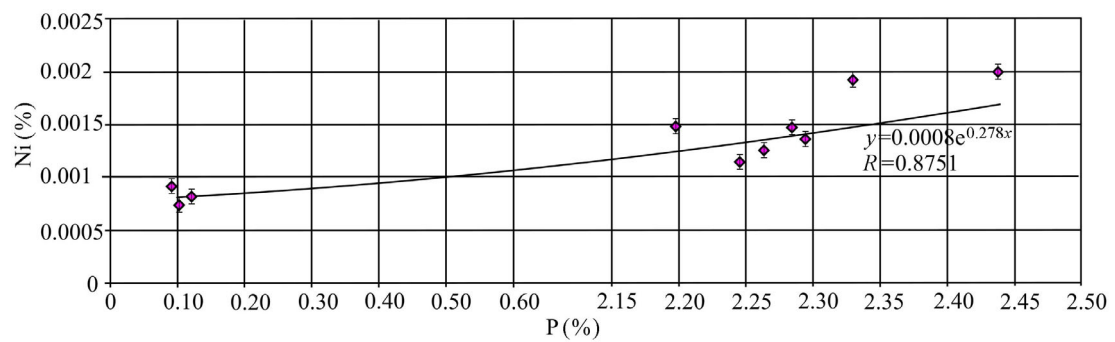

Fig. 5. Nickel and phosphorus contents in sediments from drinking water supply (standard error 0.000136).
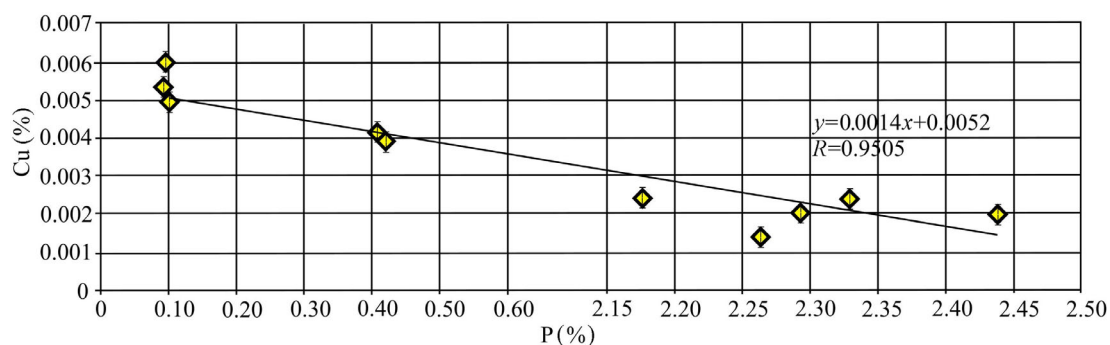
Fig. 6. Copper and phosphorus contents in sediments from drinking water supply (standard error 0.000509).

the highest phosphorus percentages (Figs 4, 5). Both metals were widely used in anticorrosive layers in metallic pipelines and different water supply equipment (e.g. reservoirs, pumps, fittings). In addition, it can be seen from Figs 4 and 5 that Zn and Ni can be accumulated with phosphorus compounds, showing the dependence on the internal surfaces of water supply pipelines.

These research results indicate that Zn concentration can be dependent on water supply pipe materials and it accumulates preferentially in pipes with an increased phosphorus concentration. A similar variation was found by Nawrocki et al. (2010): Zn concentration in steadily flowing water varied between 0.002 and 1.0 mg/L depending on water sources and treatment.

Nickel can be accumulated in sediments (Fig. 5) from cast iron pipes. In cases of appropriate hydraulic conditions, such as high water flow velocity following stagnation, it will appear in drinking water from the users' taps. These findings are in agreement with a statement by the WHO that the primary source of nickel in drinking water is it being leached from metals in contact with drinking water, such as pipes and fittings (WHO 2007).

The aim of all phosphorus accumulation systems is to immobilize metals through the formation of metal phosphates with reduced solubility in a wide range of environmental conditions (Zhang et al. 2008).

As explained by Vila et al. (2012), in the case of Cu occurring as heavy metal cations in water supply, the principal immobilization mechanism by phosphorus compounds is the ion-exchange process. The lowest percentage of copper was obtained with the highest percentage of phosphorus (Fig. 6).

All results relating to Cu concentrations can be compared with research by Lehtola et al. (2004) who reported copper incorporation into the biofilm on an internal pipe surface. But a contrasting observation was made on copper concentrations in biofilms from a groundwater plant at Riga (Latvia) where the concentration was

4.29 $\mu g/cm^2$, nearly half of the 2.38 $\mu g/cm^2$ obtained in a biofilm from a water supply network (Lehtola et al. 2004). Some other research showed that the increase in nitrifier activity, over time, in brass pipes occurred only after levels of copper leaching to water dropped below about 0.1 ppm as the pipe metal aged (Zhang et al. 2008).

Phosphorus compounds are known to affect the accumulation of Pb, Zn, Ni, Cu (Zhang et al. 2008; Fang et al. 2009; Ching-Yu et al. 2010; Vila et al. 2012) in the groundwater extraction and drinking water supply system through various processes (Fig. 7). These include pipe material as a phosphorus and heavy metals source, microelement (Me) balance in settled sediments of water systems, direct heavy metals adsorption by P compounds, direct precipitation of heavy metals as phosphate compounds and additional biological precipitation (organic matter).

For all samples collected at the water supply network, the sampling sites with the highest phosphorus contents usually had the smallest Pb, Cr and Cu amounts (Figs 2, 3 and 6), but the levels of Zn and Ni were higher (Figs 4, 5). The concentrations of the investigated Zn, Cr, Cu and Ni transition metals were found to depend on phosphorus compounds with different statistical correlations (Figs 3–6). All metals are used practically in different parts of water supply networks because of their anticorrosion properties. Phosphorus compounds are actually not efficient adsorbers of Pb, Cr and Cu according to reactions presented in Fig. 7. Lead and copper compounds appear in linear statistical correlations because of simplifying assumptions of the presented models. The sediment interactions with pipeline materials including release and anion exchange reactions (Fig. 7) are adopted here.

Lead introduced to the water supply layer, with less phosphate, will be more easily leached from the sediments and hence becomes more available. Chromium compounds are used for different anticorrosive layers in water supply and multi-solute reactions in Fig. 7 are all
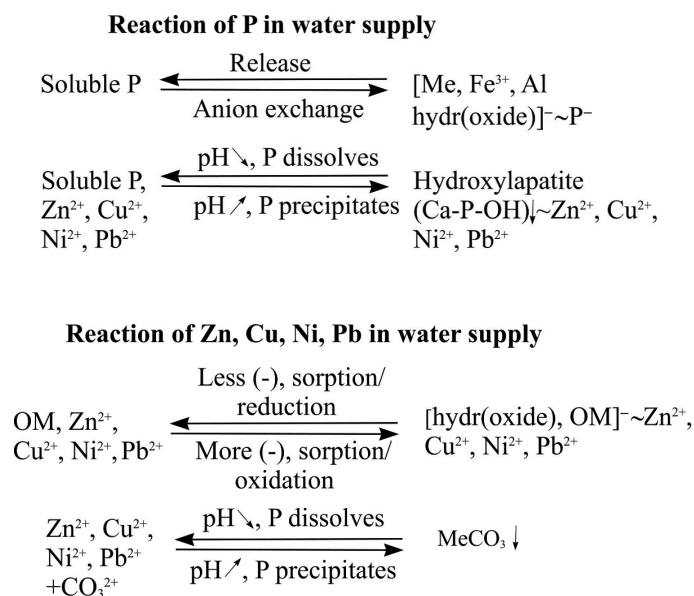
Reaction of P in water supply

Soluble P $\xleftarrow[\text{Anion exchange}]{\text{Release}}$ [Me, Fe^{3+}, Al hydr(oxide)]$^-$~P^-

Soluble P, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} $\xleftarrow[\text{pH}\nearrow, \text{ P precipitates}]{\text{pH}\searrow, \text{ P dissolves}}$ Hydroxylapatite (Ca-P-OH)$\downarrow$~Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}

Reaction of Zn, Cu, Ni, Pb in water supply

OM, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} $\xleftarrow[\text{More (-), sorption/ oxidation}]{\text{Less (-), sorption/ reduction}}$ [hydr(oxide), OM]$^-$~Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}

Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} +CO_3^{2+} $\xleftarrow[\text{pH}\nearrow, \text{ P precipitates}]{\text{pH}\searrow, \text{ P dissolves}}$ $MeCO_3\downarrow$

Fig. 7. Reactions of phosphorus and Pb, Zn, Ni, Cu in the water supply system. OM, organic matter.

accounted for through the description of logarithmic statistical correlation. Microelements Zn and Ni adsorb independently (there are no counteractions or/and cross-flows, for each microelement) such that different adsorption statistical correlations occur – exponential for Ni and linear for Zn. Zinc compounds are widely used for anticorrosive layers in water supply systems. Zinc has a linear relationship to phosphorus concentration in water supply sediments according to anion exchange and precipitation reactions in Fig. 7. Nickel compounds are more toxic than Zn compounds (Table 2) and are less used in water supply systems (occasionally used in nickelled layers). These were found to be an exponential function of phosphorus concentration in pipeline sediments according to sorption reactions in Fig. 7.

The formation of complexes of the investigated metals with phosphorus reflects the nature of reactions controlling their solubility and is actually dominated by different functions such as adsorption, ion exchange and chelation under different concentrations. According to previous research, metal–phosphorus interactions in the water supply cannot be described by one equation or statistical correlation (Zhang et al. 2008). According to Table 3, groundwater from Vilnius water intakes exploiting Quaternary aquifers is not the source of the investigated metals. Different insoluble substances can be formed in sediments from water supply networks as a result of the destructive impact of decomposing corrosion admixture on anticorrosive layers of water pipelines. The overall conclusion is that the investigated

heavy metals are expected to occur in only relatively small amounts in sediments in cast iron and steel pipes of drinking water supply.

DISCUSSION

All living organisms rely on carbon, nitrogen, phosphorus and some micronutrient (including certain metals) cycles. Phosphorus is the sixth most prevalent element, with a median concentration of 1400 mg/g at twenty drinking water utilities that participated in a study in the USA (Ching-Yu et al. 2010). It was found that the 10th and 90th percentile phosphorus concentrations were 450 mg/g and 4300 mg/g (0.43% of total weight), respectively and this amount is approximately similar to the results obtained in this study. Further, it was mentioned in the article cited above that phosphorus occurrence in the corrosion scale can be associated with the formation of hydroxyapatite, adsorption of orthophosphate into various mineral surfaces and phosphorus uptake/accumulation in biofilm and cellular materials (Fang et al. 2009; Vila et al. 2012). The results of Paustenbach et al. (2003) and Zhang et al. (2008) showed that thicker biofilms were formed on more extensive surfaces with the addition of phosphorus at levels of 30 and 300 μg/L. It is also stated by Sarin et al. (2004) that orthophosphates, poly-phosphates and silicates are commonly used as corrosion inhibitors that are applied primarily to reduce lead and copper concentrations in drinking water systems.

Naturally obtained (Yang et al. 2015) or artificially added phosphorus can accumulate in water supply sediments and interact with heavy metals obtained from internal surfaces of steel and iron pipelines. A linear dependence has been observed between heterotrophic bacterial abundance in biofilm and available phosphorus in the water supply systems of Kuopio (Finland) and Riga (Latvia) (Lehtola et al. 2004). This Finnish and Latvian research proves that a high content of phosphorus in supplied water may enhance the formation of biofilms within distribution pipelines. Groundwater phosphate concentrations of 55.40 µg/L and a relatively higher concentration of 76.80 µg/L were observed in users' tap water in the Benin water supply system (Agatemor & Okolo 2007). It has also been stated that pipe surface deposits containing phosphate might serve as reservoirs for bioavailable phosphorus (Zhang et al. 2008).

An observation that 1 g of phosphatic clay can accumulate 37.2 mg of Pb and 1 g of activated phosphate rock will adsorb 15.47 mg of lead was made by Singh et al. (2001). Lead concentrations in steadily flowing water (Zhang et al. 2009) varied between 0.01 and 0.14 mg/L, with depending on different water sources and at different water treatment plants. The Pb concentrations observed in actual field data were much lower than those observed in earlier laboratory experiments involving only the standing water within submersible pumps (the lead–brass alloy) that exhibited average 300 µg/L overnight internal water concentrations over 10 to 30 days.

All results from Vilnius water supply pipes revealed approximately similar amounts of Pb in all samples of both steel and cast iron pipelines and at the outlet of water treatment plants. A possible explanation is that Pb is not accumulated in water supply pipeline sediments because even its small amounts can be toxic to biofilm microorganisms. It has been found (Zhang et al. 2008) that solid $Pb_3(PO_4)_2$ would have formed and controlled soluble lead levels. Lead concentration in biofilm from the groundwater plant at Riga (Latvia) was 7.38 µg/cm^2, nearly four times less than the concentration of 2.01 µg/cm^2 obtained in biofilm from the water supply network (Lehtola et al. 2004).

The statement by the WHO about Pb presence in tap water as a result of its dissolution from natural sources, but primarily from household plumbing systems (WHO 2011), will need additional research. Those findings are in accordance with the relatively low mean concentration values of 5.6 mg/kg indicated for lead in the sampled heavy metals of the Kouris water reservoir (Cyprus) (Karydas et al. 2015). The results of our research revealed no reliable dependence of copper amounts in pipelines.

The total dissolved concentrations of heavy metals are small because solid phases containing the metals are associated with phosphorus compounds. Also, heavy metals interact with iron compounds that form in all metal-based pipelines even if the internal surface is coated with an anticorrosive layer. Our observations demonstrate that anticorrosive layers in pipelines are partly destroyed by abrasive materials, e.g. sand particles or effects of the maintenance of water supply networks.

All of these findings relate to heavy metal and phosphorus compounds in solid phase sediments from water supply pipelines. Further research will be needed to evaluate possible preventive and/or maintenance practices to improve and develop resistant inner protective layers for water supply pipelines and appropriate water supply maintenance techniques.

CONCLUSIONS

As an example of the application of the drinking water safety approach, the rankings of heavy metals and phosphorus concentrations in internal pipeline sediments were evaluated. Lead, chromium, zinc, nickel and copper concentrations measured in pipeline sediments indicated a significant dependence on phosphorus concentrations. The measured concentrations of heavy metals pose no health threats that might concern users about drinking water quality. Problems arise when phosphorus interferes with those metals, causing higher concentrations of compounds and discoloured water being delivered through users' taps, leading to complaints to water supply companies.

An assessment of the quality of the sediments from water supply pipelines can serve as an efficient instrument for generating information necessary for the evaluation and development of a proper strategy for the improvement of the quality of supplied water and creation of a system with reliable water supply. Consequently, to reduce a negative effect of heavy metals on water quality, measures for water supply improvements should be undertaken. These should achieve balanced use of different pipeline materials. Use of alternative materials (e.g. glass-fibre-based materials) would eliminate the consequences of the excessive amounts of heavy metals. However, it would be useful to investigate the characteristics of alternative materials under different hydrogeological and environmental conditions.

REFERENCES

Agatemor, C. & Okolo, P. O. 2007. University of Benin water supply system: microbiological and physico-chemical assessments. *Environmentalist*, **27**, 227–239.

Cerrato, J. M., Reyes, L. P., Alvarado, C. N. & Dietrich, A. M. 2006. Effect of PVC and iron materials on Mn(II) deposition in drinking water distribution systems. *Water Research*, **40**, 2720–2725.

Ching-Yu, P., Korshin, G. V., Valentine, R. L. & Hill, A. S. 2010. Characterization of elemental and structural composition of corrosion scales and deposits formed in drinking water distribution systems. *Water Research*, **44**, 4570–4580.

Diliūnas, J., Jurevičius, A. & Zuzevičius, A. 2006. Formation of iron compounds in the Quaternary groundwater of Lithuania. *Geologija (Vilnius)*, **55**, 66–73.

[EC] European Council. 1998. Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *Official Journal*, L**330**, 32–54.

Fang, W., Hu, J. Y. & Ong, S. L. 2009. Influence of phosphorus on biofilm formation in model drinking water distribution systems. *Journal of Applied Microbiology*, **106**, 1328–1335.

Friedman, M. J., Reiber, S. H., Hashim, M. A., Mukhopadhyay, S., Sahu, J. N. & Sengupta, B. 2011. Remediation technologies for heavy metal contaminated groundwater. *Journal of Environmental Management*, **92**, 2355–2388.

Karydas, C. G., Tzoraki, O. & Panagos, P. 2015. A new spatiotemporal risk index for heavy metals: application in Cyprus. *Water*, **7**, 4323–4342.

Lehtola, M. J., Juhna, T., Miettinen, I. T., Vartiainen, T. & Martikainen, P. J. 2004. Formation of biofilms in drinking water distribution networks, a case study in two cities in Finland and Latvia. *Journal of Industrial Microbiology and Biotechnology*, **31**, 489–494.

[LMH] Lithuanian Ministry of Health. 2003. *Lietuvos higienos norma HN 24:2003 "Geriamojo vandens saugos ir kokybės reikalavimai"* [*Lithuanian hygiene norm HN 24: 2003 "Drinking water safety and quality requirements"*]. V-455. Vilnius [in Lithuanian].

Nawrocki, J., Raczyk-Stanisławiak, U., Swietlik, J., Olejnik, A. & Sroka, M. J. 2010. Corrosion in a distribution system: steady water and its composition. *Water Research*, **44**, 1863–1872.

Paustenbach, D. J., Finley, B. L., Mowat, F. S. & Kerger, B. D. 2003. Human health risk and exposure assessment of chromium (VI) in tap water. *Journal of Toxicology and Environmental Health*, **66**, 295–339.

Sarin, P., Snoeyink, V. L., Lytle, D. A. & Kriven, W. M. 2004. Iron corrosion scales: model for scale growth, iron release, and colored water formation. *Journal of Environmental Engineering*, **130**, 964–973.

Singh, S. P., Ma, L. Q. & Harris, W. G. 2001. Heavy metal interactions with phosphatic clay: sorption and desorption. *Journal of Environmental Quality*, **30**, 1961–1968.

Valentukevičienė, M. & Ignatavičius, G. 2012. Presence and fate of manganese substances in drinking water supply systems. *Ekologija*, **58**, 23–31.

Valentukevičienė, M., Ignatavičius, G. & Amosenkienė, A. 2011. The sustainable development assessment of drinking water supply system. *Technological and Economic Development of Economy*, **17**, 688–699.

Valentukevičienė, M., Karczmarczyk, A., Jurkienė, A. & Grigaitytė, A. 2013. Research on correlation between nitrogen compounds, iron and manganese concentrations in drinking water supply systems. *Journal of Environmental Engineering and Landscape Management*, **21**, 216–223.

Vila, M., Sịnchez-Salcedo, S. & Vallet-Regị, M. 2012. Hydroxyapatite foams for the immobilization of heavy metals: from waters to the human body. *Inorganica Chimica Acta*, **393**, 24–35.

[WHO] World Health Organization. 2003. *Nutrients in Drinking Water; Potential Health Consequences of Long-Term Consumption of Demineralized, Remineralized and Altered Mineral Content; Drinking Water Expert Consensus Meeting Group Report*. WHO Office for the European Region, 12 pp.

[WHO] World Health Organization. 2004. *Guidelines for Drinking-Water Quality – Volume 1: Recommendations. Third edition*. 515 pp.

[WHO] World Health Organization. 2007. *Nickel in Drinking-water. Background Document for Development of WHO Guidelines for Drinking-Water Quality*. 30 pp.

[WHO] World Health Organization. 2011. *Lead in Drinking-water. Background Document for Development of WHO Guidelines for Drinking-Water Quality*. 26 pp.

Yang, X., Huang, T. & Zhang, H. 2015. Effects of seasonal thermal stratification on the functional diversity and composition of the microbial community in a drinking water reservoir. *Water*, **7**, 5525–5546.

Zhang, Y., Griffin, A. & Edwards, M. 2008. Nitrification in premise plumbing: role of phosphate, pH and pipe corrosion. *Environmental Science & Technology*, **42**, 4280–4284.

Zhang, Y., Griffin, A., Rahman, M., Camper, A., Baribeau, H. & Edwards, M. 2009. Lead contamination of potable water due to nitrification. *Environmental Science & Technology*, **43**, 1890–1895.

Peamiste mikroelementide ja fosfori sisaldus joogivee süsteemi setetes

Marina Valentukeviciene, Ramune Zurauskiene ja Jonas Satkunas

Põhjavesi on Leedus ainuke joogiveeallikas. Vilniuse veevarustuses kasutatakse rohkem kui 20 Kvaternaari põhjaveekihi veehaaret. Käesoleva töö peamine eesmärk oli iseloomustada raskmetallide sisaldusi joogiveetrasside torude sisepinnale akumuleeruvates fosfaatsetes setetes. Uurimistulemused näitavad, et kõrgema sisaldusega mikroelementideks olid Pb, Ni, Zn ja Cu. Lisaks näitavad tulemused, et antud mikroelementide ja fosfaatsete setete akumulatsioonil on omavaheline seos.