

# Comparison of Pb, Zn, Cd, As, Cr, Mo and Sb Adsorption onto Natural Surface Coatings in a Stream Draining Natural As Geochemical Anomaly

Petr Drahota · Pavel Škaloud · Barbara Nováková ·  
Martin Mihaljevič

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**Abstract** Natural surface coatings (biofilms) were collected on glass slides in the shallow, arsenic-rich stream and were used to compare biofilm trace element adsorption properties. Biofilm element retention and affinities were element specific indicating different processes control their sequestration. Distribution coefficients ( $K_d$  values), calculated as the ratio between biofilm and dissolved trace element concentrations, revealed solid phase enrichment that, depending on the trace element, extended from  $10^{0.18}$  to  $10^{3.17}$ . Elements were specifically scavenged by the organic constituents of the biofilm itself (Fe, Pb, Zn, Cr) and associated biominerals of poorly ordered Mn oxide (Cd, As, Mo, Sb). The results provide an evidence for the significant role that microbial activity can play in trace element geochemistry in freshwater environment.

**Keywords** Biofilm · Trace elements · Distribution coefficient · Biogenic Mn oxide

Natural surface coatings are ubiquitous in freshwater environments where they can play an important role in the

accumulation of metals and metalloids from surrounding waters (Headley et al. 1998; Haack and Warren 2003; Dong et al. 2007). Trace metal and metalloid adsorption is expected to be governed by the composition of the solid phase, in addition to the effects of solution chemistry (e.g. pH, element speciation). Metal oxides, especially iron, manganese and aluminum oxides, and organic materials, are expected to be the dominant components of natural surface coatings as well as major scavengers of trace elements because of their high specific surface areas (Dong et al. 2000; Warren and Haack 2001). These sorbents have diverse binding abilities for trace metals and metalloids and have contrasting influence on the element mobilization and bioavailability. So the determination of relative trace element scavenging abilities of the organic versus oxide components within complex assemblage of natural surface coating is of great significance.

Most researches concerning the natural surface coatings are focused on adsorption of Pb, Zn and Cd, but trace oxyanions adsorption onto solid phases was relatively fewer, and for Mo and Sb have not been reported previously in literature. Since the relative roles of organic and oxide components are affected by the nature of trace element itself (Warren and Haack 2001) and distribution of one kind of trace element among the components is very different from others (Dong et al. 2007), we have measured the distribution of trace metals and metalloids in a stream draining natural As geochemical anomaly where the As concentrations in water, soil and sediments have been found to exceed a number of Czech standards (Drahota et al. 2011). Our aim was to estimate and compare adsorption efficiency of natural surface coatings as well as the relative roles of metal oxides and organic matter within mixed mineral-organic assemblage in adsorption of Pb, Zn, Cd, As, Cr, Mo, and Sb.

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P. Drahota (✉)  
Institute of Geology, Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 269, 165 00 Prague 6, Lysolaje, Czech Republic  
e-mail: petr.drahota@natur.cuni.cz

P. Škaloud  
Department of Botany, Faculty of Science, Charles University, Benátská 2, 128 43 Prague 2, Czech Republic

B. Nováková · M. Mihaljevič  
Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

## Materials and Methods

All laboratory glass- and plastic-ware was exhaustively cleaned as for trace analyses (e.g. Drahotka et al. 2013). Nitrocellulose filters were treated with 50 mL 0.1 M HNO<sub>3</sub> (suprapure, Merck), 100 mL MilliQ water and then dried at 50°C for 15 h in an oven. All sampling equipment was sealed in clean polyethylene bags until used.

Natural surface coatings (biofilms) were sampled every 2 or 4 h during the diel investigation of the Mokrsko Stream chemistry (Drahotka et al. 2013) conducted during August 2–3, 2010 and June 20–21, 2011. The Mokrsko Stream is located near the village of Mokrsko in the Psí Hory gold district (central Czech Republic), approximately 50 km south of Prague. The sampling location was approximately 250 m downstream from the source, which represents the mouth of the short (tens of meters) subsurface drainage system. The Mokrsko Stream at sampling location is 30 cm wide with an average depth of 5 cm, and an average streamflow of 0.2 L/s during baseflow. Biofilms developed on a precleaned glass microscope slides that were fixed vertically (short edge) at about 1 cm under the water surface in polypropylene racks for a period of 4 weeks. At the time of sampling, 4–8 microscope slides were rinsed with filtered stream water that has been collected simultaneously. To avoid dehydration and contamination of the biofilms, they were stored in Petri dishes containing a small amount of filtered stream water until further processing. The surface coating was scratched from the slide with a clean microscopic cover-glass, resuspended in filtered stream water and collected on acid-washed and preweighted filters (0.45 µm, cellulose nitrate, Millipore®) to obtain the dry weight of each sample after 15 h drying at 50°C. Filters were digested with 3 mL of concentrated HNO<sub>3</sub> (65 % Suprapure, Merck) and 0.5 mL of H<sub>2</sub>O<sub>2</sub> (30 % Suprapure, Merck) in closed Teflon beakers (Savillex®). After dilution to 25 mL with MilliQ water, the trace element concentrations of the samples were measured by ICP-MS (ThermoScientific XSeries II). The measured concentrations of trace elements (Mn, Fe, Pb, Zn, Cd, As, Cr, Mo, Sb) in the certified and synthetic standard (NIST 1640) were within ±2 % of their certified values. The digestion procedure was performed with blank filters to check the quality and the accuracy of the measurements.

Composite natural surface coating sample collected during June, 2011 was extracted using the sequential extraction (SE) method. The SE procedure employed here was the modification of the extraction techniques successfully used and tested for assessing the solid speciation of trace elements in the biofilm by Dong et al. (2000) and Hua et al. (2012). The SE procedure seeks to partition trace elements into: 0.02 M NH<sub>2</sub>OH·HCl + 0.01 M HNO<sub>3</sub> for 30 min (Mn oxides), 0.4 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> for 40 min at pH 6

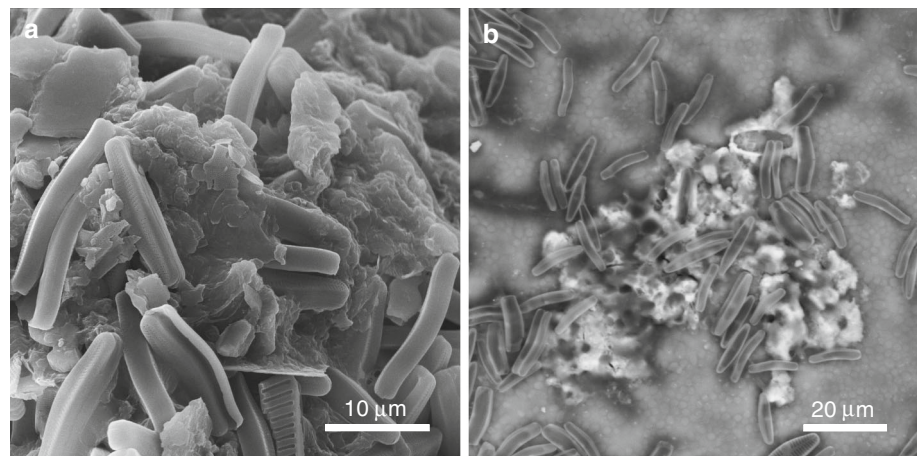
adjusted using 0.1 M NaOH (Fe (hydr)oxides), and 10 % oxalic acid for 60 h (organic material and acid extractable residual phases). After each extraction step the suspension was centrifuged for 10 min at 5,000 rpm. The supernatant was filtered through 0.2-µm membrane filter (nylon, Pro-Fill), acidified by HNO<sub>3</sub> (Merck, Suprapure), and elemental concentrations were determined by ICP-MS. The extractions were performed in three replicates; blank extractions were used with the same process for the control experiment. All reagents used here were trace metal grade.

Several slides with natural surface coatings were air-dried immediately and then used for observation by SEM-EDS (Vega3XM, Tescan/Quantax 200, Bruker). One set was carbon-coated for elemental mapping, and replicate sections gold-coated to enable fine-resolution imaging of sample structure and topography. The X-ray diffraction (XRD) analyses of the surface coatings were performed using a PANalytical X'Pert Pro diffractometer. The analysis conditions were as follows: Cu Kα radiation, 40 kV, 30 mA, step scanning at 0.02°/550 s in the range 3–80° 2θ.

## Results and Discussion

Brownish green natural surface coatings that developed on glass slides after 4 weeks in Mokrsko Stream consisted of assemblages of microorganisms and mineral deposits. Microscopic examinations of some natural biofilm samples indicated that the biofilms contained large number of diatoms (*Gomphonema*, *Achnanthes*; Fig. 1a); green algae (*Coelastrrella*) and protozoa represented minor component. The mineral composition of the natural coating (quartz, albite, muscovite/illite, hornblende and kaolinite), determined by XRD, was similar to floc particles (Drahotka et al. 2013), suggesting their development could be attributed to the attachment of flocculated suspended particles. Micrographs and EDS analyses of natural surface coatings developed after 4 weeks confirmed the presence of aluminosilicate minerals, but they also showed a heterogeneous distribution of Mn. Manganese was concentrated in the fine-grained hydrous Mn oxide mineral precipitates (Fig. 1b) that were always associated with accumulations of small bacterial cells. Such an association is not surprising since the formation of Mn(III/IV) oxides from soluble Mn<sup>2+</sup> is believed to be a biologically controlled process in most of freshwater environments (Tebo et al. 2004). The XRD patterns of the samples rich in biogenic Mn oxides indicated that these biogenic precipitates were poorly crystalline (broad *hk* bands corresponding to 2.4 and 1.4 Å d-spacings) and thus probably structurally related to hexagonal birnessite (Villalobos et al. 2006). X-ray emission spectra from Mn oxide were characterized by strong peaks for Mn but also in several

**Fig. 1** Scanning electron micrographs of natural surface coating showing large diatoms within attached mineral particles (a) and newly-formed Mn oxides (brighter aggregate) (b). Maximum value of arsenic concentration in Mn oxide is 1.6 wt%  $\text{As}_2\text{O}_5$  (based on 15 analyses)



analyses showed higher Fe (up to 3.3 wt%  $\text{Fe}_2\text{O}_3$ ) and As (up to 1.6 wt%  $\text{As}_2\text{O}_5$ ). Other metals and metalloids (Pb, Zn, Cd, Cr, Mo, and Sb) were not detected in the biogenic Mn oxides as well as in the other components of the natural surface coatings by EDS. The Mn oxides were similar in morphology, poor-ordering and chemical composition to the biogenic Mn oxides from the Mokrsko Stream's streambed described by Drahota et al. (2011). These were also characterized by higher contents of Fe (up to 6.3 wt%  $\text{Fe}_2\text{O}_3$ ) and As (up to 2.21 wt%  $\text{As}_2\text{O}_5$ ). The data presented above demonstrate the importance of biogenic Mn oxide formation for As sequestration from the aqueous phase at the Mokrsko Stream.

Surface concentrations of Fe, Mn, Pb, Zn, Cd, As, Cr, Mo, and Sb solubilized by concentrated  $\text{HNO}_3/\text{H}_2\text{O}_2$  (defined as 100 % of total extractable) are given in Table 1. Biofilm metal and metalloid dynamics were element specific. Manganese and Fe were the most abundant elements in the biofilm. The mean biofilm total Mn and Fe concentrations of 20 and 11 g/kg, respectively, represented together approximately 3 % by mass of the biofilm. Mean biofilm total concentrations for the other elements decreased in the following order: As (703  $\mu\text{g/g}$ ) > Zn (109  $\mu\text{g/g}$ ) > Cr (51  $\mu\text{g/g}$ ) > Pb (30  $\mu\text{g/g}$ ) > Sb (10.5  $\mu\text{g/g}$ ) > Mo (2.7  $\mu\text{g/g}$ ) > Cd (1.0  $\mu\text{g/g}$ ). In comparison to the dissolved concentrations (Drahota et al. 2013), the metal and metalloid concentrations in the biofilm were relatively high, implying that the dissolved elements had been sorbed and retained by the solid phase accumulates. To assess the solid phase partitioning of the metals and metalloids, distribution coefficients ( $K_d$ , L/kg) were calculated following the conventional operational definition as the ratio between solid ( $\text{Me}_{\text{biofilm}}$ ) and dissolved ( $\text{Me}_{\text{dissolved}}$ ) element concentrations (Stumm and Morgan 1996):

$$K_d = (\text{Me}_{\text{biofilm}})/(\text{Me}_{\text{dissolved}})$$

Mean  $K_d$  indicated substantive differences in relative element affinities for the biofilm.  $K_d$  values for Pb (log  $K_d$

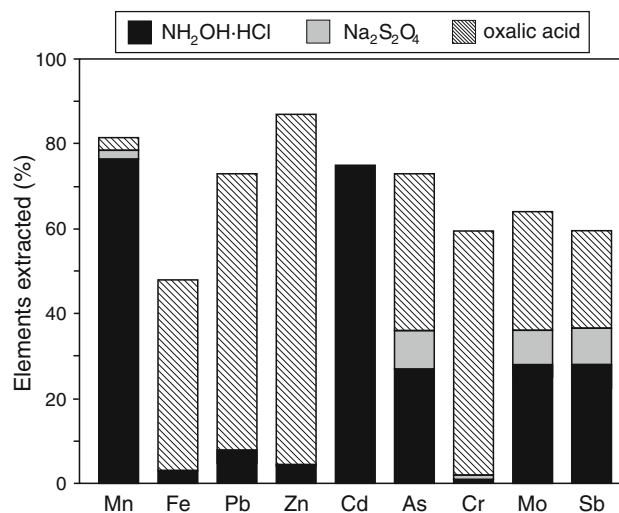
3.17), Cr (log  $K_d$  2.93), Zn (log  $K_d$  2.56) and Mn (log  $K_d$  2.30), were three and two orders of magnitude above those for Cd, Fe, Sb, Mo, and As (log  $K_d$  1.97, 1.57, 0.60, 0.32, and 0.18, respectively; Table 1). A paucity of reported literature  $K_d$  values for biofilm environments preclude direct comparison to other systems. However, the observed element trends are consistent with those reported in the literature. For instance, lower partitioning of elements between biofilms and bulk solution has been reported in acidic systems compared to circumneutral systems (Ferris et al. 1989), where  $K_d$  values of  $10^2$ – $10^3$  for Mn, Fe, Pb, Zn and Cr have been measured (Ferris et al. 1999, 2000; Haack and Warren 2003). Many studies have shown that the solid phase partitioning of dissolved elements and associated  $K_d$  values are quite sensitive to the composition of reactive materials (Warren and Haack 2001). Because of this sensitivity, the different  $K_d$  values obtained for Mn, Fe, Pb, Zn, Cd, As, Cr, Mo, and Sb in the Mokrsko biofilm are not unusual, but rather illustrate the inherent variability that can be anticipated for trace element uptake and retention by heterogeneous solid materials.

The extractant reagents in the SE employed were intended to selectively remove specific adsorbing phases without removing other components.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was used to extract easily reducible Mn oxides, and  $\text{Na}_2\text{S}_2\text{O}_4$  was used to extract Fe oxides.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  removed 77 % of the biofilm Mn, but also removed 3 % of Fe (Fig. 2). Extraction with  $\text{Na}_2\text{S}_2\text{O}_4$  removed only 0.1 % of Fe. These results agree closely with that obtained from SEM–EDS study. Biogenic Fe-bearing Mn oxides represent major component of the biofilm, whereas Fe (hydr)oxides are absent. In accordance to these findings, the two most important geochemical components in the SE have been identified as Mn oxides and organic matter including acid extractable residual fraction (Fig. 2). Among the trace elements studied the highest values of first fraction ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) were observed for Cd (75 % of the total concentration). The high capability of Mn oxides (especially biogenic Mn oxides) to adsorb Cd, Pb and

**Table 1** Biofilm total element concentrations (Mn, Fe: mg/g; Pb, Zn, Cd, As, Cr, Mo, Sb:  $\mu\text{g/g}$ ), their detection limits (DL), and partition coefficients ( $K_d = [\text{Me}_{\text{biofilm}}]/[\text{Me}_{\text{dissolved}}]$ , L/kg)

(DL)	n	Mn (0.0002)	Fe (0.007)	Pb (0.8)	Zn (5)	Cd (0.01)	As (0.08)	Cr (2.4)	Mo (0.09)	Sb (0.03)
2010, August	13	15.95 $\pm$ 5.19	9.63 $\pm$ 2.60	26.8 $\pm$ 7.6	102.1 $\pm$ 55.5	0.8 $\pm$ 0.2	728.1 $\pm$ 176.3	52.5 $\pm$ 25.9	2.9 $\pm$ 1.0	7.8 $\pm$ 1.2
2011, June	7	24.57 $\pm$ 8.71	12.46 $\pm$ 2.09	32.4 $\pm$ 13.9	115.9 $\pm$ 26.4	1.1 $\pm$ 0.5	677.0 $\pm$ 122.9	49.0 $\pm$ 5.3	2.5 $\pm$ 0.4	13.2 $\pm$ 5.5
$\log K_d$		2.30 $\pm$ 0.07	1.57 $\pm$ 0.16	3.17 $\pm$ 0.06	2.56 $\pm$ 0.04	1.97 $\pm$ 0.10	0.18 $\pm$ 0.03	2.93 $\pm$ 0.08	0.32 $\pm$ 0.00	0.60 $\pm$ 0.13

other metal cations in freshwater environments has been observed by many researchers (e.g. Dong et al. 2000, 2007; Haack and Warren 2003). When compared with Cd, the adsorption of Pb, Zn and Cr was dominated by organics (including acid extractable residual fraction) in the studied samples (Fig. 2). One reason for this may be the different forms of biofilm used. Specifically, samples of scraped biofilm were used for SE in this study, which resulted in full contact between the solid and leaching solution, while in previously conducted studies (e.g. Dong et al. 2000, 2007), the extraction and adsorption was conducted using biofilm attached to glass slides, and the contact was consequently inadequate. As shown in the Fig. 2, the distribution patterns of oxyanions As, Mo and Sb were similar. Specifically, the relative contribution of Mn oxides was similar to that of organics (including acid extractable fractions), i.e. 23 %–37 % of the total concentration. Evidence of the association of As, Mo and Sb species with Mn oxides has been already shown (e.g. Takamatsu et al. 1985; Thanabalasingam and Pickering 1990; Tani et al. 2003). Mn oxides exhibit an ability to oxidize As(III) and Sb(III), and to adsorb both oxidized species. Although the processes of As and Sb sequestration by Mn oxides are somewhat intricate, and depended strongly on the experimental conditions, it has been generally accepted that the predominant mode of As sequestration by biogenic Mn oxide is the concurrent sorption of As(V) and divalent cations such as Mn(II), Zn(II) (Takamatsu et al. 1985; Watanabe et al. 2012).



**Fig. 2** Relative proportion of Mn, Fe, Pb, Zn, Cd, As, Cr, Mo, and Sb observed in sequential extraction of composite natural surface coating collected during June, 2011. Values indicated average of three replicates. Elements were sequentially extracted in three steps: (1) Mn oxides (0.02 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  + 0.01 M  $\text{HNO}_3$ ), (2) Fe (hydr)oxides (0.4 M  $\text{Na}_2\text{S}_2\text{O}_4$ ), and (3) organic material and acid-extractable residual phases (10 % oxalic acid)

In conclusion, it is clear that benthic biofilms did not play a dominant role in regulating pH and O<sub>2</sub> dynamics in the Mokrsko Stream, and consequently, the trace elements diel cycles (Drahota et al. 2013). On the other side, the accumulation of biofilm is of great interest as microorganism-induced mineral precipitation reactions serve to localize poorly-ordered Mn oxide deposition in places where microorganisms are growing and microorganism-derived organic matter enhances solid phase metal retention. Presently, we can only speculate as to the processes involved in trace elements association with these biogenic Mn oxides. However, these processes appear to be responsible for seasonal trace oxyanion cycles (Drahota et al. 2011). Thus, the geochemical microenvironment of the biofilm, regulated largely by microorganism activity and attendant ecological controls, has the potential to discernibly affect trace metal dynamics.

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