HELMHOLTZ
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antimony 2015

3rd International Workshop on Antimony in the Environment

6 - 9 October, 2015

Leipzig (Germany)

Organizers:

Montserrat Filella
University of Geneva, Switzerland

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Department Analytical Chemistry, Germany

Cite as: Filella, M., Daus, B. (eds., 2015): antimony 2015: 3rd International Workshop on Antimony in the Environment, 6 - 9 October, 2015 Leipzig (Germany) - Helmholtz Centre for Environmental Research - UFZ, Leipzig.

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Dear participants of Antimony 2015,

With a great pleasure we welcome you to the **3rd International Workshop on Antimony in the Environment.**

We believe it is time for a new workshop on this topic after 2005 in Heidelberg and 2011 in Jena. This workshop will address the current and future status of the research on antimony. The program includes keynote lectures, oral presentations and poster sessions covering recent developments in the study of this element in environmental and biological systems.

We would like to thank the journal Environmental Chemistry for their generous support of the poster prices.

Environmental Chemistry

We also thank the Fonds der chemischen Industrie for its kind financial support the workshop.

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We wish all colleagues interesting lectures, very fruitful discussions and a pleasant stay at the KUBUS of the Helmholtz Centre for Environmental Research – UFZ in Leipzig.

Montserrat Filella Birgit Daus

Montserrat Filella & Birgit Daus

Programme

Thuesday 6/10/2015

18:00 - 20:00	Leipziger KUBUS foyer: icebreaker party and registration

Wednesday 7/10/2015

8:30 - 9:00	Registration
9:00 - 9:10	Opening

Session 1 Environmental fate and behaviour: Sb versus As

9:10 - 9:50	**Keynote 1: Kirk Nordstrom,** USGS *Antimony and arsenic geochemistry: How far does the comparison go?*
9:50 - 10:10	**Susan Wilson,** University of New England, Australia *Antimony and arsenic in an Australian river catchment: evidence for element specific risk assessment*
10:10 - 10:30	**Anezka Borcinova Radkova,** Queen's University, Canada *Antimony and arsenic geochemistry in tailings and pH neutral drainage water at Beaver Brook Antimony Mine, Newfoundland*
10:30 - 10:50	**Ekaterina Markelowa,** University Waterloo, Canada *The contrasting redox behavior of antimony and arsenic in soil and argillaceous environments*
10:50 - 11:20	coffee break, poster session
11:20 - 11:40	**Asmaa Rouwane,** Université de Limoges, France *Chemical fractionation of antimony compared to arsenic in wetland soil: influence of reducing conditions, nitrates and phosphates addition*
11:40 - 12:00	**Susan Tandy,** ETH Zurich, Switzerland *Antimony and toxic metal uptake by plants growing on drained and waterlogged shooting range soil*
12:00 - 12:20	**Birgit Daus,** Helmholtz Centre for Environmental Research -UFZ, Germany *Differences between arsenic and antimony concerning sorption and biotransformation*
12:20 - 13:40	lunch break and poster session

Session 2 Analytical methods and procedures

13.40 - 14:00	**Matthias Grob,** University of Bern, Switzerland *A novel trapping technique to quantitatively and qualitatively measure minute amounts of stibine and trimethylstibine*
14:00 - 14:20	**Matthew Tighe,** University of New England, Australia *Development of a colorimetric method for the determination of total antimony and antimony species in contaminated waters*

14:20 - 14:40	**Franz Lehmann,** Helmholtz Centre for Environmental Research -UFZ, Germany *Analytical investigations on the stability of Sb(III) in a metal rich bioleaching solution*
14:40 - 14:50	coffee break
14:50 - 15:10	**Mehmet Dogan,** Hacettepe University, Turkey *Speciation of inorganic antimony by using solid phase extraction in natural water samples by atomic absorption spectrometry*
15:10 - 15:30	**Daniel Sánchez-Rodas Navarro,** University of Huelva, Spain *Microwave assisited vs. Ultrasound probe extraction for antimony speciation in atmospheric particulate matter*
15:30 - 15:50	**Bin Chen,** PS Analytical, UK *Online analysis of antimony in various wastewater streams using hydride generation-AFS*
18:00	**Guided City Tour Leipzig**

Thursday 8/10/2015

Session 3 Toxicological effects including pharmaceutical applications

9:00 - 9:40	**Keynote 2: Daniel Argaw Dagne,** WHO *Antimonials in the treatment of leishmaniasis*
9:40 - 10:00	**Frederic Frezard,** Universidade Federal de Minas Gerais, Brazil *Amphiphilic antimony(V) complex or oral tratment of cutaneous leishmaniasis*
10:00 - 10:20	**Cynthia Demicheli,** Universidade Federal de Minas Gerais, Brazil *New antimony complexes as potential antileishmanial agentes against Sb(III)-sensitive and -resistant parasites*
10:20 - 10:40	**Robert Rice,** University of California Davis, US *Inorganic antimonite - human skin cancinogen?*
10:40 - 11:10	coffee break, poster session

Session 4 Environmental fate and behaviour: chemical processes

11:10 - 11:30	**Mengchang He,** Beijing Normal University, China *Rapid photechemical oxidation of Sb(III) by Fe(III)-oxalate complexes*
11:30 - 11:50	**Montserrat Filella,** University of Geneva. Switzerland *Kinetics of ligand substitution reactions in antimony studies*
11:50 - 12:10	**Jurai Majzlan,** University Jena, Germany *Behaviour of antimony during weathering of the tetrahedrite-tennantite* $[Cu_{12}(Sb,As)_4S_{13}]$ *minerals*
12:10 - 13:40	lunch break and poster session

Session 5 Environmental fate and behaviour: environmental problems

13.40 - 14:00	**Reiner Schulin,** ETH Zürich, Switzerland *Antimony in shooting range soil – an environmental problem in Switzerland*
14:00 - 14:20	**Zengpink Ning,** Chinese Academy of Science, China *Spatial distribution and temporal variation of Antimony in PM10 and PM2.5 around a large Sb smelting areas, Southwest China*
14:20 - 14:40	**Gudny Okkenhaug,** Norwegian Geotechnical Institute, Norway *Antimony in waste: mobility in different wastes from various handling facilities*
14:40 - 15:00	**Alexia Molina,** Universidad Nacional Autónoma de México, Mexico *Geochemistry and distribution of antimony in mine tailings of Zimapán (Hidalgo, México)*
15:00 - 15:15	coffee break
15:15 - 16:00	Poster minutes
16:00 - 17:00	**Round table discussion**
20:00	**Conference Dinner Ratskeller Leipzig**

Friday 9/10/2015

Session 6 Microbial and intake processes

9:00 - 9:40	**Keynote 3: Markus J. Tamás,** University of Gothenburg, Sweden *Molecular biology of arsenic and antimony toxicity and tolerance: lessons learned from yeast*
9:40 - 10:00	**Christopher Rensing,** University of Copenhagen, Denmark *Identification of a bacterial antimonite oxidase in agrobacterium tumefaciens*
10:00 - 10:20	**Lars Duester,** Federal Institute of Hydrology, Germany *Release of antimony from sediments into the pore water in incubation experiments: high resolution microprofiling and fractionation*
10:20 - 10:40	coffee break
10:40 - 11:00	**Jing Ji,** ETH Zurich, Switzerland *Sb(III) and Sb(V) uptake by different plants under hydroponic conditions*
11:00- 11.20	**Jelle Mertnes,** International Antimony Association, Belgium *Use of antimony and antimony compounds is safe for human health and the environment*
11:20 - 11:40	**Closing session**

Abstracts

Lectures

ANTIMONY AND ARSENIC GEOCHEMISTRY: HOW FAR DOES THE COMPARISON GO?

D. Kirk Nordstrom 15

ANTIMONY AND ARSENIC IN AN AUSTRALIAN RIVER CATCHMENT: EVIDENCE FOR ELEMENT SPECIFIC RISK ASSESSMENT

Susan C. Wilson, Matthew Tighe, Peter V. Lockwood, Paul M. Ashley, William A. Maher, Anne M. Taylor 18

ANTIMONY AND ARSENIC GEOCHEMISTRY IN TAILINGS AND PH NEUTRAL DRAINAGE WATER AT BEAVER BROOK ANTIMONY MINE, NEWFOUNDLAND

Anežka Borčinová-Radková, Heather Jamieson, Kate Campbell 20

THE CONTRASTING REDOX BEHAVIOR OF ANTIMONY AND ARSENIC IN SOIL AND ARGILLACEOUS ENVIRONMENTS

Ekaterina Markelova, Raoul-Marie Couture, Christopher T. Parsons, Igor Markelov, Philippe Van Cappellen, Benoit Madé, Laurent Charlet 21

CHEMICAL FRACTIONATION OF ANTIMONY COMPARED TO ARSENIC IN WETLAND SOIL: INFLUENCE OF REDUCING CONDITIONS, NITRATES AND PHOSPHATES ADDITION

Asmaa Rouwane, Marion Rabiet, Malgorzata Grybos and Gilles Guibaud 24

ANTIMONY AND TOXIC METAL UPTAKE BY PLANTS GROWNING ON DRAINED AND WATERLOGGED SHOOTING RANGE SOIL

Kerstin Hockmann, Susan Tandy, Björn Studer, Markus Lenz, and Rainer Schulin 26

DIFFERENCES BETWEEN ARSENIC AND ANTIMONY CONCERNING SORPTION AND BIOTRANSFORMATION

Birgit Daus 28

A NOVEL TRAPPING TECHNIQUE TO QUANTITATIVELY AND QUALITATIVELY MEASURE MINUTE AMOUNTS OF STIBINE AND TRIMETHYLSTIBINE

Matthias Grob, Adrien Mestrot, Wolfgang Wilcke 29

DEVELOPMENT OF A COLORIMETRIC METHOD FOR THE DETERMINATION OF TOTAL ANTIMONY AND ANTIMONY SPECIES IN CONTAMINATED WATERS

Matthew Tighe, Susan Wilson, Millie M. Edwards 30

ANALYTICAL INVESTIGATIONS ON THE STABILITY OF Sb(III) IN A METAL RICH BIOLEACHING SOLUTION

Franz Lehmann, Birgit Daus 31

SPECIATION OF INORGANIC ANTIMONY BY USING SOLID PHASE EXTRACTION IN NATURAL WATER SAMPLES BY ATOMIC ABSORPTION SPECTROMETRY

Mehmet Dogan, Mustafa Soylak, Latif Elci 33

MICROWAVE ASSISTED VS. ULTRASOUND PROBE EXTRACTION FOR ANTIMONY SPECIATION IN ATMOSPHERIC PARTICULATE MATTER

D. Sánchez-Rodas, L. Alsioufi, A. Sánchez de la Campa 34

ONLINE ANALYSIS OF ANTIMONY IN VARIOUS WASTEWATER STREAMS USING HYDRIDE GENERATION-AFS

Bin Chen, Warren Corns and Peter Stockwell 35

PENTAVALENT ANTIMONIALS IN THE TREATMENT OF LEISHMANIASIS

Daniel Argaw Dagne 36

AMPHIPHILIC ANTIMONY(V) COMPLEX FOR ORAL TREATMENT OF CUTANEOUS LEISHMANIASIS

Juliane S. Lanza, Flaviana R. Fernandes, José M. C. Vilela, Rogério M. Paniago, Lucas A. M. Ferreira, Margareth Spangler, José M.C. Vilela, Maria N. Melo, Cynthia Demicheli, Frédéric Frézard 37

NEW ANTIMONY COMPLEXES AS POTENTIAL ANTILEISHMANIAL AGENTS AGAINST Sb(III)-SENSITIVE AND -RESISTANT PARASITES

Arshad Islam, Bernardo L. Rodrigues, Juliane S. Lanza, Frédéric Frézard, Cynthia Demicheli 38

INORGANIC ANTIMONITE – HUMAN SKIN CARCINOGEN?

Marjorie A. Phillips, Angela Cánovas, Pei-Wen Wu, Alma Islas-Trejo, Juan F. Medrano, Robert H. Rice 39

RAPID PHOTOCHEMICAL OXIDATION OF Sb(III) BY Fe(III)-OXALATE COMPLEXES

Linghao Kong, Mengchang He 41

KINETICS OF LIGAND SUBSTITUTION REACTIONS IN ANTIMONY STUDIES

Montserrat Filella, Luis M. Laglera 42

BEHAVIOR OF ANTIMONY DURING THE WEATHERING OF THE TETRAHEDRITE-TENNANTITE [$Cu_{12}(Sb,As)_4S_{13}$] MINERALS

Juraj Majzlan, Anežka Borčinová-Radková, Heather Jamieson, Martin Števko, Martin Chovan 43

ANTIMONY IN SHOOTING RANGE SOIL – AN ENVIRONMENTAL PROBLEM IN SWITZERLAND

Kerstin Hockmann, Susan Tandy, Björn Studer, Martin Keller, Markus Lenz, Rainer Schulin....... 45

SPATIAL DISTRIBUTION AND TEMPORAL VARIATION OF ANTIMONY IN PM10 AND PM2.5 AROUND A LARGE Sb SMELTING AREAS, SOUTHWEST CHINA

Zengping Ning, Tangfu Xiao, Enzong Xiao, Yizhang Liu 47

ANTIMONY IN WASTE: MOBILITY IN DIFFERENT WASTES FROM VARIOUS WASTE HANDELING FACILITIES

Gudny Okkenhaug, Åsgeir Ålmås, Nicolas Morin, Sarah Hale, Hans Peter H. Arp 48

GEOCHEMISTRY AND DISTRIBUTION OF ANTIMONY IN MINE TAILINGS OF ZIMAPÁN (HIDALGO, MÉXICO)

A. Molina, M.A. Armienta, G. Villaseñor 50

MOLECULAR BIOLOGY OF ARSENIC AND ANTIMONY TOXICITY AND TOLERANCE: LESSONS LEARNED FROM YEAST

Markus J. Tamás 51

IDENTIFICATION OF A BACTERIAL ANTIMONITE OXIDASE IN AGROBACTERIUM TUMEFACIENS

Li J., Wang Q., Li M., Yang B., Shi M., Guo W., McDermott T.R., Rensing C., Wang G. 52

RELEASE OF ANTIMONY FROM SEDIMENTS INTO THE PORE WATER IN INCUBATION EXPERIMENTS: HIGH RESOLUTION MICROPROFILING AND FRACTIONATION

Anne-Lena Fabricius, Lara Löhr, Dennis Ecker, Lars Duester 53

Sb(III) AND Sb(V) UPTAKE BY DIFFERENT PLANTS UNDER HYDROPONIC CONDITIONS

Ying Ji, Susan Tandy, Pierre Vollenweider, Rainer Schulin 55

USE OF ANTIMONY AND ANTIMONY COMPOUNDS IS SAFE FOR HUMAN HEALTH AND THE ENVIRONMENT

Jelle Mertens 56

Poster

ANTIMONY GEOCHEMISTRY AND BIOAVAILABILITY AT A FORMER MINING SITE

Bauda P., Grybos M., Masfaraud J.F., Aran D., Blaudez D., Brill H., Billet D.,
Montarges-Pelletier M., Boiron M.C. .... .61

GEOCHMICAL CHARACTERIZATION OF COLLOIDS FROM MINE DRAINAGE WATERS AND THEIR ROLE IN Sb AND As TRANSPORT

Anežka Borčinová-Radková, Heather Jamieson, Elizabeth Phillips, Bronislava Lalinská-Voleková,
Peter Šottník 63

IMMOBILIZATION OF ANTIMONY IN LEAD SMELTER-AFFECTED SOILS BY AMENDMENT WITH AMORPHOUS MANGANESE OXIDE

Vojtěch Ettler, Zdeňka Tomášová, Martin Mihaljevič, Michael Komárek 64

SPATIOTEMPORAL DISTRIBUTION OF INORGANIC ANTIMONY ALONG THE GIRONDE FLUVIAL-ESTUARINE CONTINUUM AND BIOACCUMULATION IN WILD OYSTERS AT THE ESTUARY MOUTH: A PRELIMINARY APPROACH TO THE FATE OF REGIONAL ACCIDENTAL RADIONUCLIDE RELEASES

Teba Gil-Díaz, Linda Makni, Jörg Schäfer, Frédérique Pougnet, Mélina Abdou, Mathilde
Mikolaczyk, Jérôme C.J. Petit, Alexandra Coynel, Lionel Dutruch, Cécile Bossy, Angélique Husson,
Jean-François Chiffoleau, Hervé Derriennic, Gérard Blanc 66

ANTIMONY DEPOSITION AND ACCUMULATION IN BIOMONITORING PLANTS AT A TRAFFIC AFFECTED SITE COMPARED TO RURAL SITES IN BAVARIA / GERMANY

Margit Krapp, Ludwig Peichl.. 68

MINERALOGY OF WEATHERING PRODUCTS OF MINE WASTES AT SEVERAL Sb AND Cu DEPOSITS IN SLOVAKIA

Bronislava Lalinská-Voleková, Anežka Radková, Juraj Majzlan, Tomáš Klimko, Martin Chovan, Peter Šottník, Lubomír Jurkovič, Jana Brčeková 70

ANTIMONY IN SOILS OF SOME HISTORICAL MINING SITES IN THE CENTRAL SUDETES, POLAND

Karolina Lewińska, Anna Karczewska, Bernard Gałka, Marcin Siepak, Michał Stysz........ 72

IDENTIFICATION OF CRITICAL RESIDUES FOR TRANSPORT ACTIVITY OF ACR3P, THE *SACCHAROMYCES CEREVISIAE* As(III)/H^+ ANTIPORTER

Katarzyna Markowska, Ewa Maciaszczyk-Dziubinska, Magdalena Migocka, Donata Wawrzycka, Robert Wysocki 74

ANTIMONY EFFECTS ON NON-TARGET DIAZOTROPHIC SOIL BACTERIUM, *AZOSPIRILLUM BRASILENSE* SP7

Maximilian Obinna Obiakor, Lily Pereg, Susan C. Wilson, Matthew Tighe 75

LEACHABILITY OF ANTIMONY AND OTHER TOXIC ELEMENTS FROM IMPOUNDMENT SEDIMENTS AT ABANDONED Sb-DEPOSIT POPROČ

Katarína Peťková, Ľubomír Jurkovič, Peter Šottník, Andrea Černeková 77

INORGANIC Sb(V) REACTIVITY AND UPTAKE PATHWAYS IN HUMAN ERYTHROCYTES

Waldo Quiroz, Manuel Bravo, Luis Felipe Aguilar, Luis Mercado, Silvana López, Camila Barrera 79

ROLE OF MICROBIAL ACTIVITY IN ANTIMONY AND ARSENIC RELEASE FROM WETLAND SOIL UNDER REDUCING CONDITIONS

Asmaa Rouwane, Isabelle Bourven, Malgorzata Grybos, Marion Rabiet, Lucie Mallet, Gilles Guibaud 81

EXPERIMENTAL PILOT SCALE TREATMENT OF MINE WATER AFTER ANTIMONY MINING AT LOCALITY POPROC (SLOVAKIA)

Peter Šottník, Peter Sekula, Ľubomír Jurkovič, Jaroslav Vozár 83

CORRELATING MICROBIAL COMMUNITY PROFILES WITH ANTIMONY CONTAMINATION DATA IN A WATERSHED HEAVILY CONTAMINATED BY AN ANTIMONY TAILING MINE

Enzong Xiao, Tangfu Xiao , Zengping Ning, Xiaolong Lan, Weimin Sun 86

Lectures

(in order of programme)

ANTIMONY AND ARSENIC GEOCHEMISTRY: HOW FAR DOES THE COMPARISON GO?

D. Kirk Nordstrom

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Arsenic and antimony are often thought to behave very similarly in geochemical processes. Located in Group 15 (or Group 5B or VA) of the periodic table, antimony and arsenic are congeners of nitrogen, with antimony directly below arsenic. They both have filled *d* electronic shells and s^2p^3 outermost shells, but arsenic has a $3d^{10}$ shell whereas antimony has a $4d^{10}$ shell. As expected they have the same oxidation states of -3, 0, 3, and 5. There are two reasons why the antimony atom or ion is larger than the comparable arsenic atom or ion, larger electronic shell and less d-block contraction. Chemical bonding characteristics, or valency, depend on electronic shell configuration, the nature and direction of bonds, and atom size. Antimony radius is about 20 pm larger than arsenic, regardless of oxidation state, atomic radius, or covalent radius. Antimony is also heavier with atomic weight of about 122 compared to 75 for arsenic. Consequently, the chemical properties of arsenic and antimony have reasons to be similar and dissimilar. The larger size of the antimony V atom has an important consequence on the pentavalent oxyanions. The arsenic atom in the structure of arsenic acid is small enough and the one double bond with oxygen strong enough that it forms an approximate tetrahedral structure with 3 replaceable hydrogens (H_3AsO_4) , whereas the antimony atom in antimonic acid is too large and it is octahedrally coordinated ($HSb(OH)_6$). Another result is that antimony easily forms mixed oxidation state compounds and arsenic does not. For example, there are three known mixed oxidation antimony oxide minerals, stibiconite ($Sb^{III}Sb_2^{V}O_6(OH)$), cervantite, and clinocervantite (dimorphs of $Sb^{III}Sb^{V}O_4$). The substance $(NH_4)_2SbCl_6$ was shown to be a mixed valence compound in 1934.

Geochemically, there is a considerable difference in upper continental crust abundance with arsenic at 5.7 ppm and antimony at 0.75 ppm (Hu and Gao, 2008) resulting in an As/Sb ratio of 7.6. This difference is caused by light element differentiation during early formation of the earth combined with the abundance of elements produced through nucleosynthesis in the galaxies and the solar nebula. For the total crust the As/Sb ratio is 12 whereas the As/Sb ratio for the mantle is about 5.5, suggesting some enrichment in arsenic from the mantle to the crust (or depletion in antimony or both).

Hydrothermal mineral deposits form over a large range of pressures, temperatures, and fluid compositions. These deposits are the source material for most of our metal products. Gold, silver, mercury, arsenic, and antimony form strong complexes with aqueous sulfide over a wide range of pressures and temperatures and as hydrothermal solutions carrying these complexes rise to the surface they reach a point where they will boil through adiabatic decompression. This decompression will cool the fluid phase and lose sulfide through volatilization, promoting precipitation of these elements as sulfide minerals. The similarity in the stability of the sulfide complexes contributes to the common association of these elements in mineral deposits. As one of the best examples, hydrothermal gold is nearly always found with arsenic. The arsenic occurs in pyrite and in arsenopyrite and several studies have examined the gold content of these minerals. However, there are also processes that separate arsenic and antimony because some mineral deposits are predominantly or only arsenic-rich and others are predominantly or only antimony-rich. Numerous mineral deposits in southern China are antimony-rich. Carlin-type gold deposits in Nevada are arsenic-rich.

Oxidation and weathering of arsenic compounds seems to behave differently from those of antimony. Because these processes are catalyzed by microorganisms, it is also important to know how microbes interact with arsenic and antimony. Microbes that oxidized reduced antimony have been known for some time but only recently has it become clear that dissimilatory antimony reduction also occurs. Abin and Hollibaugh (2014) formed a mixture of sénarmontite and valentinite by reduction of antimonate solution using a bacterium in the *Bacillales* order with lactate as an electron donor. The conversion was complete within 85 hours. Arsenite is known to undergo reduction during mammalian digestion and human keratinocytes were used to follow the rate of arsenate and antimonate reduction (Patterson, 2003). A substantial portion of the arsenate was reduced to arsenite within a few days but antimonite was not detected in keratinocyte cells.

The rate of aqueous arsenite and antimonite oxidation seems to be similar for acid conditions such as acid mine waters but not for circumneutral waters. Oxidation of arsenite using biofilm from the Giant mine was two orders of magnitude faster than antimony oxidation (Asta et al., 2012) and faster than oxidation in acid waters. When dissolved Fe(III) concentrations reach a high enough ratio to As(III) in an acid water, arsenite oxidation can proceed fast enough abiotically by Fe(III). To further complicate matters, apparently Sb(III) can be photooxidized in the presence of humic acids (Buschmann et al., 2005).

Studies on mine drainage from an antimony mine and foundry show that in circumneutral carbonate-rich waters, antimony and arsenic are attenuated very little and can travel downstream as conservative constituents for some distance (Dore, 2015). When acid waters, rich in dissolved iron, begin to precipitate, both arsenic and antimony are attenuated with a tendency for a faster attenuation rate of arsenic. Examination of pore waters and sediments exhibiting oxidizing and reducing conditions in circumneutral soils and sediments contaminated by high levels of both arsenic and antimony show that arsenic is more easily oxidized and reduced in the pore waters whereas antimony remains oxidized regardless of redox conditions (Fawcett et al., 2015). Arsenic also appears to be more mobile than the antimony under all redox conditions. Also, whether in dissolved form or associated with sediment surfaces, antimony (V) is fairly stable.

The myriad of factors that can oxidize and reduce arsenic and antimony are slowly being recognized. Mounting evidence demonstrates that arsenic and antimony, although they might be derived from the same source material and have some comparable chemical characteristics clearly behave differently in hydrogeochemical processes.

References

Abin, C.A., Hollibaugh, J.T. (2014) Dissimilatory antimonate reduction and production of antimony trioxide microcrystals by a novel microorganism. Environ. Sci. Technol. 48, 681-688.

Asta, M.P., Nordstrom, D.K., McCleskey, R.B. (2012) Simultaneous oxidation of arsenic and antimony at low and circumneutral pH, with and without microbial catalysis. Appl. Geochem. 27, 281-291.

Buschmann, J., Canonica, S., Sigg, L. (2005) Photoinduced oxidation of antimony (III) in the presence of humic acid. Environ. Sci. Technol. 39, 5335-5341.

Dore, E. (2015) Geochemical studies on antimony: antimony dispersion in water draining Su Suergiu mine area; removal of Sb(V) from aqueous solution by layered double hydroxides (LDH). Ph.D. dissertation, University of Cagliari, Sardinia, Italy.

Fawcett, S.E., Jamieson, H.E., Nordstrom, D.K., McCleskey, R.B. (2015) Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. Appl. Geochem. (online: **http://dx.doi.org/10.1016/j.apgeochem.2014.12.012**)

Hu, Z., Gao, S. (2008) Upper crustal abundances of trace elements: A revision and update. Chem. Geol. 253, 205-221.

Patterson, T.J., Ngo, M., Aronov, P.A., Reznikova, T.V., Green, P.G., Rice, R.H. (2003) Biological activity of inorganic arsenic and antimony reflects oxidation state in cultured human keratinocytes. Chem. Res. Toxicol. 16, 1624-1631.

ANTIMONY AND ARSENIC IN AN AUSTRALIAN RIVER CATCHMENT: EVIDENCE FOR ELEMENT SPECIFIC RISK ASSESSMENT

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The 11,000 km^2 Macleay River catchment, in northern NSW, represents the most extensive known dispersion of Sb contamination in the southern hemisphere. The Sb, co-occurring with As, is derived from historical mining activities at Hillgrove Mine in the upper catchment, which is highly contaminated [1]. The contamination has dispersed, mainly by flooding, through 300 km of high country gorge lands to the coastal floodplain 300 km to the east, where 90% of the area is contaminated above background concentrations [2]. This is a unique case of Sb and As large scale contamination through a range of different ecosystem environments, impacting soil, sediment, water, biota and humans. Over 10 years, the research team at University of New England, collaborating with University of Canberra, have been working to answer the many unknowns needed to understand the risk to the environment and humans presented by the Sb and As contamination, and to quantify differences in distribution, biogeochemistry, mobility and bioavailability.

The research has shown that both metalloids follow similar patterns of distribution and dispersion throughout the Macleay River environment as a result of the flood mediated mobilisation of the contaminated sediment [2]. Field sampling of river water and soil pore water measurements, however, show that the relative mobility of the two metalloids depends on site specific soil and water conditions and cannot be assumed either similar or dissimilar [3,4]. Associations with soil phases also differ between the two metalloids [2]. Studies on the accumulation and transfer in plants (aquatic, riparian and human food crops in both glasshouse trials and field sampling) indicate plant accumulation of both metalloids, but both the extent of accumulation and translocation to above ground plant parts is dependent on plant species. Often As translocation observed is greater than Sb, and apparent mechanisms of uptake are different [2,5]. Both metalloids can transfer to upper trophic levels of the aquatic food chain [5] although the accumulation and ecotoxicity of both metalloids differs depending on the organism and its physiology. In oral bioaccessibility studies on contaminated soil samples, the bioaccessible fraction for As (<7 % total As) was significantly greater than that of Sb (<3 % total Sb) [3].

The research in the Macleay River Catchment has filled many knowledge gaps in our understanding of Sb and has also clearly demonstrated that this metalloid cannot be assumed to behave similarly or dissimilarly to its sister element, As, in the environment. It is critical that risk assessment for these two metalloids is element specific for development of appropriate and scientifically sound environment management and protection guidelines.

References

[1] Ashley, P.M., Graham, B., Tighe, M., Wolfenden, B.J., 2007: Aust. J. Earth Sci. 54, 83-103.

[2] Tighe, M., Ashley, P., Lockwood, P., Wilson, S.C., 2005: Sci. Total Environ. 347, 175-186.

[3] Wilson, S.C., Tighe, M., Paterson, E., Ashley, P.M., 2014: Environ. Sci. Pollut. R. 21, 11671-11681.

[4] Tighe, M., Lockwood, P.V., Ashley, P.M., Murison, R.D., Wilson, S.C., 2013: Sci. Total Environ. 463-464, 151-160.

[5] Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M.J., Ashley, P.M. , Lockwood, P.V., Wilson, S.C., 2009: Environ. Chem. 6, 133-143.

ANTIMONY AND ARSENIC GEOCHEMISTRY IN TAILINGS AND pH NEUTRAL DRAINAGE WATER AT BEAVER BROOK ANTIMONY MINE, NEWFOUNDLAND

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One of the largest antimony deposits in the world outside China is the Beaver Brook deposit located in central Newfoundland, Canada. The underground operation was opened in 1996 and is currently closed due to low Sb prices. The Sb mineralization is located within two closely spaced fault zones as massive stibnite in fault-related zones. Two tailings impoundments are used for flotation tails. This study focuses on Sb and As associated with secondary phases in tailings and factors controlling their formation and stability. We collected tailings and co-existing surface and pore water. Scanning electron microscopy and electron microprobe analyses were combined with synchrotron-based µ-XRD, µ-XRF to determine the element distribution and Sb host phases in tailings. Water samples were collected within the tailings by lysimeters and from surface waters draining the tailings piles as well as underground mine drainage. Oxidation state of Sb and As were determined by HG-AAS. In addition, the samples of tailings and biofilms are analyzed to assess the microbial diversity and possible influence on weathering kinetics and formation of secondary minerals. Near neutral to alkaline pH is characteristic for all collected water samples. The average concentration of Sb and As in tailings sediments is high with values of 3952 ppm and 2940 ppm, respectively. The dominant gangue minerals in tailings sediment are quartz, Fe-dolomite and illite. The most common sulphide in the tailings is arsenopyrite, followed by pyrite. Stibnite is observed rarely in near-surface samples and appears to be easily dissolved in oxidizing conditions. SEM analysis shows oxidation rims enriched in Fe, Sb and As are formed on arsenopyrite, and, more rarely, on pyrite grains. Sb-Fe-Si rims also form on Fe dolomite and quartz grains. The portion of As in Sb-Fe-Si secondary phases is low, and is often undetected; except for arsenopyrite oxidation rims where As is common. Amorphous Fe-precipitates enriched in As, Si, Ca and Mn are present in tailings drainage water only in minor amounts with no Sb detected. These results show that though the concentrations of both Sb and As are elevated in drainage waters, they are partly controlled by the crystallization of secondary phases, which are formed in active recently deposited tailings.

THE CONTRASTING REDOX BEHAVIOR OF ANTIMONY AND ARSENIC IN SOIL AND ARGILLACEOUS ENVIRONMENTS

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Introduction. Natural solid materials can immobilize antimony (Sb) and arsenic (As) from the aqueous phase. A range of chemical, physical and microbial processes controls contaminant fate, depending on the environmental conditions (e.g. pH, E_H and temperature). Both Sb and As are sensitive to redox conditions and may be present in the aqueous phase as a variety of chemical species, mainly in their penta- and trivalent forms (i.e., Sb(V), As(V) and Sb(III), As(III)). These species differ in their physical and chemical properties, which determine their toxicity and bioavailability, as well as sorption affinity and chemical reactivity.

Fresh soils from the top horizon are often considered to be effective sorbing materials in remediation strategies due to the presence of a variety of reactive mineral surfaces, rich microbial diversity and availability of labile organic matter. In contrast, the retardation capacity of the deeper, clay-rich soil horizons, which tend to be more homogeneous, have been less rigorously evaluated. In this study, we contrast a published study on the mobility of Sb and As in a soil suspension [1] with new results for the same elements in an argillaceous (clay-rich) suspension. We estimate sorption affinity and speciation changes of the two contaminants in each case. We focus on the mineralogical characterization of the solid phases (XRD, ICP-OES of acid extracts), speciation of the aqueous (HPLC-ICP-OES) and solid-bound (ICP-OES of leached oxidized species) metalloids and microbial activity (adenosine triphosphate (ATP) concentrations as a proxy) over time. Inverse modeling using Excel solver and PHREEQC v.3.1.7 [2] is performed to estimate the equilibrium and kinetic parameters of the hypothesized processes controlling the fate and behavior of Sb and As [3].

Experimental conditions and scenarios. Experiments included natural solid material (soil or clay-rich) suspensions to which a mixture of oxidized aqueous contaminants (As(V) and Sb(V)) was added. The top horizon of a Mollic Fluvisol was sampled from the first flood stage of the Saône River close to the town of Trévoux (France) and suspended in river water to obtain a solid-liquid ratio of 100 g L^{-1}. A natural clay-rich formation was sampled in northern France at a depth of about 25-30 m and was suspended in artificial clay pore water solution (50 g L^{-1}). Contaminants were added to achieve initial concentrations of 50 μmol L^{-1} for soil experiments and 500 μmol L^{-1} for clay-rich experiments. Experiment “Soil I” was performed with the soil under oxic conditions and experiment “Soil II” under oscillating oxic/anoxic conditions with ethanol additions. Experiment “Clay I” included the clay-rich material, which was maintained sterile under oscillating oxic/anoxic conditions, while in experiment “Clay II” microbial activity was enhanced by adding ethanol and an inoculum of microbiota extracted from the Saône topsoil.

All batch experiments were performed using a previously described computer-controlled bioreactor system monitored using pH and E_H electrodes [4]. Redox oscillations were induced by alternate sparging with anoxic and oxic gases for consecutive periods of 7 days for a total duration of at least 7 weeks. Gaseous mixtures differed between soil and clay-rich experiments by adjusting the carbon dioxide content to represent near-surface and subsurface conditions (0.03% and 1% CO_2, respectively). Meanwhile, CO_2 fugacity was kept constant in the oxic and anoxic periods within the same experiment in order to maintain stable pH and carbonate chemistry. In Clay I experiment, strict abiotic conditions were ensured by high-temperature sterilization and addition of microbial inhibitors. In biotic experiments, microbial activity was stimulated by the addition of ethanol as electron donor and source of labile organic carbon. Ethanol was added at the beginning of every anoxic period.

Sorption on the mineral matrix. The experimental results provide us with valuable information on the im/mobilization mechanisms of Sb and As under oscillating redox conditions with two different, natural sorbent materials. Sorption affinities of Sb(V) and As(V) to the sorbent matrices were evaluated for soil and clay-rich sorbent materials in the experiments “Soil I” and “Clay I”, respectively. Sorption rate order, sorption (ks), desorption (kd) and irreversible (ki) rate constants, as well as equilibrium constants (log K), were estimated by fitting a multi-reaction model to the time series of aqueous contaminant concentrations. Modeling results suggest that sorption of both Sb and As was controlled by coupled equilibrium and kinetic reactions. The latter could be represented by first-order rate expressions. Sorption of Sb was similar for both sorbent materials and was mainly kinetically-controlled. In general, Sb was found to be more mobile than arsenic, with residual Sb(V) concentrations persisting in the solution. In contrast, the extent of As sorption was greater, but differed substantially between the two sorbent materials. For the soil, As sorption followed a two step process: fast sorption described by an equilibrium constant, followed by slow uptake. Removal of aqueous As by the clay-rich material was two orders of magnitude lower than by the soil. The zeta potential of the clay suspension was more negative than for the soil (-28 mV vs -18 mV), resulting in greater electrostatic repulsion between sorbent and dissolved oxyanions consistent with the lower sorption affinity for the clay material. The soil was likely a better sorbent for As due to a greater abundance of Fe- and Mn-oxy(hydr)oxide minerals.

Effects of redox oscillations. In the abiotic clay suspension experiment (Clay I), measured E_H values varied by less than 20 mV between oxic and anoxic periods, due to sterilization of the sorbent material and a lack of redox transformations. The E_H in Clay II experiment fluctuated over a greater range of 100 mV (from +350 mV to +250 mV), but remained suboxic throughout the experiment at pH 6.9. In contrast, in the Soil II experiment, E_H values varied between oxidizing (+500 mV) and reducing (-300 mV) conditions, with corresponding pH changes from 7.5 to 8.

In the soil suspension (exp. “Soil II”), we observed contrasting im/mobilization of aqueous Sb and As: Sb was immobilized during reducing periods and remobilized during oxic periods, while As was mobilized during anoxic periods and immobilized during oxic periods. In experiment “Clay II”, reduction of As and, to a lesser extent, Sb occurred within the first anoxic period, but subsequent oxic periods did not result in the re-oxidation or remobilization of Sb or As. Residual aqueous As concentrations were found to occur entirely as As(III), which persisted in solution for the remainder of the experiment. Sb reduction immobilized it as Sb(III), while Sb(V) was found to persist in the aqueous phase.

According to thermodynamic modelling, Sb immobilization during anoxic periods occurs due to (presumably microbial) reductive precipitation of $HSbO_2(s)$. The latter phase subsequently oxidatively dissolves during oxic periods, concurrent with the oxidation of aqueous Fe and Mn. Given that oxidation of $HSbO_2(s)$ is slow in the presence of molecular oxygen, we hypothesize that reactive oxygen species formed during Fe oxidation [5] accelerate the oxidative Sb dissolution. The mobility of As during oxic periods was predicted to be limited by the formation of surface complexes of As(V) on Fe(III) oxyhydroxides. During anoxic periods, the reduction of As(V) to As(III) resulted in the partial desorption of As(III) causing an increase in the mobile fraction of As. Due to the lack of Fe and Mn mineral sorbents in the clay material, aqueous Sb and As concentrations did not oscillate in the clay-rich suspensions during the redox cycles.

Conclusion. The results of the batch experiments highlight pronounced differences in the behavior of Sb and As under controlled, but environmentally relevant, conditions. In particular, under oscillating redox conditions, Sb and As reversibly sorb and desorb from the soil suspension, while they are irreversibly reduced and immobilized by the clay-rich material. In the soil suspension, Sb is more strongly immobilized under anoxic conditions, while the opposite is observed for As.

Acknowledgments. We acknowledge the French National Radioactive Waste Management Agency (Andra) for funding of the experimental expenses and salary of E. Markelova.

References

[1] Couture, R.-M., Charlet, L., Markelova, E., Madé, B., & Parsons, C. T., 2015: Environ. Sci. Technol., 49, 3015–3023;

[2] Parkhurst, D. L., Appelo, C. A. J., 2013: U.S. Geological Survey Techniques and Methods, 6 (43), 1−497;

[3] Zhang, H., Selim, H. M., 2005: Environ. Sci. Technol., 39 (16), 6101−6108

[4] Parsons, C. T., Couture, R. M., Omoregie, E. O., Bardelli, F., Greneche, J. M., Roman-Ross, G., & Charlet, L., 2013: Environmental Pollution, 178, 254–263;

[5] Leuz, A. K., Hug, S. J., Wehrli, B., & Johnson, C. A., 2006: Environ. Sci. Technol, 40(8), 2565–2571.

CHEMICAL FRACTIONATION OF ANTIMONY COMPARED TO ARSENIC IN WETLAND SOIL: INFLUENCE OF REDUCING CONDITIONS, NITRATES AND PHOSPHATES ADDITION

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In wetlands, the release of antimony (Sb) and arsenic (As) during soil reduction is related to several processes such as desorption, mineral dissolution and organic matter (OM) solubilization [1] [2]. Nowadays, many wetlands are exposed to agricultural activities and may be enriched with nitrates and phosphates which could impact these processes and thus the mobility of both metalloids. Our previous study showed that soil enrichment with NO_3^- and PO_4^{3-} enhanced the release of geogenic Sb and As under reducing conditions. In order to better understand which processes are involved in the release of Sb and As in NO_3^- and PO_4^{3-} enriched soil, we investigated the chemical distribution of Sb and As among the different host phases in soil before and after soil reduction through the application of a modified sequential extractions procedure (SEP) [3]. The aims of this study were to assess Sb and As fractionation during soil reduction and to identify the potential impact of nitrates and phosphates on this fractionation.

Two series of batch incubation experiments were performed during 36 days to simulate progressive soil reduction. In the first series, soil was enriched with 50 $mg.L^{-1}$ of both NO_3^- and PO_4^{3-} prior to incubation whereas in the second series, soil was not enriched. Dissolved As, Sb, Mn, Al, Fe(II) and organic carbon (DOC) as well as pH and Eh were measured during the incubation. A 6 step SEP (F1 to F6) was performed on soil sampled before (non-reduced soil) and after (strongly reduced soil) soil incubation.

In both non-enriched and enriched soil incubations, the concentrations of dissolved Sb in solution firstly increased by a factor of 7 then decreased by a factor of 3 indicating that mobilized Sb from the weakly reduced soil partly precipitated and/or was resorbed onto soil surfaces during stronger soil reduction. In the enriched soil incubation, the release of Sb was slightly higher. However, dissolved Sb concentrations reached at the end of both soil incubations were similar.

The SEP performed on the non-reduced soil showed that Sb was distributed mostly among 3 fractions: “amorphous Fe-Mn-Al (oxy)hydroxides-bound” (F4) (20%), “well cristallized (oxy)hydroxides-bound” (F5) (13%) and “organic matter-bound” (F6) (20%). The average distribution of the others fractions of Sb was: phosphate exchangeable (F2) (2%) > acetate exchangeable (F1) (1%) and carbonates-bound (F3) (<0.1%). The fractionation profile of Sb showed that F2, F5 and F6 slightly increased after 36 days of soil reduction suggesting a resorption and/or precipitation of Sb under stronger soil reducing conditions.

In the enriched soil, only the fraction bound with "organic matter" (F6) increased compared to the non-enriched soil, suggesting that the enrichment of soil with PO_4^{3-} lowered the resorption of Sb onto soil sorption sites by phosphate ions during soil reduction.

Dissolved As concentrations increased considerably during soil reduction. Even though the rate of As mobilization in the enriched soil was faster, the amounts of released As at the end of the non-enriched and enriched soil incubations were similar. The SEP performed on non-reduced soil showed that As is mainly associated with the "amorphous Fe-Mn-Al (oxy)hydroxides (F4)" which accounts for 57% of total As. The average distribution of the others fractions of As was: F2 (5%) > F5 (3%) > F6 (3%) > F1 (0.2 %) and F3 (0.1%).

After soil reduction, As was mainly mobilized from "amorphous Fe-Mn-Al (oxy)hydroxides" (F4). We also noted redistribution among As fractions under stronger reducing conditions. The amount of As in F4 decreased by 30% whereas it increased in F2, F3, F5 and F6. These findings suggest that As previously associated with "amorphous Fe-Mn-Al (oxy)hydroxides" was released into soil solution during soil reduction and then was partly resorpted and/or precipitated under stronger soil reducing conditions, thus limiting its release into soil solution. In the enriched soil, results of SEP after soil reduction showed that As was redistributed similarly to the non-enriched soil.

This work showed that the mobility of Sb under reducing conditions was restricted compared to As. Indeed, only less than 4% of total Sb in soil was released in solution against up to 20% for As. This work also showed that Sb is highly combined with organic matter in soil compared to As which exhibited a higher affinity for "Fe-Mn-Al amorphous (oxy)hydroxides".

References

[1] Mansfeldt, T., Overesch, M., 2013: Journal of Environmental Quality 42, 1130–1141;
[2] Nakamaru, Y M., Altansuvd, J., 2014: Chemosphere 111, 366–271;
[3] Javed, M B., Kachanoski, G., Siddique, T., 2013: Analytica Chimica Acta 787, 102–110;

ANTIMONY AND TOXIC METAL UPTAKE BY PLANTS GROWNING ON DRAINED AND WATERLOGGED SHOOTING RANGE SOIL

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Contamination of shooting range soils by hazardous metal(oid)s such as antimony (Sb), lead (Pb), copper (Cu), and zinc (Zn) has become an issue of public concern in various countries[1]. Remediation of such sites is difficult and expensive, so it is important that alternative management strategies and the associated risks are investigated. One such management strategy is the use of sites for animal grazing, however metal(loid) uptake by plants and thus the risks of contaminants entering the food chain are still poorly understood, especially for antimony. In particular, the effect of waterlogging, a widespread phenomenon in poorly-drained soils, has not yet been assessed on a field scale.

Here, we compared metal(loid) uptake by plants growing on moderately contaminated (Pb 500, Sb 21 mg kg^{-1}) calcareous shooting range soil under waterlogged and drained conditions, using four large outdoor lysimeters (17m^2, depth = 0.7 m). Two of the lysimeters were subjected to waterlogging with a water table fluctuating in the sub-soil according to natural rainfall infiltration[2]. Meadow vegetation was grown on the soil and shoot samples from four plant species (*Lolium perenne*, *Trifolium repens*, *Plantago lanceolata*, and *Rumex obtusifolius*) were collected at three times during the growing season. In order to understand the effect of waterlogging on metal(loid) bioavailable concentrations, soil solution samples were extracted every three to five weeks during the growing season at three soil depths (20 cm, 37 cm and 54cm). There was a strong focus on the fate of the redox-sensitive element Sb, due to the lack of knowledge about its behaviour.

At the start of sampling the lysimeters had been waterlogged for seven months and reducing conditions were established, as seen by an increase in manganese (Mn) and iron (Fe) concentrations in soil solution. Sb soil solution concentrations were greatly reduced from ~60 to ~10 µg l^{-1} by waterlogging at all depths. Pb, Cu and Zn soil solution concentrations showed a little difference between treatments at 20 cm but were similar at lower soil depths.

Antimony shoot concentrations did not differ between the drained and waterlogged treatments despite there being a large drop in Sb solution concentrations in the waterlogged lysimeters. This meant that the bioaccumulation factor for Sb was higher in the waterlogged than in the drained lysimeters. This may be due to the fact that the reduced form of antimony, $Sb(OH)_3$ is more efficiently taken up than the oxidised form $Sb(OH)_6^-$. It is hypothesised that this is due to the former being taken up by aquaglyceroporins while the latter probably follows the apoplastic uptake route. For most plants, Pb, Cu, and Zn shoot concentrations were higher in the drained treatment than in the waterlogged treatment. There was also a trend of increasing concentration of these metals in plants over the season. All plant metal concentrations were below the Swiss regulations for animal feed (Pb, Cu, Zn), and while Sb has no regulatory value it remained about background level for plants.

Thus we conclude that the risk of transfer of these metal(loids) to the food chain under these conditions is low and that it is not increased by waterlogging as long as Fe (hydr)oxide dissolution under reducing conditions remains low.

References

[1] Wan, X. M., Tandy, S., Hockmann, K., Schulin, R., 2013: Environ. Pollut. 172, 53-60;

[2] Hockmann, K., Tandy, S., Lenz, M., Reiser, R., Conesa, H. M., Keller, M., Studer, B., Schulin, R., 2015: Chemosphere. 134, 536-43;

DIFFERENCES BETWEEN ARSENIC AND ANTIMONY CONCERNING SORPTION AND BIOTRANSFORMATION

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Antimony and arsenic not only co-occur often in the environment, they show also a number of chemical similarities. Both exist in identical oxidation states -3, 0, +3, and +5 and Sb(III)/Sb(V) and As(III)/As(V) are the dominant redox pairs in aqueous solutions. The pK_{s1}-values of $Sb(OH)_3$ and $As(OH)_3$ are 11.8 and 9.2, respectively, and hence both exist as neutral solutes ($Sb(OH)_3$ and $As(OH)_3$) in aqueous solutions showing similar diameters. The pentavalent species occur as anions in neutral waters. However, there are many differences observed in the environmental behavior of both elements.

A first study was carried out the compare the sorption behavior onto iron hydroxides in single species solutions and with competitive ions [1]. The general trend for both metalloids is that the methylated species sorb much less than the inorganic ones. However, the competitive sorption shows large differences between arsenate and antimonate.

The question arises whether this has a direct influence on the bioavailability of the metalloids. Leaching test also with dynamic systems were carried out with mining affected samples having relatively high concentrations of As and Sb [2]. Surprisingly, the mobilization behavior is very similar with a little higher mobilization rates for arsenic which correlates with the higher contents.

Having a look at plants, the uptake and transfer of the metalloid specie are of interest. Pot experiments with the fern *Pteris vittata* were done with different concentration of antimony and arsenic [3]. Here the differences between the two elements are big in uptake rates as well as in transformation of the species.

References:

[1] Kolbe, F., Weiss, H., Morgenstern, P., Wennrich, R., Lorenz, W., Schurk, K., Stanjek, H., Daus, B. (2011): Sorption of aqueous antimony and arsenic species onto akaganeite, *Journal of Colloid and Interface Sciences* 357, 460 – 465.

[2] Wennrich R., Daus B., Müller K., Stärk H.-J., Brueggemann L., Morgenstern P. (2012): Behavior of metalloids and metals from highly polluted soil samples when mobilized by water - evaluation of static versus dynamic leaching.- *Environm. Pollution* 165, 59-66.

[3] Müller, K., Daus, B., Mattusch, J., Vetterlein, D., Merbach, I., Wennrich R. (2013): Impact of arsenic on uptake and bio-accumulation of antimony by arsenic hyperaccumulator Pteris vittata. *Environmental Pollution* 174, 128-133

A NOVEL TRAPPING TECHNIQUE TO QUANTITATIVELY AND QUALITATIVELY MEASURE MINUTE AMOUNTS OF STIBINE AND TRIMETHYLSTIBINE.

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High antimony (Sb) concentration in Swiss soils results from shooting activities and the associated weathering of Sb-containing ammunitions in shooting ranges. Sb can be transformed through biomethylation and biovolatilisation. These two biological mechanisms, which are not well understood, can fundamentally change the mobility, availability and toxicity of Sb, especially under reduced or flooded conditions, making soil pollution assessment in hydromorphic soils difficult. On the other hand, both processes could potentially be used for the bioremediation of contaminated soils. However, due to the inherent instability of the species involved and their presence in the environment at trace levels, very little information is available on this topic. In order to quantify and identify the volatile Sb species released into the atmosphere, (1) a HPLC-ICP-MS method for the low-level separation of inorganic and organic Sb was developed and (2) an efficient and "field-suitable" trapping method for environmentally relevant amounts of volatile organic (trimethylstibine) and inorganic (stibine) Sb species was established. To test the efficiency of the developed trapping method, a hydride generation technique was used to produce volatile Sb. The trapping liquid was composed of a mix of nitric acid and hydrogen peroxide. The recovery of the trapping set-up was 84 ± 2 % (n=3) for stibine and 102 ± 9 % (n=3) for trimethylstibine. During the trapping, the volatile species are converted to their non-volatile counterparts: Sb(III) and Sb(V) for stibine and trimethylantimony for trimethylstibine. The species in their liquid form did not convert or degrade for at least 18 days, providing sufficient time between environmental sampling and analysis. The limit of detection, based on the analysis of three procedural blanks was 1.6 ng Sb and the hydride generation of Sb was quantitative (>99.98%). Possible applications are "on-site" measurements of volatile Sb in shooting ranges, sewage sludge and waste deposits. Our final aim is to use this method to trap volatile Sb generated by soils incubated under various climatic and land-use scenarios to understand the mechanisms leading to the atmospheric release of Sb.

DEVELOPMENT OF A COLORIMETRIC METHOD FOR THE DETERMINATION OF TOTAL ANTIMONY AND ANTIMONY SPECIES IN CONTAMINATED WATERS

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Several colorimetric methods for Sb determination exist, which vary in complexity and achievable detection limits. Colorimetric methods for Sb detection have potential application in rapid response to water pollution events and quantification of Sb in waters with known high Sb concentrations in the context of mining and environmental monitoring. In this work we modified the potassium iodide based colorimetric method first developed by McChesney[1] for determining total antimony (Sb) in biological samples. The adapted method was successfully used to quantify total Sb in contaminated waters, including the historic and high concentration adit waters at Hillgrove Mine, NSW, Australia. Trialled standard ranges had a strong linear correlation (R^2 >0.99), high precision (RSD <10%) and high accuracy (approximately 100% Sb recovery) for sample concentrations >0.5 µg ml^{-1} Sb. Conversely, Sb concentrations <0.5 µg ml^{-1} produced weaker colour development and had decreased precision. The method detection limit was 0.297 µg ml^{-1} for high range Sb (0 to 25 µg ml^{-1}), 0.113 µg ml^{-1} for low range Sb (0 to 2.5 µg ml^{-1}), 0.289 µg ml^{-1} for Sb (III) and 0.173 µg ml^{-1} for Sb (V) standards. Due to the variability in colour development at lower concentrations, the practical maximum limit of reporting was considered to be 1.5 µg ml^{-1} Sb. Realistic concentrations of Ca and Fe increased Sb quantification to approximately 120%, while S and Al decreased Sb quantification to approximately 87% and between 70.3% and 92.3% respectively. Extreme levels of humic acid caused significant interference, with Sb recovery beyond 120%, but simple filtering procedures typical of field practices were shown to reduce this to acceptable levels. Field application of the colorimetric method successfully quantified Sb to within 87.8% of values recovered via ICP-MS analysis, with the advantage of being extremely rapid, and potentially field based. Preliminary work showed the method could be used to successfully separate Sb(III) and Sb(V) when applied in conjunction with SPE anionic filtering columns, and to preconcentrate Sb(V), resulting in a new potential detection limit of 0.09 ug ml^{-1}.

References

[1] McChesney, E.W., 1946. Ind. Eng. Chem. Anal. Ed. 18(2), 146-149.

ANALYTICAL INVESTIGATIONS ON THE STABILITY OF Sb(III) IN A METAL RICH BIOLEACHING SOLUTION

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Several speciation techniques for analyzing Sb(III) and Sb(V) have been developed in recent years. The application of an ion chromatographic separation coupled to the element specific detection like ICP-MS is widespread used. However, dealing with the analysis of instable redox species, the stability of the species in the sample is of special concern.

Leuz et al. [1] showed that a high Fe:Sb ratio and a low pH value comes along with a higher oxidation rate of Sb(III) by oxygen in aqueous solutions. Half-lives of Sb(III) were reported to be in the range of some minutes to hours. Taking samples in reducing environments (e.g. groundwater or seepage waters) a preservation procedure of the reduced antimony species (Sb(III)) is necessary to ensure high quality speciation results. The time span between sampling and analysis might vary between hours and several days for typical environmental sampling campaigns. Concerning the presence of Fe next to Sb(III), Daus and Wennrich [2] demonstrated a good stability of Sb(III) even for samples with high iron concentrations using EDTA as preservation agent (final concentration 20 mM), while phosphoric acid, tartrate and citric acid turned out to be not suitable as preservation agent for such samples. The EDTA forms stable complexes with Sb(III) as well as with the iron and prevent effectively the oxidation to Sb(V) by this way.

In a new project the antimony species have to be analysed in samples generated by bioleaching of material rich in metals, the so called Theisen sludge, a by-product of the copper shale smelting industry in central Germany. This leaching solution contains, among others, 227 mg L^{-1} Ca, 111 mg L^{-1} Cu, 501 mg L^{-1} Fe, 79 mg L^{-1} Mg and 2910 mg L^{-1} Zn (analysed by ICP-OES). The antimony concentrations are in the range of several hundreds of µg L^{-1}. However, the competition of so many cations for EDTA complexes might disturb the Sb(III) preservation. Therefore, the influence on the stability of Sb(III) under these conditions was investigated.

The original bioleaching sample and samples diluted by a factor of 10 with de-ionized water were used for the preservation tests. A spiking solution of Sb(III) was freshly prepared by dissolving Sb_2O_3 in de-ionized water. The leaching solution (undiluted and 1:10 diluted) with different EDTA concentrations (20, 40, 60 mM) was spiked with 100 µg L^{-1} Sb(III) each. In addition, a 1:10 diluted leaching solution without EDTA was spiked with 100 µg L^{-1} Sb(III). All samples were stored in the dark at 4 °C and analysed immediately, after 1, 3, 6, and 10 days.

Applying HPLC-ICP-MS with a Hamilton PRP-X100 column (150 mm x 2.1 mm, 10 µm) and element-specific detection (ICP-MS, Agilent 7700, m/z = 121) the Sb(III) and Sb(V) concentrations were analysed (for details of the analytical procedure see [3]) in the samples. Stock solutions of $K[Sb(OH)_6]$ and $K_2(SbO)_2C_8H_4O_{10} \cdot 3H_2O$ were used for calibration. EDTA was added to each blank and standard solution up to a final concentration of 20 mM before every measurement.

The preservation efforts failed for the original sample even for the highest EDTA concentration. The Sb(III) concentration in the 1:10 diluted leaching solution without EDTA decreased significantly within a few hours. However, the stabilization was successful for all chosen EDTA concentrations in the 1:10

diluted leaching solution. This underpins the necessity of a preservation agent and the applicability of EDTA for such purpose. The final concentration of 20 mM EDTA is sufficient to avoid the oxidation of Sb(III). The suggested procedure for samples with generally high cation concentrations is to dilute the sample first by a factor of 10 with de-ionized water and add EDTA immediately to preserve the antimony speciation. Cool and dark storage is advised as usual. The only limitation of the procedure is the presence of high enough antimony concentrations for the dilution step which is the case in our project.

References

[1] Leuz, A.-K., Hug, S.J., Wehrli, B., Johnson, C.A., 2006: Environmental Science & Technology 40, 2565-2571;

[2] Daus, B., Wennrich, R., 2014: Analytica Chimica Acta 847, 44-48;

[3] Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W., Daus, B., 2012: Fresenius Environmental Bulletin 21, 11c, 3453-3458;

SPECIATION OF INORGANIC ANTIMONY BY USING SOLID PHASE EXTRACTION IN NATURAL WATER SAMPLES BY ATOMIC ABSORPTION SPECTROMETRY

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Antimony is a ubiquitous element in the environment that has been extensively used for various industrial applications including batteries, semiconductors and fire proof textiles. Due to its toxicity and biological effects, antimony has been considered as a priority pollutant [1–3]. The permissible limit of antimony in drinking waters prescribed by the US Environmental Protection Agency (EPA) is 6 µg L^{-1}. Antimony is known to be one of the most toxic elements and has serious effects on plants, animals and human health. Inorganic compounds of antimony are more toxic than it's organic forms. Actually, the toxicity of Sb(III) is ten times higher than Sb(V), hence this expressed the importance of determination of these two ions separately.

In this presentation, speciation schemes investigated by our research group for inorganic antimony species based on solid phase extraction on amberlite XAD-8, chromosorb 102 resins have been discussed in order to speciate Sb(III), Sb(V) and total antimony in natural water samples by using atomic absorption spectrometry.

MICROWAVE ASSISTED VS. ULTRASOUND PROBE EXTRACTION FOR ANTIMONY SPECIATION IN ATMOSPHERIC PARTICULATE MATTER

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An extraction method for Sb(V) and Sb(III) speciation in airborne particulate matter (PM) collected upon quartz filters has being developed, based on microwave assisted extraction at 90 W with an 0.05 mol L^{-1} hidroxilammonium chlorhidrate solution. The analysis of the extracts was performed by coupling of high performance liquid chromatography (HPLC) with atomic fluorescence spectrometry (AFS).

The parameters optimized were the volume of the extractant (5 mL or 10 mL, depending on the Sb concentration of the samples) and the time of extraction (6 min). The proposed microwave extraction method was compared to an existing one based on ultrasound probe [1]. The purpose of the proposed method is to represent an alternative to the use of ultrasound probe, which produces a high frequency and disrupting noise during its operation that can be harmful and a possible health hazard for the operator.

Both extraction methodologies were applied to Sb spiked blanks (extracting solutions and quartz filters), and PM samples with particles of diameter lower than 10 microns (PM10) containing Sb at the ng m^{-3} level. PM10 samples were collected at an urban location of southern Spain. Similar and satisfactory results were obtained for spiked blanks with both methods. However, for PM10 samples, quantitative results considering extraction efficiency (> 95 %) were obtained only by the proposed method based on microwave assisted extraction, higher than using ultrasound probe extraction (<70%). Both Sb(V) and Sb(III) were found in the samples, Sb(V) being the main antimony species.

References

[1] Bellido Martín, A., Gómez Ariza, J.L., Smichowsky, P., Sánchez-Rodas, D., 2009: Anal. Chim. Acta 649, 191-195

ONLINE ANALYSIS OF ANTIMONY IN VARIOUS WASTEWATER STREAMS USING HYDRIDE GENERATION-AFS

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Antimony is one of the most commonly found toxic heavy metals in wastewaters due to its extensive usage in such as flame retardants, plastics, alloys, semiconductors, batteries, pigments, glassware and ceramics. Severe antimony contaminations are found in areas affected by mining activities, copper smelters and power plants. Online analysis of Sb in wastewater streams enables the possibilities of precise monitoring of the complete water treatment process and ensures the compliance with discharge regulations. However the analytical challenges remain due to the complexity of the wastewater matrix. Hydride generation is also oxidation state dependent and therefore online chemistries have to be developed to ensure accurate measurements are achieved. In this presentation, various industrial wastewater streams are successfully analysed by online analysis based on hydride generation atomic fluorescence spectrometry (HG-AFS). Detection limits of 200 ppt with linearity to 100 ppm are achievable with the online instrumentation. The results were compared and cross examined by HPLC-HG-AFS and HG-AFS methodologies after the appropriate sample treatments.

PENTAVALENT ANTIMONIALS IN THE TREATMENT OF LEISHMANIASIS

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Leishmaniasis is a parasitic disease caused by several species of the genus leishmania protozoan and intracellular parasites. The disease manifests in three major clinical forms, cutaneous, mucocutaneous and visceral. The visceral form is the most severe and is fatal if left untreated. The diseases prevail in over 98 countries and territories globally causing over 1.3 million estimated new cases annually altogether.

Pentavalent antimonials have been extensively used for the treatment of both cutaneous and visceral leishmaniasis for over seven decades. The two pentavalent antimonials in use are meglumine antimoniate and sodium stibogluconate. They are chemically similar, and their toxicity and efficacy are related to their antimonial content. As per the current manufuturing practice by the major pharmas, Meglumine antimoniate solution contains 8.1% Sb^{5+} (81 mg/ml), whereas Sodium Stibogluconate 10% Sb^{5+} (100 mg/ml). The efficacy of antimonials varies depending on the endemic region, clinical form of the diseases and the type of leishmania species. Due to high level of toxicity and other side effects, quality assurance of antimonials is a critical concern as substandard medicines can cause severe toxicity and death.

Development parasite resistance to antimonials in the Indian subcontinent has led to changing the treatment policies to other antileishmanial medicines in this south east Asia region. Although in the past few years a numbers of alternative and new treatment options are developed, still in many developing countries pentavalent antimonials are the main stay of treatment for leishmaniasis either as monotherpy or in combination with other drugs.

AMPHIPHILIC ANTIMONY(V) COMPLEX FOR ORAL TREATMENT OF CUTANEOUS LEISHMANIASIS

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Pentavalent antimonial drugs such as meglumine antimoniate (Glucantime) have been used to date in the treatment of visceral and cutaneous leishmaniasis, besides the need for parenteral administration for long periods and severe side effects. An amphiphilic Sb(V) complex was recently synthesized from octanoyl-N-methylglucamide (L8) with the purpose of enhancing the permeation of Sb(V) across biological barriers and thereby achieving topically- and orally-active antimonial drugs. The SbL8 complex was found to form kinetically stabilized nanoassemblies in water (W) and this simple aqueous dispersion exhibited antileishmanial activity when given by oral route in a murine model of visceral leishmaniasis [1]. The objective of the present work was to interfere in the structural organization of these nanoassemblies, so as to investigate its influence on the oral bioavailability of Sb and, ultimately, optimize an oral formulation of SbL8 for treatment of cutaneous leishmaniasis (CL). Interference in the structural organization of SbL8 was achieved by manipulating the solvent polarity through addition of propylene glycol (PG) to the aqueous dispersion of SbL8. The presence of 50%(v/v) PG resulted in the loss of hydrophobic microenvironment, as evidenced by fluorescence probing. However, nanostructures were still present, as shown by dynamic light scattering (DLS), small angle X-Ray scattering (SAXS) and atomic force microscopy (AFM) analyzes. A remarkable property of these nanoassemblies, as revealed by AFM and SAXS studies, is the flexibility of their supramolecular organization which showed changes as a function of solvent and substrate polarities. The formulation of SbL8 in 1:1 W:PG given orally to mice promoted significantly higher and more sustained serum levels of Sb, when compared to SbL8 in W. The same formulation, when given as repeated doses (200mg Sb/kg/day) to BALB/c mice infected with *Leishmania amazonensis*, was significantly more effective in reducing the parasite burden than SbL8 in W and, even, the conventional drug Glucantime given intraperitoneally at the same dose. In conclusion, this work introduces a new concept of polarity-sensitive nanocarrier, that was successfully applied for optimizing an oral formulation of Sb(V) for treatment of CL. Financial support: Brazilian agencies FAPEMIG, CNPq and CAPES.

Reference

[1] Fernandes FR. et al. 2013. Antimicrob Agents Chemother. 57(9), 4229–4236.

NEW ANTIMONY COMPLEXES AS POTENTIAL ANTILEISHMANIAL AGENTS AGAINST Sb(III)-SENSITIVE AND -RESISTANT PARASITES

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Hydrosoluble pentavalent antimony complexes with N-methylglucamine (meglumine antimonate or Glucantime®) or sodium gluconate (sodium stibogluconate or Pentostam®) are still first-choice medications in most developing countries to treat all forms of leishmaniasis. Because antimonial drugs require repeated parenteral injections and exert toxicities, patients frequently interrupt the treatment, causing resistant microorganisms to emerge. In this context, the World Health Organization has recommended the search for new drugs and formulations. In this work, novel organoantimony(V) complexes of the type $M(L)_2$ were synthesized, in which L = deprotonated 3-(dimethylamino)benzoic acid (HL1) or deprotonated 2-acetylbenzoic acid (HL2) and M = triphenylantimony(V) (M). Complexes, $[M(L1)_2]$ (1) and $[M(L2)_2]$ (2), were characterized by elemental analysis, IR, UV-Vis and NMR. Crystal structures of solid state complexes **1** were determined by single crystal X-ray diffraction revealing that **1** adopted five-coordinated extremely distorted trigonal bipyramidal geometry. The organometallic complexes, metal precursors and free ligands were evaluated *in vitro* for their antiparasitic activity *against Leishmania infantum* and *L. amazonensis* promastigotes and their cytotoxicity towards murine macrophages. Both organometallic complexes showed good anti-leishmanial activity (IC_{50} in the range of 2.1-14.3 µM). Organoantimony(V) complexes **1** and **2** were further assessed for their activity against antimony-resistant *L. infantum* and *L. amazonensis* promastigotes, as well as antimony-sensitive *L. Infantum* and *L. amazonensis* intracellular amastigotes in comparison to Glucantime®. **1** and **2** were active at ∼10 µM against amastigotes forms and at ∼10.0–24.0 µM concentration against antimony-resistant *leishmania* promastigotes. Both organoantimony(V) complexes were more active than Glucantime® against amastigote forms of both *Leishmania* strains. Thus, these compounds constitute promising antileishmanial drugs candidates. Financial support from Brazilian agencies CNPq, FAPEMIG and CAPES.

INORGANIC ANTIMONITE – HUMAN SKIN CARCINOGEN?

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Inorganic arsenic in drinking water is a known human carcinogen. Inorganic antimony is an animal carcinogen and a possible human carcinogen. Comparison of the actions of arsenite (AsIII) and antimonite (SbIII) revealed considerable parallels in responses of cultured human epidermal cells, a well-known arsenic target cell type, where antimonite displayed half the potency of arsenite. Both induce persistent heme oxygenase expression and suppress differentiation, while maintaining cellular proliferative potential. Both disrupt key cellular signaling pathways resulting in elevated extracellular regulated kinase (Erk) activity while preventing activation of bone morphogenetic protein (BMP), Notch and protein kinase C pathways. To further such analysis, global measurements of alterations in protein and miRNA levels in treated cells were performed to determine whether arsenite and antimonite might display commonalities indicative of similar mechanisms of action.

Shotgun protein profiling was performed using mass spectrometry of tryptic peptides obtained from whole cell extracts from untreated cells or cells treated with 3 µM sodium arsenite or 6 µM potassium antimony tartrate. Initial analysis revealed that of the ≈450 proteins reproducibly detected, nearly 10% were suppressed by each agent, and >90% of these overlapped. Among these were differentiation marker proteins such as filaggrin and keratin 10 and members of the SPRR and S100A families. Levels of nearly 5% of the proteins were increased by antimonite. Half as many were stimulated by arsenite, of which 80% overlapped those simulated by antimonite. Among the latter were glyceraldehyde phosphate dehydrogenase, ferritin heavy chain, heme oxygenase 1 and quinone reductase NQO1. Although the keratinocyte responses to the two treatments were not a complete overlap, the correspondence was high.

Results of the more sensitive next generation sequencing also indicate that inorganic AsIII and SbIII produced highly similar, although not identical, transcriptional responses in human keratinocytes. In addition to confirming effects detected at the protein level listed above, the analysis recognized an order of magnitude more differentially expressed genes. The large majority were affected in the same direction by both AsIII and SbIII. At a high level of statistical stringency ($p<0.01$) and fold change >2, comparison of the expression changes revealed a fraction of the changes that differed with the two treatments. Analysis of the differential expression may help understand differences in their biological effects.

Finally, since miRNAs have important regulatory roles in cells, alterations in miRNA expression levels were determined using real time PCR arrays. Among the 315 most highly expressed miRNAs, arsenic and antimony produced the same response for 79%. Only 4% of all expressed miRNAs were increased by these compounds while 29% were decreased and 67% were unchanged. Several of the miRNAs found to be decreased by arsenic and antimony treatments were verified by single real time PCR Taqman assays, including miR-143, miR-146a and miR-203. To investigate a potential link between suppression of mi-RNAs and differentiation markers, miR-143, miR-146a and miR-203 were separately over-expressed in cultured keratinocytes, resulting in a 4-fold increase for miR-203, 100-fold for miR-143 and 400-fold for miR-146a. While the latter two mi-RNAs appeared to accelerate cell growth, miR-203 over-expression was growth inhibitory, which may explain the relatively modest levels of miR-203 over-expression achieved. None of these miRNAs had much effect on expression of differentiation markers or on the ability of arsenic or antimony to suppress their expression. Since arsenic and antimony preserve proliferative potential while miR-203 expression results in its loss, we investigated whether the decrease in miR-203 levels by arsenic and antimony could contribute to this phenomenon. Over-expression of miR-203 resulted in the expected loss in colony forming efficiency while arsenic and antimony increased it. Over-expression of miR-203 was able to block the increased colony forming efficiency elicited by arsenic and antimony. The possibility that antimonite exposure could contribute to human skin cancer is supported by its preservation of proliferative potential as well as its reported interference with DNA repair.

RAPID PHOTOCHEMICAL OXIDATION OF Sb(III) BY Fe(III)-OXALATE COMPLEXES

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High concentrations of Antimony (Sb) detected in certain kinds of soils and waters, particularly near mining and smelter areas, industrially contaminated soils and shooting-range soils has attracted extensive attention. The environmental fate and toxicology of Sb primarily depend on its chemical speciation. Sb(III) and Sb(V) are the two common Sb inorganic forms, Sb(III) is much more toxic than Sb(V), and the latter is more mobile. Photochemical reactions involving aqueous ferrioxalate complexes are known to generate free radical species that might be able to oxidize Sb(III) to Sb(V). However, the mechanisms of Sb(III) oxidation in irradiated ferrioxalate solution are poorly understood.

In this study, the mechanisms of Sb(III) oxidation in irradiated ferrioxalate solution were investigated systematically involving the effect of pH (3-7), oxygen, free radical scavenger and Fe(II). The pH greatly influenced the photooxidation efficiencies of Sb(III) by control the speciation of Fe(III)-oxalate complexes, the cycle of Fe(III)/Fe(II) and $HO_2\bullet/O_2\bullet^-$. The photooxidation efficiency of Sb(III) was favored in acidic solutions. Molecular oxygen is the crucial factor on Sb(III) oxidation in irradiated ferrioxalate solution. •OH and Fe(IV) generated by the irradiation of ferrioxalate complexes are responsible for Sb(III) oxidation. In acidic solutions, •OH generated by the reaction of FeII(ox) and H_2O_2 is the main oxidant for Sb(III), but with the increasing solution pH, the hypothetical Fe(IV) generated by the reaction of $FeII(ox)_2^{2-}$ and H_2O_2 gradually become to be the main oxidant for Sb(III). This study shows that the irradiated ferrioxalate complexes-induced oxidation of Sb(III) can be an important oxidation pathway in surface aquatic environment.

KINETICS OF LIGAND SUBSTITUTION REACTIONS IN ANTIMONY STUDIES

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Studies and predictions in environmental studies have been mostly based on thermodynamic equilibrium assumptions. However, knowledge of the kinetics of the ligand substitution reactions involved is needed in order to understand (i) the environmental behaviour of chemical elements, (ii) the results obtained by many analytical techniques, (iii) element bioavailability and toxicity.

So far, when kinetics of ligand substitution has been taken into consideration in the environmental field, approaches have been nearly exclusively based on the so-called Eigen-Wilkins mechanism [1,2] even if its applicability to the systems under study has rarely been tested. This is partly due to the simplicity of the approach but also to the way kinetics has been presented so far in environmental textbooks [3,4] and to the fact that a reduced number of 'well-behaved' transition elements have been repeatedly considered (i.e., Cu, Cd, Pb, Zn, etc.).

The recent interest in elements heavily hydrolysed in solution (e.g., Fe in oceans in global warming studies; As, involved in massive toxic episodes; Ga, In, Ta, Nb due to their criticality) has evidenced the many limitations of the approach usually followed [5]. A gap seems to exist between what has been well-established in coordination chemistry for many years [6,7] and what has been applied in environmental chemistry. Antimony, an extensively hydrolysed element, belongs to this category of elements. Moreover, in the case of Sb, the wide-spread and increasing use of potassium antimony tartrate (PAT) as a source of Sb(III) in solution adds an additional complication to the subject. Not only the use of PAT raises the question of which of the species existing in solution is responsible of the observed effect (i.e., toxicity, absorption on solid phases, etc.) [8] but it may also introduce an unexpected kinetic effect in the response observed.

References

[1] W. Eigen and K. Tamm, Z. Elektrochem., 66, 107 (1962).
[2] M. Eigen and R.G. Wilkins, Adv. Chem. Ser., 49, 55 (1965).
[3] F.M.M. Morel and J. G.Hering, Principles and Applications of Aquatic Chemistry. Wiley, New York (1993).
[4] W. Stumm and J.J. Morgan, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters. Wiley, New York (1996).
[5] L.M. Laglera and M. Filella, Mar. Chem., 173, 100 (2015).
[6] L. Helm and A.E. Merbach, Chem. Rev., 105, 1923-1959 (2005).
[7] S.E. Lincoln, Helv. Chim. Acta, 88, 523-545 (2005).
[8] M. Filella and P.A. Williams, Environ. Toxicol., 25, 431 (2010).

BEHAVIOR OF ANTIMONY DURING THE WEATHERING OF THE TETRAHEDRITE-TENNANTITE [$Cu_{12}(Sb,As)_4S_{13}$] MINERALS

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Using samples from an oxidation zone at Špania Dolina (formerly Herrengrund) in Slovakia, we were able to characterize the behavior of antimony during weathering of tetrahedrite-tennantite (ttd-tnn) minerals and compare it to that of the other elements in this complex solid solution.

The primary mineralization consists of ttd-tnn, with a lesser amount of chalcopyrite and traces of pyrite. The ore minerals form lenses and veinlets parallel to the layering or schistosity of weakly metamorphosed Permian arcoses, with or without accompanying quartz. Secondary minerals are distributed throughout the profile sampled (~ 3 meters) and there is a distinct vertical zonality. The uppermost zone contains the Cu carbonates malachite and azurite. The bulk of the oxidation zone consists of completely or partially weathered ttd-tnn grains, replaced by olive-green "trombolite", a mixture of secondary minerals and mineraloids. The name trombolite was used for such mixtures at least since mid-19th century (e.g., [1]). The bottom of the profile is enriched by Cu sulfates, such as antlerite and brochantite. All minerals were identified by powder X-ray diffraction (XRD).

Antimony released from ttd-tnn minerals is hardly mobile and is re-located in thin veinlets which dissect the ttd-tnn grains. The electron microprobe analyses document great variability of the trombolite veinlets, with a wide range of the Sb/(Sb+As) ratio. The products identified in an optical microscope as trombolite also contains an appreciable amount of iron. According to our micro-XRD data, antimony is present there as a mixture of tripuhyite ($FeSbO_4$) and romeite-type minerals [$(Ca,Pb,Sb^{3+})Sb^{5+}{}_2O_6$]. It is not clear yet what is the exact composition of the romeite-type minerals; our micro-X-ray absorption spectroscopy (XAS) data indicate that the prevailing oxidation state of antimony is Sb^{5+}. The primary ttd-tnn minerals have always Sb/Fe ratios greater than 1 [2] and this could be possibly the reason why the romeite-type minerals appear consistently in all samples.

Our results compare well with our previous findings that Sb in mining wastes is stored in the form of tripuhyite, to a lesser extent iron oxides with adsorbed or incorporated antimony [3]. In the mine wastes with abundant stibnite, pyrite, and arsenopyrite, that is, excess of Fe over Sb, the romeite-type minerals are found very rarely. Trombolite is a complex mixture of copper sulfides, arsenates of various metals, the minerals of antimony, and possibly iron oxides. Antimony is one of the least mobile elements in that mixture, but other elements, especially Cu and S, are much more mobile.

References

[1] Zepharovich, V.v., 1873: *Mineralogisches Lexicon für das Kaiserthum Österreich*. Band II.

[2] Sejkora, J., Števko, M., Macek, I., 2013: Contribution to chemical composition of tetrahedrite from the Piesky copper deposit, the Špania Dolina ore district, central Slovakia. *Bull. mineral.-petrolog. Odd. Nár. Muz. (Praha)* 21, 89-103.

[3] Majzlan, J., Lalinská, B., Chovan, M., Bläß, U., Brecht, B., Göttlicher, J., Steininger, R., Hug, K., Ziegler, S., Gescher, J., 2011: A mineralogical, geochemical, and microbiogical assessment of the antimony- and arsenic-rich neutral mine drainage tailings near Pezinok, Slovakia. *American Mineralogist* 96, 1-13.

ANTIMONY IN SHOOTING RANGE SOIL – AN ENVIRONMENTAL PROBLEM IN SWITZERLAND

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Contamination of shooting range soil by antimony (Sb) released from corroding ammunition has become an issue of public concern in many countries. In Switzerland, up to 25 tons of Sb enter the pedosphere every year by shooting on more than 2,000 shooting ranges. Although locally restricted to small areas in most cases, contamination of shooting range soils is a major environmental problem in Swtzerland due to the high abundance of sites that now require treatment.

A key concern is the leaching of antimony from contaminated soils through the subsurface zone into ground and surface water. The latter risk is in particular given in soils subject to permanent or periodic waterlogging. Waterlogging not only leads to lateral subsurface flow, but also strongly affects soil redox potential, thereby influencing the entirety of soil chemical and biological conditions that control the transport behavior of a solute. Under aerobic conditions, Sb is stable as the monovalent anion $Sb(OH)_6^-$ (antimonate) in soil solution. Under reducing conditions, the neutral species $Sb(OH)_3$ (antimonite) becomes dominant [1]. The two species strongly differ in their affinity to iron (Fe) and manganese (Mn) (hydr)oxides. The interplay of Sb redox transformations, differential sorption and reductive dissolution of Mn and Fe (hydr)oxides during waterlogging and their effect on Sb mobility has received little attention so far, and in particular, almost nothing is known how it affects the transport behavior of Sb in water-logged soils under field conditions.

In this study, we investigated Sb leaching from contaminated soil in terms of changing redox conditions using lysimeter field experiments. In order to identify the role of specific factors and processes that affect Sb mobility, the lysimeter experiment was accompanied by laboratory batch and column experiments. The same calcareous soil collected from a large shooting range in eastern Switzerland was used throughout all experiments.

In the lysimeter experiment [2], we compared Sb leaching from four large lysimeters filled with the experimental soil under field conditions. Leachate samples and soil solution samples were taken at bi-weekly intervals. After monitoring all four lysimeters for >1.5 years under drained conditions, two of the lysimeters were subjected to waterlogging through a valve that opened when the water table exceeded a depth of 30 cm below the soil surface and closed again as soon as the water table dropped to a depth of 50 cm. Otherwise, the water table fluctuated according to natural weather conditions. The resulting soil water regime simulated that of a gley soil, which is a frequently found soil type on Swiss shooting ranges.

Antimony leachate concentrations under drained conditions showed a strong seasonal fluctuation between 110 $\mu g\ l^{-1}$ in summer and <30 $\mu g\ l^{-1}$ in winter. With the development of anaerobic conditions upon waterlogging, Sb leachate concentrations decreased to <10 $\mu g\ l^{-1}$ Sb and remained stable at this level. Antimony speciation measurements in soil solution revealed that after waterlogging, Sb leaching decreased due to the reduction of Sb(V) to Sb(III) and the retention of the latter by Fe phases.

To further understand the dynamics of Sb retention and speciation under water-logging conditions, we incubated batch microcosms with the same soil as used in the lysimeter experiment under anaerobic conditions for up to 64 days [3]. Lactate was added to some of the microcosms as an external electron donor to promote reducing conditions by enhancing indigenous microbial activity. Similar to the lysimeter experiment, the transition to reducing conditions at first led to the immobilization of Sb. However, when reducing conditions continued, previously sorbed Sb(III) was gradually released into solution due to reductive dissolution of Fe (hydr)oxides. Speciation measurements in the solid phase by X-ray absorption near edge structure (XANES) spectroscopy and in the soil solution by liquid chromatography (LC) ICP-MS provided evidence that Sb(III) predominated at low redox conditions (Eh<0.05 V) in both phases (>90%).

The soil microcosms also indicated that Sb(V) may be released with the reductive dissolution of Mn (hydr)oxides. However, the effect of Mn reduction on Sb mobility was not clearly separated from the initial desorption of Sb(V) and the concomitant reduction of Sb(V). Therefore, we also performed column experiments in order to better resolve the sequence of the postulated reduction and desorption reactions [4]. Five columns packed with the study soil were eluted for 5 days with 15 mM sodium lactate solution at a flow rate of 33 mm d^{-1}, the flow was interrupted for 37 days, and then resumed for another 4 days. With the transition to moderately reducing conditions after 1 day of flow, effluent Sb (identified as Sb(V) by LC-ICP-MS) and Mn concentrations showed a concomitant increase, providing evidence that sorbed Sb(V) was indeed released, as hypothesized, under moderately reducing conditions by reductive dissolution of Mn minerals. The release of Sb(V) was then counteracted by the reduction to Sb(III), which was first scavenged by Fe (hydr)oxides and then slowly liberated again when the redox potential further decreased to Fe-reducing conditions.

In conclusion, this study indicates that conversion of Sb(V) to Sb(III), which may take weeks to months under field conditions, but occurred within hours to days in the microcosm experiment, is an important mechanism for Sb retention in poorly drained soils in the environment. While the decrease in total dissolved Sb concentrations upon reduction of Sb(V) may indicate a reduced risk of Sb leaching from waterlogged than well-drained soils, it must be considered that Sb(III) is more toxic than Sb(V). Furthermore, the microcosm experiments indicate that prolonged duration of waterlogging could enhance Sb leaching again, as Sb(III) may be released upon reductive dissolution of Sb(III)-hosting Fe (hydr)oxides. This study also showed for the first time that Mn (hydr)oxides may play an important role for the mobility of Sb(V) in moderately-reduced soils.

References

[1] Filella, M., Belzile, N., Chen, Y.W., 2012: Earth-Science Reviews 59, 265-285.

[2] Hockmann, K., Tandy, S., Lenz, M., Reiser, R., Conesa, H. M., Keller, M., Studer, B., Schulin, R., 2015: Chemosphere 134, 536-43;

[3] Hockmann, K., Lenz, M., Tandy, S., Nachtegaal, M., Janousch, M., Schulin, R., 2014: Journal of Hazardous Materials 275, 215–221.

[4] Hockmann, K., Tandy, S., Lenz, Schulin, R., 2014: Environmental Chemistry11, 624–631;

SPATIAL DISTRIBUTION AND TEMPORAL VARIATION OF ANTIMONY IN PM10 AND PM2.5 AROUND A LARGE Sb SMELTING AREAS, SOUTHWEST CHINA

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Antimony (Sb) is a typical non-essential and toxic heavy metal, and recently has been identified as an emerging global contaminant. Moreover, research has shown that people who inhale high concentration of Sb from air for long time would develop various diseases, but it remains largely unknown of Sb in atmospheric particulate matter (APM), especially around smelting area.

APM was collected at the rooftop (approximately 10 m above ground) of a building at two sites (Site 1: next to the gate of the smelting factory, Site 2: about 3.5 km far away from the smelting factory), each lasting for 6 days from January to December 2014 in Dushan country, Guizhou province, China. Two medium volume air samplers (Laoying 2050, Qingdao Laoshan Applied Technology Research Institution, China) were used to collect PM10 and PM2.5 at each site, respectively. The quartz fiber filter (Diameter= 90 mm, Pallflex 2500 QAT-UP; Pallflex Products Co., USA) was used.

APM sample and filter were digested using a heated acid mixture (15 mL of 15 M HNO_3 and 5 mL of 10 M HF) in screw top PTFE-lined stainless steel bombs. Milli-Q water (18.2 MΩ cm) was used for all experiments, and reagents used were of super pure grades.

The contents of major elements (Fe, Al, Mn, K, Mg, Ca and Na) in APM were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP6500, Thermo Scientific, Germany). The concentrations of trace elements in APM were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer, ELAN DRC-e, USA).

Results showed that mass concentrations of PM10 ranged from 44.9 to 106.2 $\mu g/m^3$ in site 1, and from 24.3 to 98.3 $\mu g/m^3$ in site 2, respectively, which were lower than the Chinese standard level- II value (150 $\mu g/m^3$) of ambient air quality standards (GB3095-2012). Meanwhile, compared to American daily mean value standard (65 $\mu g/m^3$) and Chinese daily mean value standard (75 $\mu g/m^3$), mass concentrations of PM2.5 were also not high for site 1 and site 2. However, Sb contents in PM10 and PM2.5 were extremely high, up to 531.4 mg/kg in PM10 and 403.9 mg/kg in PM2.5 at site1. Sb contents in PM10 and PM2.5 decreased with the increase of distance from the smelting factory. At site 2, Sb contents in PM10 and PM2.5 were just <35.2 mg/kg and <29.4 mg/kg, respectively. Moreover, during suspend operation from April to July, Sb contents in PM10 and PM2.5 sharply reduced and kept in low level (<21.8 mg/kg in PM10, <18.0 mg/kg in PM2.5), which suggested that Sb contents in APM were strongly impacted by the smelting activities.

ANTIMONY IN WASTE: MOBILITY IN DIFFERENT WASTES FROM VARIOUS WASTE HANDELING FACILITIES

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Increased use of antimony (Sb) in plastics and other products has resulted in an increased and often uncontrolled release of Sb compounds into the environment. Waste handling facilities can be a substantial source of Sb emissions to their surrounding environment, though such data is scarce. In the EU the supply of antimony is considered to be of critical importance, due to its economic importance and to its relatively high supply risk related to flame retardant and micro capacitors. It is important to understand how much antimony ends up in different types of waste handling facilities, and their environmental emissions.

This study presents a systematic field investigation of Sb concentrations in diverse types of waste from waste handling facilities in Norway [1]. The wastes included were; waste electrical and electronic equipment (WEEE), glass, vehicle fluff, combustibles, bottom ash, fly ash and digested sludge. The highest solid Sb concentrations were found in WEEE and vehicle plastic (1452 ±746 mg kg^{-1}) and vehicle fluff (1245 ± 4680 mg kg^{-1}). The type of acid used to digest the diverse solid waste materials was also tested. It was found that HNO_3:HCl extraction gave substantially lower, non-quantitative yields compared to HNO_3:HF. The highest water-leachable concentration for wastes when mixed with water at a 1:10 ratio were observed for plastic (1.34 ±0.79 mg kg^{-1}) and bottom ash (0.61 ±0.13 mg kg^{-1}). For all of the considered waste fractions, Sb(V) was the dominant species, even though Sb(III) as Sb_2O_3 is mainly used in plastics and other products, indicating rapid oxidation in water.

Antimony concentrations in leachate at waste handling facilities were investigated using both active grab samples and Diffusive Gradient in Thin Films (DGT) passive samples. Grab samples target the total suspended Sb concentration, whereas DGT targets the free- or chemically labile concentration. The results from grab sample concentrations (from 0.5 to 50 µg L^{-1}) were lower than the predicted no-effect concentration of 113 µg L^{-1}. The DGT concentrations were substantially lower (from 0.05 to 9.93 µg L^{-1}) than the grab samples, indicating much of the Sb is present in non-available colloidal form. In addition, air samples were taken from the chimney and areas within combustible waste incinerators, as well as from the vent of a WEEE sorting facility.

This work is a part of the research project WASTEFFECT funded by the Norwegian Research Council where the main goal is to develop robust waste emission and exposure models for waste regulators and companies to anticipate and reduce risks from emerging contaminants. One of the main part of the project is to determine how emerging contaminants behave in different waste streams, like landfilling, incineration and recycling. Priority contaminants included in this project are brominated flame retardants (BFRs), PCBs, bisphenol A along with antimony.

References

[1] Okkenhaug, G., Almås, Å.R, Morin, N., Hale, S., Arp, H.P.H, 2015: Submitted to Environmental Science Processes & Impacts.

GEOCHEMISTRY AND DISTRIBUTION OF ANTIMONY IN MINE TAILINGS OF ZIMAPÁN (HIDALGO, MÉXICO)

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Zimapán mining district has a complex sulphide mineralization containing Fe, Pb, Zn, Sb, As, Cu and Ag. The most abundant sulphides are sphalerite (ZnS) and galena (PbS) followed by pyrite (FeS_2), arsenopyrite (FeAsS), pyrrotite (Fe1-xS) chalcopyrite ($CuFeS_2$) and numerous sulphosalts. The occurrence of Pb-Sb sulphosalts is notable in this deposit, being boulangerite ($Pb_5Sb_4S_{11}$) and jamesonite ($Pb_4FeSb_6S_{14}$) the most common[1]. The mining development started in 1632 and has been one of the most important economic activities in the area[2]. However, mining tailing disposal has led to several environmental issues as soil pollution and contamination of streams and groundwater.

Besides natural sources, mining activities are one of the major anthropogenic source of antimony in the environment[3]. In Mexico there are few studies concerning the contents, behavior and geochemical processes that control the Sb distribution in mine wastes.

The aim of the present research is to study the distribution of antimony in primary minerals and mine tailings in order to assess the geo-availability of Sb in the environment. Samples were taken from historic and recent mine wastes within an ore processing plant. The mineralogy of tailings was studied by X- ray diffraction (XRD) and the total content of Sb and other metal was analyzed by X-ray fluorescence. Sb minerals in parental rocks were identified by SEM (scanning electron microprobe). Mineralogical characterization is essential to establish the solid phases where Sb could associate.

References

[1] Simons, Frank S. y Mapes, 1956. Geology and ore Deposits of the Zimapán Mining District, State of Hidalgo Mexico. Geological Survey Professional.

[2] Armienta, M.A., Villaseñor, G., Cruz, O., Aguayo, A., Morton, O., 2012. Geochemical processes and mobilization of toxic metals and metalloids in an As-rich base metal waste pile in Zimapán, Central Mexico. Applied Gechemistry 27, 2225-2237.

[3] Levresse, G., Lopez, G., Tritlla, J., López, Cardellach.E., Chavez, Carrillo. A.,Salvador, Mascuñano. E., Soler, A., Corbella, M., Sandoval,Hernández, G.L., Esquivel-Corona, R., 2012. Phytoavailability of antimony and heavy metals in arid regions: The case of the Wadley Sb district (San Luis, Potosí, Mexico). Science of the Total Environment 42-428, 115-125.

MOLECULAR BIOLOGY OF ARSENIC AND ANTIMONY TOXICITY AND TOLERANCE: LESSONS LEARNED FROM YEAST

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Arsenic [As] and antimony [Sb] are toxic metalloids that are naturally present in the environment, and long-term exposure can cause a range of human diseases. In addition, As and Sb have long histories of usage as chemotherapeutic agents and are important constituents of currently used pharmacological drugs. The impact of these metalloids on the environment and human health underscores the importance of elucidating toxicity and tolerance mechanisms. For about 15 years now, my team has investigated (i) transport proteins through which As/Sb enter or leave cells, (ii) signal transduction and transcriptional regulatory mechanisms that cells use to sense and respond to As/Sb, and (iii) proteins and cellular processes that are targeted by As/Sb. We use budding yeast (*S. cerevisiae*) as a powerful eukaryotic model organism to elucidate fundamental aspects of metalloid biology and as a heterologous expression system to study tolerance factors from other organisms such as plants, parasites and mammals.

This presentation will highlight some of our key achievements including; (i) the first demonstration that aquaporins constitute major entry pathways for As and Sb into eukaryotes such as yeast and plants [1, 2]. Defining the routes of metalloid entry into cells is imperative for understanding the biology of these agents as causative and therapeutic agents of disease, and has important implications for human health. Moreover, this discovery is an important step for engineering ‘safe’ crop plants that do not accumulate As. (ii) My team demonstrated that stress-activated protein kinases regulate aquaporin-mediated metalloid transport and tolerance in yeast and the parasite *Leishmania* [3, 4]. This finding suggests that pharmacological modulation of stress-activated protein kinase activity may be an effective way to sensitize cells and to reverse metalloid resistance by increasing influx. (iii) We recently demonstrated that As interferes with protein folding and triggers widespread protein aggregation in living cells [5, 6]. This novel mechanism of As toxicity may explain its suggested role in the pathogenesis of protein folding disorders associated with As poisoning.

References

[1] Wysocki, R., Chéry, C.C., Wawrzycka, D., Van Hulle, M., Cornelis, R., Thevelein, J.M., Tamás, M.J., 2001: Mol Microbiol 40, 1391-1401;

[2] Bienert, G.P., Thorsen, M., Schussler, M.D., Nilsson, H.R., Wagner, A., Tamás, M.J., Jahn, T.P., 2008: BMC Biol 6, 26;

[3] Thorsen, M., Di, Y., Tangemo, C., Morillas, M., Ahmadpour, D., Van der Does, C., Wagner, A., Johansson, E., Boman, J., Posas, F., Wysocki, R., Tamás, M.J., 2006: Mol Biol Cell 17, 4400-4410;

[4] Mandal, G., Sharma, M., Kruse, M., Sander-Juelch, C., Munro, L.A., Wang, Y., Vilg, J.V., Tamás, M.J., Bhattacharjee, H., Wiese, M., Mukhopadhyay, R., 2012: Mol Microbiol 85, 1204-1218;

[5] Jacobson, T., Navarrete, C., Sharma, S.K., Sideri, T.C., Ibstedt, S., Priya, S., Grant, C.M., Christen, P., Goloubinoff, P., Tamás, M.J., 2012: J Cell Sci 125, 5073-83;

[6] Ibstedt, S., Sideri, T.C., Grant, C.M., Tamas, M.J., 2014: Biol Open 3, 913-923;

IDENTIFICATION OF A BACTERIAL ANTIMONITE OXIDASE IN AGROBACTERIUM TUMEFACIENS

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Antimony (Sb) and its compounds are listed by the United States Environmental Protection Agency (USEPA, 1979) and the European Union (CEC, 1976) as a priority pollutant. Microbial redox transformations are presumed to be an important part of antimony cycling in nature; however, regulation of these processes and the enzymology involved are unknown. In this study, comparative proteomics and reverse transcriptase-PCR analysis of Sb(III)-oxidizing bacterium Agrobacterium tumefaciens GW4 revealed an oxidoreductase (anoA) is widely distributed in microorganisms, including at least some documented to be able to oxidize Sb(III). Deletion of the anoA gene reduced Sb(III) resistance and decreased Sb(III) oxidation by ∼27%, whereas the anoA complemented strain was similar to the wild type GW4 and a GW4 anoA overexpressing strain increased Sb(III) oxidation by ∼34%. Addition of Sb(III) up-regulated anoA expression and cloning anoA to Escherichia coli demonstrated direct transferability of this activity. A His-tag purified AnoA was found to require NADP(+) as cofactor, and exhibited a Km for Sb(III) of 64 ± 10 µM and a Vmax of 150 ± 7 nmol min(-1) mg(-1). This study contributes important initial steps toward a mechanistic understanding of microbe-antimony interactions and enhances our understanding of how microorganisms participate in antimony biogeochemical cycling in nature.

RELEASE OF ANTIMONY FROM SEDIMENTS INTO THE PORE WATER IN INCUBATION EXPERIMENTS: HIGH RESOLUTION MICROPROFILING AND FRACTIONATION

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Results on the pore water concentration of antimony in different laboratory scale incubation experiments with sediments are presented. The incubation experiments addressed questions on the redox dependent release of Sb as well as on fractionation aspects. Two different experiments were conducted: (i) a microprofiling and micro sampling system (Missy) and (ii) a slurry/suspension reactor. Results presented are an excerpt from bigger datasets including also analytes like arsenic, iron or manganese and hence enabling a comprehensive presentation/interpretation on potential release and sorption mechanisms in sediment-water systems. Besides the metal(loid)s concentration, experiment specific parameters like O_2 concentration, pH and redox values were measured. In all experiments a sieved (<2 mm), shock frosted and freeze-dried freshwater sediment was used (river Lahn, Germany).

The pore water samples were obtained via direct suction-based filtration using a PES hollow fiber membrane (0.45 µm). Element concentrations were determined by means of ICP-MS. In a second study, two fractionation methods were applied to samples taken in a Missy experiment: besides the pore water total "dissolved" content (<0.45 µm); the ultrafiltration fraction (UF) and a cloud point extractable fraction (CPE) were analyzed. After sampling, all preparation steps were performed in a glove box in an Argon-atmosphere in order to avoid changes in fractionation patterns caused by, e.g. the formation of iron (hydr)oxides.

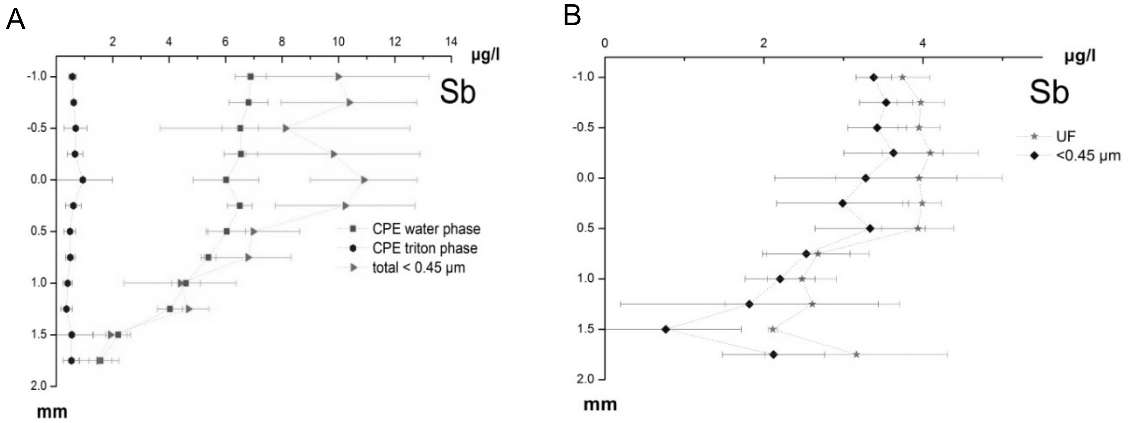

Figure 1: (A) cloud point extraction based micro profiles and (B) ultrafiltration (<3 kDa) based micro profile. <0.45 µm equals the total "dissolved" fraction based on the universal convention. Again, negative values display the distance from the sediment surface in the overlaying water.

Figure 1 displays examples (A) of CPE based antimony profiles and (B) of UF based profiles in comparison to the total "dissolved" content. The results of both fractionation methods show that almost no colloidal fraction with the upper cut-off of 0.45 µm is present in the sediment pore water. An explanation why the UF fraction concentration shown in B is not a methodological artefact will be given in the presentation.

As an example from the slurry reactor experiment, the pore water concentration of arsenic and antimony are shown in Figure 3. The sediment was rewetted in the reactor (200 g of sediment plus 1.4 L of water) and, after a preparatory period, the stirred suspension was forced to predefined redox conditions via the automated addition of either N2 (g) or air (target values/achieved value (time steps): 300/313 (0 d), 200/197 (3 d), 0/-8 (5 d), -100/-102 (18 d) and 0/-6 mV (20 d)). The results shown in Figure 2 demonstrate that the redox-dependent release of antimony and arsenic from this sediment via different fractions of the pore water were unequal.

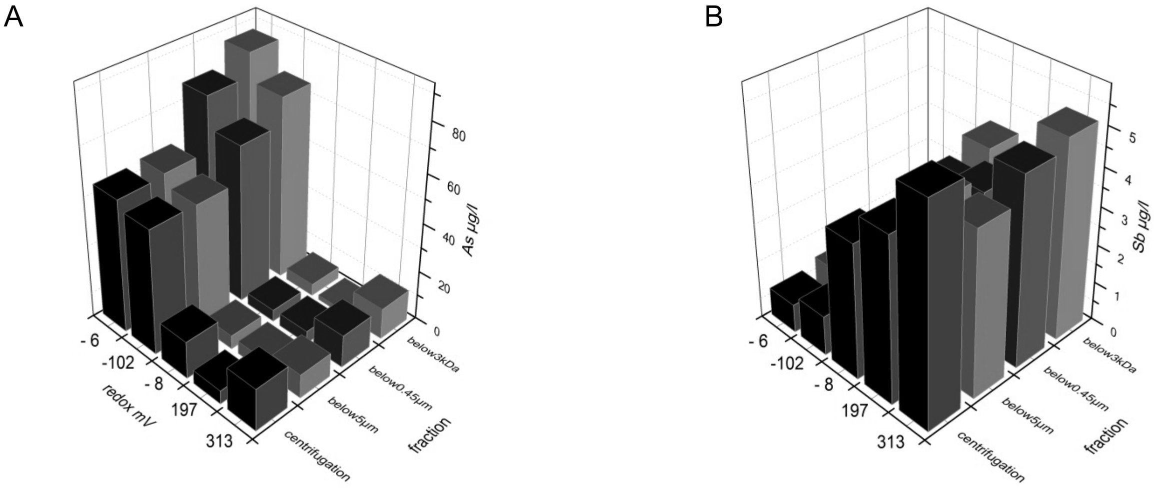

Figure 2: Concentrations of (A) arsenic and (B) antimony in sediment pore water fractions from a slurry incubation experiment with native unpolluted sediment. The way of illustration of the opposing trends of the metalloid concentrations in the pore water fractions under the different redox conditions is chosen to enable a comparison at a glance.

References

[1] Fabricius, A.-L., Duester, L., Ecker, D., Ternes A. T. 2014: Environmental Science and Technology 48(14):8053-61, doi: 10.1021/es501814b

Sb(III) AND Sb(V) UPTAKE BY DIFFERENT PLANTS UNDER HYDROPONIC CONDITIONS

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As a hardening agent in lead bullets, Sb is becoming a major contaminant in shooting range soil of some countries including Switzerland. Due to mining activities, antimony contamination is also a large problem in developing countries like China and Bolivia. Because of its high mobility, there may be a great risk of Sb transfer from contaminated soils to plants, and then the food chain. In soils, metallic Sb is rapidly oxidized to one of the two oxidation states, Sb(III) and Sb(V), which can interchange depending on soil redox conditions. Many Sb contaminated soils are temporarily or permanently waterlogged and as a result of inhibited soil aeration can show large temporal and spatial variability in Sb redox states. Little is known about how such conditions affect Sb uptake by plants growing on these soils.

In order to compare Sb(III) and Sb(V) plant uptake in a variety of agricultural plant species, we grew Lolium perenne, Helianthus annuus, Oryza sativa, Tritium aestivum, Hordeum vulgare, Secale cereale and Holcus lanatus for 4 weeks in nutrient solution without Sb and then for 8 days in nutrient solution containing either Sb(III) or Sb(V). The experimental solutions were renewed every two days and monitored for dissolved oxygen and Sb redox speciation (HPLC-ICP-MS). After harvest, all shoots and roots were washed, dried, ground and digested for elemental analysis (ICP-MS and ICP-OES).

When plants grew in Sb(III) solutions, antimony concentrations were around 100 times higher in roots (300-900 ppm) than in shoots (1-5 ppm), while in Sb(V) solutions, root concentrations (20-70 ppm) were only around 10 times higher than shoot concentrations (1-6 ppm). This may be due to the different chemical forms of Sb(III) and Sb(V) in aqueous solutions. Sb(III) forms the neutral species Sb(OH)3, whereas Sb(V) forms Sb(OH)6- anions. Antimony concentrations in shoots were higher from Sb(III) solutions than Sb(V) solutions in all plants except H. lanatus. It is thought that Sb(III) is readily taken up as Sb(OH)3via aquaglyceroporin channels. The uptake pathways of Sb(V) are still unknown. The fact that H. lanatus behaved differently to all the other plants in this study with regards to Sb concentration in shoots makes it an interesting species for further work on Sb uptake by plants. This maybe because H. lanatus has different antimony uptake mechanisms compared to other plants or the presence of an efflux system.

As there is an assumption that Sb uptake connects to the formation of iron plaque in root surface, now we are trying to find a timetable and optimized conditions for iron plaque formation of targeted plants under hydroponic environment.

USE OF ANTIMONY AND ANTIMONY COMPOUNDS IS SAFE FOR HUMAN HEALTH AND THE ENVIRONMENT

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Introduction

Antimony and antimony compounds are used in many applications in today's society. Antimony metal is used in the production of metal alloys (lead-acid batteries, foils, ammunition, semiconductors…) and the manufacture of antimony compounds. Antimony trioxide is the dominating antimony compound on the market, representing >90% of the worldwide tonnage, with widespread uses as flame retardant synergist or as catalyst in PET production, in the pigment and glass industry…

International assessments of antimony and antimony compounds

The safety of antimony and antimony compounds has often been subject to debate. Over the past 10 years, a lot of scientific work has been performed worldwide to assess the safety of these chemicals for human health and the environment. These assessments have historically focused on antimony trioxide because of its dominance in the worldwide market.

The first 'recent' risk assessment was done in the EU ('EU-RAR') following the publication of antimony trioxide on the 4th priority list of the Existing Substance Regulation 793/93/EC in 2000. In view of (i) the many critical shortcomings of existing data in the public domain, as well as (ii) essential data gaps, the International Antimony Association (i2a) provided additional data to allow for a complete and conclusive risk assessment, with Sweden as rapporteur Member State. The final version of the EU-RAR[1] was accepted May 2008. The hazard data of the EU-RAR were approved by the OECD members under the SIAP program in October 2008[2]. The conclusions of the EU-RAR have also been reviewed and copied by the Canadian (2010)[3], Dutch (2011)[4] and US (2014)[5] governments.

i2a and the EU-REACH Regulation

Since 1 June 2007, the EU has implemented one of the strictest chemical legislations worldwide: the REACH Regulation (EC) 1907/2006. This Regulation obliges companies manufacturing or importing chemical substances into the EU in quantities ≥1 **ton** per year to register these substances with the **European Chemicals Agency**. The aim of REACH is to ensure the protection of human health and the environment from the risks that can be posed by chemicals. The burden of proof of the chemicals' safety lies with industry, with the relevant EU Regulatory Bodies checking the submitted registration dossiers and taking the appropriate actions if required.

For the REACH registration of antimony trioxide in 2010, and during the dossier updates thereafter, the data of the EU-RAR have been reviewed by i2a. This review has elucidated that the data are still appropriate. Next to antimony trioxide, i2a has prepared REACH dossiers for seven other substances:

-antimony metal
-three Sb(III) substances (antimony trisulfide, antimony tris(ethylene glycolate) and antimony trichloride), and
-three Sb(V) substances (antimony pentoxide, sodium hexahydroxoantimonate and sodium antimonate(A)).

For the purpose of REACH, a whole series of physicochemical, environmental and human health data have to be gathered or generated for each chemical substance for which a dossier needs to be prepared. Therefore, i2a has gathered and reviewed all relevant international scientific publications, and performed new studies for endpoints lacking critical information (according to OECD guidelines and GLP compliant). To ensure only high quality scientific data are used to assess chemical safety, a thorough review process of the scientific literature has been performed[6]. By using study quality indicators, the regulatory process ensures that data quality is established and documented.

As mentioned in the EU REACH text, information on intrinsic properties of substances may also be generated using information from structurally related substances. For the latter, intelligent ‘grouping’ strategies were applied, allowing for ‘read-across’ of information from a reference substance to the other group members. Within i2a, critical substance characteristics were determined, compared and interpreted, and i2a’s substances are grouped as poorly water soluble Sb(III) substances (incl. antimony metal) with antimony trioxide as major reference substance and highly water soluble Sb(V) substances with sodium hexahydroxoantimonate as major reference substance.

Hazard assessment of antimony and antimony compounds

The i2a grouping strategy allowed read-across of data from the two reference substances to the other substances within the read-across group so that all human health endpoints were covered with scientific information. Based on the hazard assessments performed in the EU-RAR and for the EU-REACH registration dossiers, a brief overview will be provided of the critical threshold concentrations for the various human health endpoints and the associated classifications according to the CLP Regulation (EC) 1272/2008 at the *3rd International Workshop on Antimony in the Environment.* Key conclusion is that, based on scientific evidence, antimony trioxide requires a classification as Carcinogen cat2 ‘*Suspected of causing cancer via inhalation*’. No classification for other human health hazards are required. For precautionary reasons, this hazard classification is read-across to other chemicals in the group. Antimony tris(ethylene glycolate), antimony metal (massive) and the Sb(V) substances are not classified for human health hazards based on today’s scientific evidence.

For environmental health, the effects of antimony are expected to be exerted through dissolved antimony ions. Antimony prevails as Sb(III) and Sb(V) in the environment, and both Sb(III) and Sb(V) ions hydrolyze easily. Even though the dominant species in oxic waters is Sb(V), Sb(III) has been detected in concentrations much above what is predicted, and the reverse is true for Sb(V) in anoxic systems[7]. Because environmental conditions control the behavior of dissolved antimony in water, sediment and soil, regardless of the antimony compound added, toxicity data for antimony and all antimony compounds were considered useful for deriving threshold concentrations. As for human health, an overview will be provided of the critical threshold concentrations for the various environmental endpoints and the associated classification criteria according to CLP at the *3rd International Workshop on Antimony in the Environment*. Key conclusion is that antimony and the antimony compounds considered do not need to be classified for environmental hazards based on today's scientific evidence.

Risk assessment of antimony and antimony compounds

Using the hazard data for human health and environment, and comparing with measured or conservative estimates, a risk assessment was performed for antimony trioxide in the EU-RAR and for antimony and antimony compounds considered under EU-REACH. The risk assessments cover all industrial, professional and consumer uses identified by the members of i2a for the entire life-cycle. The risk assessments show that all uses are safe for human health and the environment, and that none of the uses identified pose a risk to the health of workers, consumers and the environment throughout the entire life-cycle.

Conclusion

Many years of experience have demonstrated the safety and efficacy of antimony and antimony compounds. The safety has been confirmed in assessments, performed by many authorities, and in the EU REACH dossiers. Using high quality scientific data, and comparing the therefrom derived critical threshold concentrations with human and environmental exposure data, it has been demonstrated that antimony and antimony compounds can be safely used as flame retardant synergist, as PET catalyst, in alloys/glass/pigments/ceramics… As such, there are no scientific reasons to avoid or replace antimony and antimony compounds for the uses identified.

References

[1] EU 2008 - **http://echa.europa.eu/documents/10162/553c71a9-5b5c-488b-9666-adc3af5cdf5f**
[2] OECD 2008 - **http://webnet.oecd.org/Hpv/UI/handler.axd?id=13e93c97-6605-4eac-961f-8af23cc6ad32**
[3] Environment and Health Canada 2010 - **https://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=9889ABB5-1#a1**
[4] DECOS 2011 - **http://www.gezondheidsraad.nl/sites/default/files/201133_Antimony_and_compounds.pdf**
[5] US EPA 2014 - **http://www.epa.gov/oppt/existingchemicals/pubs/ATO%20RA_%288-28-14%29_FINAL.PDF**
[6] Klimisch et al. 1997 Regul Toxicol Pharmacol. 25, 1-5
[7] Skeaff et al. 2013 Integr Environ Assess Manag 9, 98-113

POSTERS

(in alphabetical order of the first author)

ANTIMONY GEOCHEMISTRY AND BIOAVAILABILITY AT A FORMER MINING SITE

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Mining activities generate metal and metalloid (As, Sb, Cd, Cu, Pb, Zn…) containing wastes. Alteration, weathering and erosion of such materials contribute through oxidation, reduction, dissolution to the dispersion of these elements in soils, aquifers and in biota raising environmental concern. Abiotic alteration of metallic wastes is often studied (1-6). However biological processes can also govern metal and metalloids mobility and toxicity. Vegetation cycle can mobilize metals and geomicrobiology studies show that microorganisms activity influences mineral dissolution and secondary phases formation (7-11). Moreover, in the case of metalloids, microbial metabolisms allows detoxification and aerobic or anaerobic energy production, well described in the case of arsenic but far less for antimony (12-14). Antimony is extensively used in industrial processes (semi conductors, flame retardants, PET catalysts...) and is presently considered as a strategic element for economic activity development, which implies antimony mining development. However it is needed to consider environmental and human safety with regards to the dispersion of this element resulting from waste storage. Former antimony mining sites are appropriate to study antimony dispersion and the processes involved. The Brioude-Massiac district is the largest mine district in France, in which La Bessade mine and waste disposal site remain accessible and was chosen to investigate antimony environmental fate and associated mechanisms through a multi-compartment and interdisciplinary work (15). In La Bessade, antimony rich metallic wastes were dumped on open pits between 1760 and 1968 when the activity ceased, and for from then on underwent alteration processes.

A preliminary field study was undertaken to first described Sb distribution and collect environmental samples in order to isolate putative adapted microflora. Global area approximates 20,000 m^2, with highly variable plant cover (from forest to nude soil) and As/Sb soil contents as indicated after X-fluorescence measurements. In such heterogeneous environment, we were able to define 4 sampling sites. For each site, the surface horizon (0-10 cm) was collected for As/Sb analysis (amount, chemical fractionation, speciation) and micro-organism biomass and diversity determination. In parallel, plant diversity was assessed as well as As/Sb in biomass (roots, green and dead leaves) and endophyte root fungi determined. Additionally, soil sample from deeper horizons (10-40 cm, 40-50 cm, 50-60 cm) of one site as well as exhaure and downstream water and sediments were characterized for As/Sb concentrations and microbiological parameters.

As expected, results indicate extremely variable As/Sb concentrations in the 4 soil sampling sites. The highest As and Sb concentrations were found at the non vegetated site (6220 mg/kg DW and 113333 mg/kg DW respectively and almost 70% of disposed materials was found in fine size fraction (<2mm). According to sequential extraction procedure (16), about 16% of As and 2% Sb had be exchanged by sulfate and almost 5% and 1% of As and Sb by phosphate. This means that 21% and 3% of As and Sb can be leached from site in anionic form. At this site about 21+/-0.5% of As and Sb can be mobilized by dissolving of amorphous and/or crystalline Fe/Mn/Al (oxy)hydroxides and about 2+/-0.5% by destruction of organic or sulfidic compounds.

In vegetated sites, As and Sb concentrations were lower and reached depending on the site 95-3730 mg/kg DW and 940-33033 mg/kg DW respectively. Fine fraction decreased by comparison to nude soil (between 44 and 60%). According to sequential extraction between 6+/2% of As and 0.8+/-0.4% of Sb can be leached in anionic form, 61+/-5 of As and 35+/-4% of Sb can be mobilized by dissolving of amorphous and/or crystalline Fe/Mn/Al (oxy)hydroxides and 6+/5 % of As and 6+/6 % of Sb by destruction of organic or sulfidic compounds. The presence of vegetation relocated As/Sb distribution in soil compartments. A relative As/Sb enrichment in “Fe/Mn/Al (oxy)hydroxides” and “organic matter” pool (to a lesser extend) and important decrease in “sorbed” pool in surfaces soil horizons compared to non vegetated site suggest the role of plants and associated rhizosphere biomass in As/Sb cycling.

On the sampling site where As and Sb concentrations reached the highest values, no plant established. On the 3 other sites, forty one plant species were identified among which seven tree species were counted. Moreover, a significant transfer to roots and aerial parts of herbaceous species was demonstrated, roughly depending on soil As/Sb bulk concentrations. For tree species, As/Sb transfer to green and dead leaves was highlighted. The presence of endophyte fungi isolated from plant roots associated with different metalloid contamination level, raises the question of their role in plant metalloid resistance.

References

1.Goienaga, N., et al., *Micro-Raman spectroscopic identification of natural mineral phases and their weathering products inside an abandoned zinc/lead mine.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2011. 80(1): p. 66-74.

2.Murciego, A., et al., *Study of arsenopyrite weathering products in mine wastes from abandoned tungsten and tin exploitations.* Journal of Hazardous Materials, 2011. 186(1): p. 590-601.

3.Stromberg, B. and S. Banwart, *Weathering kinetics of waste rock from the Aitik copper mine, Sweden: scale dependent rate factors and pH controls in large column experiments.* Journal of Contaminant Hydrology, 1999. 39(1,Äì2): p. 59-89.

4.Courtin-Nomade, A., et al., *Arsenic in iron cements developed within tailings of a former metalliferous mine* Enguialès, *Aveyron, France.* Applied Geochemistry, 2003. 18(3): p. 395-408.

5.Hudson-Edwards, K.A., et al., *Processes of formation and distribution of Pb-, Zn-, Cd-, and cu-bearing minerals in the tyne basin, Northeast England: Implications for metal-contaminated river systems.* Environmental Science and Technology, 1996. 30(1): p. 72-80.

6.Parsons, M.B., et al., *Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California.* Applied Geochemistry, 2001. 16(14): p. 1567-1593.

7.Yin N.-H., Sivry Y., Avril C., Borensztajn S., Labanowski J., Malavergne V., Lens P.N.L., Rossano S., van Hullebusch E.D., (2014): *„Bioweathering of lead blast furnace (LBF) metallurgical slags by Pseudomonas aeruginosa”,* International Biodeterioration & Biodegradation 86(C), 372-381

8.Willscher S., Bosecker K. (2003): *„Studies on the leaching behaviour of heterotrophic microorganisms isolated from an alkaline slag dump”.* Hydrometallurgy 71, 257–264

9. Gadd G. M. (2010): *„Metals, minerals and microbes: geomicrobiology and bioremediation”.* Microbiology 156, 609-643.

10.Schippers, A., et al., *The biogeochemistry and microbiology of sulfidic mine waste and bioleaching dumps and heaps, and novel Fe(II)-oxidizing bacteria.* Hydrometallurgy, 2010. 104(3,Äì4): p. 342-350.

11.Wakelin, S.A., et al., *Bacterial communities associated with a mineral weathering profile at a sulphidic mine tailings dump in arid Western Australia.* FEMS Microbiology Ecology, 2012. 79(2): p. 298-311.

12.Halter D., Cordi A., Gribaldo S., Gallien S., Goulhen-Chollet F., Heinrich-Salmeron A., Carapito C., Pagnout C., Montaut D., Seby F., Van Dorsselaer A., Schaeffer C., Bertin P.,Bauda P., Arsene-Ploetze F. Taxonomic and functional prokaryote diversity in mildly arsenic contaminated sediments. Res Microbiol. 2011 Nov;162(9):877-87.

13. Heinrich-Salmeron A , Cordi A. , Brochier-Armanet C., Halter D., Pagnout C., , Abbaszadehfard E., Montaut D., Seby F., Bertin P., Bauda P**.,** Arsene-Ploetze F. The widespread distribution of the *aoxB* gene in bacteria results from horizontal gene transfer. *Appl Environ Microbiol. 2011 Jul;77(13):4685-92.*

14. Cordi A., Pagnout C., Poirel J., Devin S., Billard P., Bauda P. Physiological and molecular characterization of a culturable arsenic-resistant bacterial community. Environmental Science and Pollution Research, E pub 27 février 2015, DOI: 10.1007/s11356-014-3840-5

15. Brill H. (1983). Etude métallogenique des minéralisations a antimoine et associées du district de Brioude-Massiac (Massif Central Français): conditions géochimiques de dépôt; implications génétiques. Annales Scientifiques de l'Université de Clermont-Ferrand II. vol 35, 340 p.

16. Müller K., Daus B., Morgenstern P., Wennrich R., (2007). Mobilization of Antimony and Arsenic in Soil and Sediment Samples - evaluation of different leaching procedures. Water Air Soil Pollution 183: 427-436.

GEOCHMICAL CHARACTERIZATION OF COLLOIDS FROM MINE DRAINAGE WATERS AND THEIR ROLE IN Sb AND As TRANSPORT

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Mine drainage waters are typically filtered to < 0.45 µm to determine the concentration of potentially toxic elements. Elements in this fraction are considered to occur as a dissolved species. In fact, the fraction < 0.45 µm typically represents a mixture of inorganic and organic colloids, and "truly" dissolved ions. It is important to distinguish colloidal from dissolved species as this affects the mobility, bioavailability and toxicity of metal(loid)s. We have sampled colloids and water collected from sites impacted by Sb mining by ultrafiltration cell technology. Using SEM analyses we have investigated the chemical composition of inorganic colloids focused on their ability to host Sb and As. Antimony and As concentrations of 240 µg.l^{-1} and 35 µg.l^{-1} respectively were measured downstream of Agnes adit in abandoned Sb mine Poproc in Slovakia. In the fraction < 0.45 µm > 0.01 µm the most common colloids contained Fe-Si±As and were amorphous and spheroidal with average particle size of 150 nm. Element maps collected using synchrotron-based µXRF confirmed the close association of Fe and As in colloids. Arsenic was more likely to be present on colloidal particles compared to Sb. However, the most commonly observed colloids from mine waters at the recently operating Beaver Brook Sb mine in Newfoundland, Canada were represented mostly by Fe-Sb-Si-S phases. These field observations were supported by tailings shake flasks experiments. Water decanted from the shake flask was filtered <0.45 um and then <0.01 um. Ultrafiltration caused the Sb concentration to decrease by 54 % and As by 86%. This results reveal that colloids may play important role in Sb transport in near neutral mine drainage. Antimony can compete for binding sites of Fe colloids where significant concentration of dissolved As is present. Further study of the formation and transport of colloids can help to understand the movement of contaminants via the water path.

IMMOBILIZATION OF ANTIMONY IN LEAD SMELTER-AFFECTED SOILS BY AMENDMENT WITH AMORPHOUS MANGANESE OXIDE

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Emissions from lead (Pb) smelters are important local sources of metal/metalloid pollution. Smelter dusts deposited and weathered in soils are releasing high amounts of metals and metalloids including antimony (Sb) and arsenic (As) [1,2]. This study aims at understanding the remediation potential of amorphous manganese oxide (AMO) used as amendment for Pb smelter-polluted agricultural soil with a special emphasis on behaviour of Sb and its comparisons with As (total Sb: 48.9 mg/kg, total As: 118 mg/kg). The AMO was added to a polluted soil at a concentration of 2% (w/w) and mixtures were regularly rewetted to 30% water-holding capacity. The soils were incubated under these conditions for 2 and 6 months. The change in the chemical fractionation of contaminants in the soil after the application of the AMO was examined using the sequential extraction procedure (SEP). The pH-dependent leaching test was performed in the pH range of 3 - 8 on the original soil and the AMO-amended soils after 2 months and 6 months of incubation (L/S of 10, time 48 h, pH controlled by addition of HNO_3 or NaOH).

After 6 months of incubation, the decrease in the "labile" fraction of the metalloid contaminants was statistically significant: As (from 5.30 to 2.51 mg/kg), Sb (from 1.17 to 0.42 mg/kg). Antimony leaching from the soil increased as a function of the pH with the highest leached concentration at pH 8 (1.93 mg/kg; ~4.0% of total). The AMO treatment significantly decreased the Sb leaching (by a factor up to 9.1) under all the studied conditions. Arsenic leaching from the soil exhibited a U-shaped leaching curve with the highest leached concentration at pH 8 (3.84 mg/kg; ~ 3.3% of total As). The AMO treatment was responsible for a significant decrease in the As leaching by a factor of up to 4.9 after 6 months of incubation. The overall decrease in the leaching of Sb and As expressed as % of the control (unamended) soil was 11-45% and 20-60%, respectively. Relatively little information is available on the efficiency of soil amendments in Sb retention; a recent study by Bagherifam et al. [4] reported that, after soil treatment with 2% Mn-oxide, the DTPA- extractable Sb concentration decreased to ~ 50%, which is in agreement with our results. An increase in leaching at pH > 7 can be partly related to dissolution of soil organic matter, but may also be connected with the dissolution of soil Fe-oxides, which can be highly responsible for Sb binding in smelter-affected soils [1] (an increase in Fe leaching as a function of the pH was also documented). In addition, Wang et al. [5] recently demonstrated that Sb^V sorption onto manganite (γ-MnOOH) is efficient under acidic conditions, but Sb can be desorbed at pH > 6, which can also be partly responsible for increased Sb leaching after AMO treatments at higher pH.

In conclusion, smelter-affected agricultural soil exhibited a statistically significant decrease in the "labile" fraction of As and Sb after the AMO treatment. Moreover, the pH-static experiments indicated that, mainly under acidic conditions, the leaching of As and Sb decreased down to 20% and 11%, respectively, compared to the original soil and as a result, this chemical stabilization method was found to be relatively efficient. This study was supported by the Czech Science Foundation (GAČR 15-07117S).

References

[1] Ettler, V., Tejnecký, V., Mihaljevič, M., Šebek, O., Zuna, A., Vaněk, A., 2009: Geoderma 155, 409-418;

[2] Ettler, V., Mihaljevič, M., Šebek, O., Valigurová, R., Klementová, M., 2012: Chem. Erde 72, S4, 15-22;

[3] Ettler, V., Tomášová, Z., Komárek, M., Mihaljevič, M., Šebek, O., Michálková, Z., 2001: J. Hazard. Mater. 286, 386-394;

[4] Bagherifam, S., Lakzian, A., Fotovat, A., Khorasani, R., Komarneni, S., 2014: J. Hazard. Mater. 273, 247-252;

[5] Wang, X., He, M., Lin, C., Gao, Y., Zheng L., 2012: Antimony(III) oxidation and antimony(V) adsorption reactions on synthetic manganite, Chem. Erde 72, S4, 41-47.

SPATIOTEMPORAL DISTRIBUTION OF INORGANIC ANTIMONY ALONG THE GIRONDE FLUVIAL-ESTUARINE CONTINUUM AND BIOACCUMULATION IN WILD OYSTERS AT THE ESTUARY MOUTH: A PRELIMINARY APPROACH TO THE FATE OF REGIONAL ACCIDENTAL RADIONUCLIDE RELEASES

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The nuclear power plant accident of Fukushima Dai-ichi (Japan, 2011), has raised concern on radionuclide behaviour and dispersal in aquatic systems. Antimony (Sb) is a fission product in nuclear power plants, presenting non-negligible radioactive intensities at relatively long exposure conditions (*i.e.,* ^{125}Sb isotope: half-life of 2.76 y). Antimony is also considered a dangerous substance by the European Community [1] due to its high toxicity, comparable to that of lead (Pb) [2]. The fate of radioactive elements can be extrapolated from their natural stable isotopes due to their analogous biogeochemical behaviour. We present several approaches to describe the dynamics of total Sb in aquatic and biological compartments within the Gironde Estuary and fluvial system. Specifically, we present data on: (i) dissolved and particulate Sb concentrations and fluxes entering the Gironde Estuary via the Garonne River (from 2004 to 2014), (ii) its distribution along the salinity and turbidity gradients of the Gironde Estuary (during intermediate discharge in March 2014 and during flood in March 2015), (iii) its concentrations in wild oysters *Crassostrea gigas* at the estuary mouth (from 1981 to 2010) and (iv) recent bioaccumulation compared to wild oysters of the same species in the Arcachon Bay (for measurements in 2014 and 2015).

Within the freshwater system, Sb showed a conservative behaviour (constant Kd > 10^4 L kg^{-1}) with stable periodical seasonal patterns of dissolved (Sb_d, mean 0.19 ± 0.06 µg L^{-1}) and particulate (Sb_p, mean 3.32 ± 1.19 mg kg^{-1}) concentrations at La Réole (reference point in the Garonne River before entering the estuary) corresponding to expected ranges for the Aquitaine region [3]. Within the Gironde Estuary, first data on Sb_P concentrations suggest constant values along the salinity gradient, with higher concentrations (1.95 ± 0.07 mg kg^{-1}) during flood (3450 m^3 s^{-1}) compared to 1.57 ± 0.06 mg kg^{-1} during intermediate discharge (1203 m^3 s^{-1}). Lower Sb_p concentrations in the estuary than in the river and the dependence on hydrological situation suggest both physical dilution and/or Sb mobilisation in the saline estuary and may reflect the influence of estuarine water and particle residence times in dissolution kinetics. Dissolved Sb concentrations increased with salinity from 0.12 ± 0.01 µg L^{-1} at S=0 to a maximum of 0.4 ± 0.06 µg L^{-1} at S>27, *i.e.* within the expected values for North Atlantic coastal waters (~0.3-0.5 µg L^{-1} [4]) but with variable behaviour between discharge conditions, supporting the idea of non-conservative Sb behaviour in the hyperturbid Gironde Estuary. Distribution coefficients (Kd ≈ 10^3 - 10^4 L kg^{-1}) indicate that in the Maximum Turbidity Zone (MTZ; Suspended Particulate Matter concentrations (SPM) >1000 mg L^{-1}) ~90% of the total Sb is associated with particles, whereas at low (SPM <100 mg L^{-1}) over 90% of total Sb are in the dissolved phase.

Data from the French biomonitoring programs (RNO and ROCCH) at La Fosse (Gironde Estuary mouth) show a stable temporal trend of Sb low concentrations (mean 0.20 ± 0.11 mg kg^{-1}) and punctual peaks in annual pools of wild oysters. Recent (Spring 2014) wild oysters from the same location showed concentrations (0.022 ± 0.009 mg kg^{-1}) which are higher than in Arcachon Bay (0.011 ± 0.004 mg kg^{-1}), with the highest content found in the gills (> 60%). Low bioaccumulation factors (BAF), in accordance with exposure levels of Sb_d at each site for the Gironde Estuary, are in conformity with other studies (e.g. [5] and [6]) and are much lower than cadmium or silver BAFs.

This study shows that freshwater discharge and the resulting position and dynamics of the MTZ, both controlling water and particle residence times in the Gironde fluvial-estuarine system, will play a major role in transport and residence times of Sb radionuclides, including the risk of upstream transport of radioactive particles to Bordeaux during summer draught. These results will be of major importance for radioprotection scenarios in case of a crisis in one of the two nuclear power plants in its watershed. Its accumulation in wild oysters is expected to be low but cannot be neglected regarding consumption risks and, thus, internal exposure to radiation.

References

[1] Council Regulation (EC) 2006/11/EC of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community [2006] OJ L64/52

[2] Harmens, H., Norris, D., Mills, G. (2013). Heavy Metals and Nitrogen in Mosses: Spatial Patterns in 2010/2011 and Long-Term Temporal Trends in Europe. ICP Vegetation Programme Coordination Centre. Centre for Ecology and Hydrology, Bangor, UK p. 63

[3] Salminen, R., Batista, M.J., Bidovec, M., et al. (2005). Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps.

[4] Filella, M., Belzile, N., Chen, Y.-W. (2002). Antimony in the environment: a review focused on natural waters I. Occurrence. Earth-Science Reviews, 57: 125-176

[5] Filella, M., Belzile, N.and Lett, M.-C. (2007) Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions. Earth-Science Reviews, 80, 195–217

[6] Fu, Z., Wu, F., Mo, C., et al. (2011) Bioaccumulation of antimony, arsenic, and mercury in the vicinities of a large antimony mine, China. Microchemical Journal, 97, 12–19.

ANTIMONY DEPOSITION AND ACCUMULATION IN BIOMONITORING PLANTS AT A TRAFFIC AFFECTED SITE COMPARED TO RURAL SITES IN BAVARIA / GERMANY

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Introduction

The Bavarian Environment Agency operates, amongst others, two continuing monitoring programs analyzing the influence of airborne antimony. The antimony deposition is determined using the Bergerhoff method [1]. The effect on plants is measured using standardized grass cultures with Italian ryegrass (*Lolium multiflorum italicum*) as accumulative bioindicators [2]. The monitoring has been performed for more than 15 years at minimum seven rural sites with background levels for the pollution influence. In a project investigating traffic affected sites in Bavaria [3] striking accumulation of antimony in grass cultures had been found in the early 1990s at the sites within spitting distance of main roads, intersections or featuring stop-and-go patterns. Subsequently an additional city site affected by traffic of a major road was added to the long term monitoring but had to be removed in 2014 due to changes in the surroundings. Since the influence of traffic processes on the deposition of antimony is documented and brake pads are identified as major emission source [4,], brake pads of common brands had been analyzed for antimony and other characteristic elements to determine changes in their composition profile.

Results

The antimony deposition at the traffic site (25 m from major road, shielded by a hedge) is multiple times higher than the arithmetic mean of the rural sites. While at the traffic site the antimony deposition declined from 3.1 µg m^{-2} d^{-1} in 1999 to 0.9 µg m^{-2} d^{-1} in 2013 it declined from 0.4 µg m^{-2} d^{-1} to 0.2 µg m^{-2} d^{-1} at the rural sites. The ratio between traffic site and background sites narrows with a maximum in 2004 from 10 : 1 to 4 : 1 in 2013. After more than 10 years of almost constant decline, since 2010 stagnation of antimony deposition was observed at the rural sites as well as at the traffic site.

One reason for the spacing between the antimony deposition at the traffic site and the rural sites is a higher dust deposition at the traffic site by a factor two to four. Furthermore the dust composition shows a characteristic difference between the different kinds of sites. At the rural sites the antimony concentration is between 0.007 ‰ and 0.015 ‰ while at the traffic site the concentration was up to 0.035 ‰ in the late 1990s and declined to almost background level in 2013. The ratio between traffic site and rural site narrows with a maximum in 2005 from 4.2 : 1 to 1.4 : 1 in 2013.

The biomonitoring with standardized grass cultures at the traffic site showed a significant increase of antimony from 1998 with 0.12 µg g^{-1} to a maximum antimony concentration of 0.25 µg g^{-1} in 2004. After 2004 there was a decrease to 0.10 µg g^{-1} in 2013. At the rural sites the mean concentration from 1998 to 2006 was less than 0.05 µg g^{-1} without a significant trend. After 2006 50 % up to nearly 100 % of the data were below limit of quantification with 0.025 µg g^{-1}.

In addition to the monitoring of airborne antimony there was analysis of antimony in brake pads of up to 65 arbitrary chosen used brake pads of different brands. While at the first analysis in 2003 the brake pads showed a mean antimony concentration of more than 20 000 µg g^{-1} the concentration decreased to less than 4 400 µg g^{-1} in 2013. In contrast a couple of other elements like tin or barium showed increasing concentrations during the period of analysis.

Discussion and conclusions

Differences between the trends of antimony deposition and accumulation in biomonitoring plants result from antimony in different size fractions of dust. Whilst the Bergerhoff method gathers rather the coarse fraction (> 10 µm) the biomonitoring plants also collect finer fractions. As is documented in Fujiwara et al. [4] antimony is found to be enriched in the smaller size fractions of dust. There are different spreading characteristics of dust fractions and special mechanisms of accumulation in plants that do not allow a direct comparison of the different methods.

Nevertheless, at the traffic site there can be found a significant reduction of antimony for the last 10 years in deposition as well as in biomonitoring plants. The main reason is supposed to be the declining concentration of antimony in brake pads as the analysis shows and as is indicated in Fujiwara et al. [4].

Looking at the results in detail a disproportionate decrease for antimony as well as many other elements in 2008 is obvious. This is likely to be caused by a change in quality of traffic. Since 2008 the transit of heavy traffic through the city center was interdicted so the number of trucks dropped and lead to lower emissions of traffic induced elements.

At the rural sites antimony in deposition and accumulation after years of decrease seem to have reached a background level where at present no trend can be discovered.

References

[1] VDI/DIN-Handbuch Reinh. Luft, 4, VDI 4320 Part 2, Berlin: Beuth, Berlin, 2012;
[2] VDI/DIN-Handbuch Reinh. Luft, 1a, VDI 3957 Part 2, Berlin: Beuth, Berlin, 2003;
[3] Peichl, L., Dietl, C., Wäber, M.1996: Schrift. Bay. Landesamt f.Umwelt 136;
[4] Fujiwara, F., Rebagliati, R.J., Marrero, J. Gomez, D., Smichowski, P. 2011: Microchem. J. 97, 62-67.

MINERALOGY OF WEATHERING PRODUCTS OF MINE WASTES AT SEVERAL Sb AND Cu DEPOSITS IN SLOVAKIA

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1. Introduction

The fate of inorganic contaminants in an aqueous solution depends largely either on their interaction with minerals or their eventual precipitation. Retention of the contaminants on mineral surfaces is a decisive factor affecting pollutant mobility and the kinetics of mineral dissolution and precipitation (Kulik 2009, and references therein).

In this work, we have investigated the Fe–As–Sb and Cu bearing products of weathering from five Sb and two Cu deposits in Slovakia. The exploitation of these deposits ceased years ago. We paid special attention to the interaction of Sb with iron phases and the competition between Sb and As for a stable association with iron.

2. Material and Methods

Quantitative mineralogical analysis of the tailings samples was performed using XRD and Rietveld refinement (HighScore (Plus) software). X-ray powder diffraction data were collected with a Bruker-AXS D8 - Advance diffractometer equipped with a CuKα radiation source and a diffracted beam graphite monochromator.

Tailings samples selected for electron microprobe analyses and for micro-X-ray diffraction (μ-XRD) were homogenized and separated into light and heavy fraction by panning in water or ethanol. Selected heavy-grain concentrates were prepared for further study in a form of standard thin and polished sections, to be inspected in transmitted and reflected polarized light, respectively (Department of Mineralogy and Petrology, Bratislava, Slovakia). Mineral phases were subsequently analyzed by a Cameca SX-100 electron microprobe in a wavelength-dispersive mode (WDS) under the conditions of 20 kV, 20 nA, and beam size of 1-5 μm (Geological Institute of Dionýz Štúr in Bratislava, Slovakia).

Samples of interest were prepared for μ-XRD experiments as special thin sections using epoxy that could be detached easily from the supporting glass. The μ-XRD data were collected at the SUL-X beamline of the synchrotron light source ANKA (Karlsruhe, Germany) and at undulator beamline 20-ID at the Advanced Photon Source (Argonne, IL, USA). The images were integrated with the program Fit2D (Hammersley et al. 1996) and the 1D XRD patterns were further used for Rietveld refinement with the program GSAS and HighScore (Plus) after background subtraction.

3. Results and Discussion

Sb deposits

Primary Sb sulfides oxidize rapidly and are either replaced by the weathering products or release their constituents into aqueous solution. Pyrite and arsenopyrite do not alter so quickly, and usually develop an oxidation rim whose composition is, to some extent, controlled by the parent sulfide mineral, but is also able to scavenge significant amounts of other elements.

Under acidic conditions, pyrite and arsenopyrite also oxidize and decompose rapidly. The Fe/(Fe + Sb) value of the analyzed minerals may attain a range from 0 to 1. At a relatively high Fe/(Fe + Sb) value, antimony is stored in goethite or HFO. These minerals may accumulate a considerable amount of Sb: HFO 1.02–13.91 wt% Sb (average 6.84 wt%), and goethite, up to 14.49 wt% Sb (average 3.96 wt%). A wide range of intermediate Fe/(Fe + Sb) values can be assigned to the mineral tripuhyite. This inconspicuous mineral can be easily overlooked. Its particles usually are nanometric, and the XRD patterns consist only of a few broad peaks. We suspect that this mineral is abundant at each contaminated site where Fe and Sb mingle together and Sb concentrations are reasonably high. In the tailings and soils rich in Sb and Ca, secondary calcium antimonates with the pyrochlore structure crystallize. These phases are rich in Sb (up to 52.90 wt%), Fe (up to 21.22 wt%) and Ca (up to 7.40 wt%).

Cu deposits

Oxidation products contain significant amounts of hazardous elements, mostly Sb (with average content 40.55 wt%), together with Cu (average 22.09 wt%), As (average 9.79 wt%) and Bi (average 1.55 wt%), for samples where the primary mineral chemical composition is close to tetrahedrite end member. These phases were identified as a mixture of tripuhyite and romeite group mineral with pyrochlore structure. For samples where the primary sulphosalt is close to tennantite composition, the oxidation products contain Sb (average 3.23 wt%), As (average 28.34 wt%), Cu (average 26.22 wt%) and Fe (average 22.32 wt.%). Some of the secondary phases associated with tennantite are pharmacosiderite and goethite (Radková et al., 2014).

4. Conclusion

Results obtained from both types of deposits showed that Sb and As in observed oxidation products are hosted differently: Sb concentration is highest in samples identified as tripuhyite and romeite group mineral with pyrochlore structure, arsenic is preferentially hosted by amorphous Fe phases.

Acknowledgements

This study was supported by the Slovak Research and Development Agency under the contracts No. APVV-0344-11 and APVV-0663-10.

References

Kulik, D.A. 2009: Thermodynamic concepts in modelling sorption at the mineral–water interface. In Thermodynamics and Kinetics of Water–Rock Interaction (E.H. Oelkers & J. Schott, eds.). Rev. Mineral. Geochem. 70, 125-180.

Radkova, A., Jamieson, H., Stevko, M., Lalinska Volekova, B., Chovan, M., 2014: Mineralogy and geochemistry of tetrahedrite-tennantite oxidation products from abandoned waste rock piles. Synchrotron Environmental Science VI conference, APS, Chicago, September 2014.

ANTIMONY IN SOILS OF SOME HISTORICAL MINING SITES IN THE CENTRAL SUDETES, POLAND.

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The Sudetes, a mountain range situated partly in south-western Poland, and northern Czech Republic, is well known as a region of beautiful landscapes and complex geology. There are many sites in the Sudetes, where the rocks are enriched in various metallic elements, including gold, silver, copper, nickel, lead, iron, uranium, arsenic and more. Most of such metallic deposits were the objectives of mining activities that lasted with various intensities for decades or centuries [1]. Due to the complicated history of this area, most of the former mines were abandoned and forgotten. Old mine waste dumps, however, spread in their surroundings, usually contain high concentrations of toxic metals, and may pose a risk to the environment and human health. For both historical and environmental reasons, it is still needed to search the traces of former mining. This work requires long hours of arduous exploration in the state archives, as well as further difficult field investigation.

This study was aimed to examine soil properties, and particularly the concentrations of toxic metals in soils, with special focus on antimony, in the surroundings of several former mines situated in the Central Sudetes. The knowledge on the occurrence of antimony in soils in Poland is very poor. It is known that it is usually present in the environment in association with various metallic elements, and in particular with arsenic. Therefore, local occurrence of enhanced Sb concentrations in soils should be expected in the sites of historical mining and processing of antimony, arsenic and other metal ores. This work presents the results obtained from an initial stage of project aimed to examine soil properties, the concentrations of antimony and the patterns of its speciation in soils in the close vicinities of several historical sites of metallic ore mining in the Central Sudeten Mts., with special focus on the mines where stibnite (antimonite) was acquired.

The sites with likely enrichment in antimony were selected based on available papers [2, 3] and other published, or unpublished, materials collected by Stysz. Examined were the soils in three regions in the Central Sudetes: 1) Bardzkie Mts., 2) Sowie Mts. – Bystrzyca Górna, and 3) Sowie Mts. – Rościszów. In the region of Bardzkie Mts. (1), soil samples were collected in Bardo and Dębowina. Mining activities in this area started probably at the beginning of 1406, and was focused on silver extraction. The size of ore deposits turned out to be unsatisfactory, and therefore the mines were abandoned. New exploration, that started in 1772 in Dębowina, confirmed the abundance of antimony veins. The mine was opened under the name of „Reiche Silber Glück". In the adits that have remained in good state until now, the mineralization of rocks occurs in the form of pyrite, sphalerite, arsenopyrite, galena, stibnite and chalcopyrite [4]. In Bardo, significant amounts of arsenopyrite have been confirmed, accompanied by stibnite, copper, lead and pyrite [5]. The second region of interest (2), situated in the vicinity of Bystrzyca Górna and Modliszów, was intensively explored and mined beginning from the 15th century, mainly to acquire gold and silver. Antimony and lead were mentioned in the recent papers [7] as accompanying metals. The third area of interest

(3) was located close to Rościszów village, at the foothills of the Sowie Mountains. Its history is poorly understood. Few available sources confirm the occurrence of barite veins, lead and zinc in the mines situated in that area.

In order to draw a the general picture of Sb concentrations in soils in the surroundings of former mines, at each of those sites (No 1, 2 and 3), ca. 10-20 soil samples were collected from the surface soil layer. Additionally, in representative sites, the samples were collected from the horizons distinguished within soil profiles. All the samples were examined to determine the basic soil properties and total concentrations of antimony and several other heavy metals. Total concentrations of metals were determined using ICP-MS (8800 QQQ, Agilent Technologies) after microwave digestion of samples (Milestone Inc.) in concentrated nitric acid (suprapure, Merck). The concentrations of antimony in soils ranged from <0.01 to 20.1 mg Sb kg-1. The lowest values were found in Rościszów area (3), and the highest ones - in the area of Dębowina in Bardzkie Mts (1). What is interesting, the soils of Dębowina and Bardo (region 1) contained high concentrations of arsenic, up to 2885 mg As kg^{-1}. Statistical analysis showed positive, significant correlation between the concentrations of As and Sb in the whole set of soil samples examined (R=0,44), whereas the corresponding R values determined for Sb and other metals (Pb, Ba, Hg or Zn) were much lower. Negative correlations were found between soil concentrations of Sb and several elements: Cd, Cu, Cr, Co, Ni, Sr, Se and V. Particularly strong negative correlations were found for Li and Al (R= -0,67).

The results obtained from this stage of the project will provide the basis for further study on Sb solubility, its speciation in soil solution, as well as its phytoavailability in soils in the conditions of Sb-enriched environments.

This research was supported by financial means granted by the National Science Centre of Poland; Project No. 2014/13/B/ST10/02978.

References

[1] Madziarz M. (2009). Advance of exploration work old ore mining in Bystrzyca Górna (Sowie Mts.). In: gornictwa - element europejskiego dziedzictwa kultury, red. P.P. Zagożdzon i M. Madziarz, Wyd. P.Wr. Wrocław (in Polish, with English abstract).

[2] Mikulski S. Z. (2010). Charakterystyka i geneza złotonoœnej mineralizacji arsenowo-polimetalicznej w złożu Czarnów (Sudety Zachodnie). Biul. PIG, 439, 303-320 (in Polish, with English abstract).

[3] Karczewska A., Krysiak A., Mokrzycka D., Jezierski P., Szopka K. (2013): Arsenic distribution in soils of a former As mining area and processing. Pol. J. Environ. St. 22, 1, 175-181.

[4] Mączka M., Stysz M. (2008). The mine „Reiche Silber Glück” in Dembowina – the relic of past antimony mining in the Bardzkie Mountains. In: Dzieje gornictwa - element europejskiego dziedzictwa kultury, red. P.P. Zagożdzon and M. Madziarz, Wyd. P.Wr. Wrocław (in Polish, with English abstract).

[5] Mączka M., Stysz M. (2013). Bardo-miasto z górniczą przeszłością. In: Dziedzictwo i historia górnictwa oraz wykorzystanie pozostałości dawnych robót górniczych, red. P.P. Zagożdzon, M.J. Battek, J. Szczepankiewicz-Battek and M. Madziarz, Wyd. P.Wr. Wrocław (in Polish, with English abstract).

[6] Mączka M., Stysz M. (2010). The metal ore mining in the area of Bystrzyca Górna, Lubachów and Modliszów – attempt of location and naming of the old excavations on the basis of archival sources and field research. In: Dzieje górnictwa - element europejskiego dziedzictwa kultury, red. P.P. Zagożdzon and M. Madziarz, Wyd. P.Wr. Wrocław (in Polish, with English abstract).

[7] Mączka M., Stysz M., Banduch R. (2009). The metal ore mining in the area of Bystrzyca Górna, Lubachów and Modliszów – attempt of location and naming of the old excavations on the basis of archival sources and field research. In: Dzieje górnictwa - element europejskiego dziedzictwa kultury, red. P.P. Zagożdzon and M. Madziarz, Wyd. P.Wr. Wrocław (in Polish, with English abstract).

IDENTIFICATION OF CRITICAL RESIDUES FOR TRANSPORT ACTIVITY OF ACR3P, THE *SACCHAROMYCES CEREVISIAE* As(III)/H^+ ANTIPORTER

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Acr3p is an As(III)/H^+ antiporter from *Saccharomyces cerevisiae* belonging to the bile/arsenite/riboflavin transporter (BART) superfamily. We have previously found that Cys151 located in the middle of the fourth transmembrane segment (TM4) is critical for antiport activity, suggesting that As(III) might interact with a thiol group during the translocation process [1]. In order to identify functionally important residues involved in As(III)/H^+ exchange, we performed a systematic alanine-replacement analysis of charged/polar and aromatic residues that are conserved in the Acr3 family and located in putative transmembrane segments. Nine residues (Asn117, Trp130, Arg150, Trp158, Asn176, Arg230, Tyr290, Phe345, Asn351) were found to be critical for proper folding and trafficking of Acr3p to the plasma membrane. In addition, we found that replacement of highly conserved Phe266 (TM7), Phe352 (TM9), Glu353 (TM9) and Glu380 (TM10) with Ala abolished transport activity of Acr3p, while mutation of Ser349 (TM9) to Ala significantly reduced the As(III)/H^+ exchange, suggesting an important role of these residues in the transport mechanism. Detailed mutational analysis of Glu353 and Glu380 revealed that the negatively charged residues located in the middle of transmembrane segments TM9 and TM10 are crucial for antiport activity. We also discuss a hypothetical model of the Acr3p transport mechanism.

Reference

[1] Maciaszczyk-Dziubinska, E., Migocka, M., Wawrzycka, D., Markowska, K., and Wysocki, R., 2014: Biochim Biophys Acta 1838: 747-755;

ANTIMONY EFFECTS ON NON-TARGET DIAZOTROPHIC SOIL BACTERIUM, *AZOSPIRILLUM BRASILENSE* SP7

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Antimony (Sb) is a toxic element and concentrations in our environmental systems are increasing due to a multitude of new consumer uses. Exposure results in acute and chronic effects, lowers ecosystem resilience and threatens viability [1, 2]. Microbial processes play essential roles in ecosystem health and bacteria perform numerous services in the environment. Yet, there is little known about the ecotoxic effects of Sb on microbes, including soil bacteria involved in the nitrogen cycle. *Azospirillum brasilense* Sp7, of the class alphaproteobacteria, is a well-studied free-living diazotroph that colonises plant roots and rhizospheric soil [3, 4]. Apart from nitrogen fixation, *Azospirillum* is capable of producing a number of plant signalling molecules such as phytohormones, auxins, nitrite, and other plant metabolic signals [5, 6]. In addition, the recently discovered type VI secretion system, T6SS, serves in mediation of biological relationships that promote crop yields [7]. Interference with the population structure of these bacteria could disrupt nutrient cycling and impact soil fertility. This study examined the effects of Sb on wild-type *A. brasilense* Sp7 by determining bacterial mortality and assessing mutation rates after exposure to Sb(III) and Sb(V) at different concentrations and for various periods of time.

Bacteria were exposed to either Sb(III) (as potassium antimony tartrate) or to Sb(V) (as potassium hexahydroxyantimonate) at different concentrations (50, 40, 20, 5, 2.5, 1, 0.5, 0.1, and 0.05 mg/l) for periods of 2, 6 and 24 h. Bacterial mortality and emergence of phenotypic variants (according to colony colour) were observed. Variant colonies were readily differentiated from colonies of parental strains by the reduced absorption of Congo-red dye added to the growth medium [8, 9]. Mortality rates were calculated by including a control without Sb. The frequency of mutation was calculated by counting the number of light-coloured variants in the background of dry red wild-type colonies. The stability of putative mutants was examined by subculturing the light-coloured colonies on nutrient broth medium supplemented with Congo-red. Both Sb species showed a toxic effect (mortality) on the bacterial population, which was dose-dependent over 2 h but Sb(III) maintained a non-dose response pattern after 6 h exposure.

Almost 100% of the bacterial cells died following 2 h of exposure to Sb(III) and Sb(V) at higher concentrations (50 – 20 mg/l) and the few surviving cells showed light-coloured phenotype. At lower concentrations the mortality rates at 2 h were 92, 82, 82, 80, 76, and 74 %, and 85, 77, 68, 68, 40 and 24 % at concentrations of 5, 2.5, 1, 0.5, 0.1 and 0.05 mg/l for Sb(III) and Sb(V), respectively. The Sb(III) had a greater toxic effect than Sb(V) even at the lower concentrations tested. The rate of appearance of phenotypic variants of *A. brasilense* was randomly distributed for both Sb species. Both wild-type and phenotypic-variant colonies were observed following exposure to Sb (III&V). The *A. brasilense* Sp7 phenotypic variants exhibited different pigmentation, forming pale white to pink colonies because they could not bind Congo red effectively. Some appeared to take up red coloration after an extended incubation period of 4 -6 days at 0.1 and 0.5 mg/l for Sb(III) and 0.1 mg/l Sb(V),.

Out of the small number of surviving cells, 74 and 7 % of the colonies formed showed phenotypic variations for both Sb(III) and Sb(V), y.

The study shows that, while Sb(III) seems to be more toxic, both Sb(III) and Sb(V) cause high mortality rates over a range of concentrations in *A. brasilense* Sp7 as well as leading to phenotypic mutations. Antimony has the potential to act as a mutagen even at lower concentrations where cell mortality is lower. Further studies are needed to examine the uptake and accumulation of the two Sb species in bacteria for a better understanding of the mechanisms of mutagenesis and toxicity. This study demonstrates, however, the importance of understanding the effects of Sb exposure on soil microbial communities for full assessment of ecosystem health in contaminated environments.

References

[1] Wilson, S.C., Lockwood, P.V., Ashley, P.M., Tighe, M., 2010: Environmental Pollution 158, 1169-1181;

[2] Filella, M., Belzile, N., Chen, Y.-W., 2002: Earth-Science Reviews 57, 125–176;

[3] Bashan, Y., Holguin, G., de-Bashan, L.E., 2004: Canadian Journal of Microbiology 50, 521-577.

[4] Steenhoudt, O., Vanderleyden, J., 2000: FEMS Microbiology Reviews 24, 487-506.

[5] Fibach-Paldi, S., Burdman, S., Okon, Y., 2012: FEMS Microbiology Letters: 326, 99-108.

[6] Wisniewski-Dyé, F., Borziak, K., Khalsa-Moyers, G., Alexandre, G., Sukharnikov, L.O., Wuichet, K., Hurst, G.B., McDonald, W.H., Robertson, J.S., Barbe, V., Calteau, A., Rouy, Z., Mangenot, S., Prigent-Combaret, C., Normand, P., Boyer, M., Siguier, P., Dessaux, Y., Elmerich, C., Condemine, G., Krishnen, G., Kennedy, I., Paterson, A.H., González, V., Mavingui, P., Zhulin, I.B., 2011: PLoS Genet. 7, e1002430.

[7] Smith, S.M., 2014: Honours Thesis, Biochemistry, Cellular, and Molecular Biology, The University of Tennessee, Knoxville, USA, 2014, pp. 1-39.

[8] Vial, L., Pothier, J.F., Normand, P., Moënne-Loccoz, Y., Bally, R., Wisniewski-Dyé, F., 2004: FEMS Microbiology Letters 236, 291-299.

[9] Pereg Gerk, L., Paquelin, A., Gounon, P., Kennedy, I.R., Elmerich, C., 1998: Molecular Plant-Microbe Interactions 11, 177-187.

LEACHABILITY OF ANTIMONY AND OTHER TOXIC ELEMENTS FROM IMPOUNDMENT SEDIMENTS AT ABANDONED Sb-DEPOSIT POPROČ

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Mining and processing of metallic and non-metallic materials is associated with environmental pollution and especially with formation of different types of anthropogenic wastes (tailings pond, heap, flotation sludge,...) that are characterized by the presence of high amounts of various potentially toxic trace elements (PTTEs) and substances with potential risk. From long-term view, locality Poproč represents serious environmental load with real influence on environment and human health. There is important source of contamination of PTTEs from impoundment sediments. Combination of pollutants dispersion into the environment (soil, water and stream sediments) from mining activities in Poproč ore field e.g. drainage from old mine, tailing impoundments, waste dumps, weathering and releasing of deposited waste on tailings ponds and mechanical drift of ore minerals in alluvium are a major source of high PTTEs content in studied area.

The studied solid samples were observed to have very high total concentrations of some toxic elements, mainly As (15.31-1463 ppm), Sb (1022-5825 ppm), Zn (2-1202 ppm) and Pb (43.6-424.7 ppm). According to directive to carry out risk assessments of contaminated sites, some elements (As, Sb, Pb) exceed several times indicative (As_{ID} = 65 ppm, Sb_{ID} = 25 ppm, Pb_{ID} = 250 ppm) and also intervention levels of rocks and soil for residential areas (As_{IT} = 70 ppm, Sb_{IT} = 40, Pb_{IT} = 300 ppm) and industry (As_{IT} = 140 ppm, Sb_{IT} = 80) [1].

The extractability of selected toxic elements was evaluated by single extraction with inorganic and organic extractants. Extraction with distilled water was used for the determination of mobile, easily-soluble fraction of elements from solid samples. Among the studied elements, the highest values of water-soluble fraction were observed for Sb, when the range of released percentages was 0.22-1.07 %. The obtained concentrations exceeded the criteria of US EPA drinking water guidelines (Sb_{Limit} = 0.006 $mg.l^{-1}$) by 70-925 times. The sequence of leaching efficiency and average extractabilities of monitored elements expressed as percentage of the total contents in samples were: Zn (8.03 %) > As (0.73 %) > Sb (0.66 %) > Pb (0.12 %). The sequence of extractability of As, Sb, Zn and Pb with the 1M NH_4NO_3 procedure for assessment of plant-available forms was: Zn (14.56 %) > Pb (0.30 %) > As (0.13 %) > Sb (0.06 %). Although these values are relatively low, they represent potential plant-availability concentrations of elements and so these wastes and mining soils could have potentially significant risks to public health and ecosystems. Extraction efficiency of distilled water was more effective for arsenic and antimony, while the extraction with ammonium nitrate solution was effective for lead and zinc. The highest extractabilities were found when organic single-extraction techniques were applied. The average bioleaching efficiency of elements with liquid Sabouraud medium was: Zn (55.71 %) > As (40.74 %) > Sb (14.33 %) > Pb (10.01 %). The addition of glucose to the liquid Sabouraud medium increased the release of elements due to activation of heterotrophic microorganisms and sequence of leaching efficiency was: Zn (64.90 %) > As (50.66 %) > Sb (14.55 %) >

Pb (8.5 %). The results obtained from the experiments showed, that bioleaching was found to be much more efficient for removal of As, Sb, Pb and Zn from mining soils and wastes in compare with inorganic leaching. The results of toxic elements release through microbial influence suggested that biological leaching could be used for reduction of contamination at studied site and become one of the possible alternative of bioremediation of soils at Poproč.

This research was supported by Agency to support research and development under contract no. APVV-0344-11 and VEGA Project No. 1/0321/14.

References

[1] Directive of Ministry of Environment of the Slovak Republic from 28. january 2015 number 1/2015 – 7 directive to carry out risk assessments of contaminated sites, Bratislava, 1-96;

INORGANIC Sb(V) REACTIVITY AND UPTAKE PATHWAYS IN HUMAN ERYTHROCYTES.

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In 2009 our group reported that heavy weight vehicle traffic as the most plausible hypothesis to explain the enrichment of antimony in the blood of port workers. Demonstrating that most of the antimony in human blood is able to permeate the erythrocyte membrane[1]. An enrichment of antimony from 4 to 10 times higher was detected in road dust in Valparaiso, Chile, which correlates with the enrichment reported in the blood[2]

In 2013 we report an analytical method for the determination of Sb(V) and Sb(III) in human erythrocytes fractions (plasma and cytoplasm) by high performance liquid chromatography with hydride generation atomic fluorescence spectrometry. Results showed that both Sb(V) and Sb(III) are capable to enter the red blood cell in a proportion of approximately 40–60%. On the other hand, both species are then excreted from the interior of the cell where the percentage considerably decreased from approximately 60 to less than 30% within the cell[3].

About Sb(V) in this work we assessed the reactivity of Sb(V) in human blood. Sb(V) reactivity was determined using an HPLC-HG-AFS hyphenated system. Sb(V) was partially reduced to Sb(III) in blood incubation experiments. Our results indicate that glutathione was the reducing agent in this reaction and that Sb(V) significantly decreased the GSH/GSSG ratio from 0.32±0.09 to 0.07±0.03. Moreover, the presence of 200 ng mL^{-1} of Sb(V) increased the activity of superoxide dismutase from 4.4±0.1 to 7.0±0.4 U mL^{-1} and decreased the activity of glutathione peroxidase from 62±1 to 34±2 nmol min^{-1} mL^{-1}.[4].

Our experiments with synthetic vesicles, as also with erythrocyte ghosts show that Sb(V) needs a protein channel to enter the red blood cell. Moreover our experiments with whole blood show that inorganic Sb(V) is able to enter through band 3 protein channel.

Finally by time-resolved molecular fluorescence we have determined that Sb(V) does not interact with the lipid phase of the membrane, however this interaction is significant with proteins of membrane.

References

[1] W. Quiroz, I. De Gregori, P. Basilio, M. Bravo, M. Pinto, M.G. Lobos, Journal of Environmental Monitoring, 11 (2009) 1051-1055.
[2] W. Quiroz, M. Cortés, F. Astudillo, M. Bravo, F. Cereceda, V. Vidal, M.G. Lobos, Microchemical Journal, 110 (2013) 266-272.
[3] W. Quiroz, L. Aguilar, M. Barría, J. Veneciano, D. Martínez, M. Bravo, M.G. Lobos, L. Mercado, Talanta, 115 (2013) 902-910.

[4] S. López, L. Aguilar, L. Mercado, M. Bravo, W. Quiroz, PLoS ONE, 10 (2015).

Acknowledgement: All authors gratefully acknowledge the financial support of FONDECYT (project 1150528).

ROLE OF MICROBIAL ACTIVITY IN ANTIMONY AND ARSENIC RELEASE FROM WETLAND SOIL UNDER REDUCING CONDITIONS

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The mobility of antimony (Sb) and arsenic (As) in wetland soil is largely controlled by several redox and pH dependent processes. The reductive dissolution of Fe and Mn (oxy)hydroxides leads to the release of previously bound Sb whereas pH increase promotes the desorption of oxyanions as well as the mobilization of dissolved organic matter (DOM)-Sb complexes [1] [2]. These processes are biologically mediated by soil microorganisms which use Fe(III) and Mn(IV) as terminal electron acceptors (TEA) during anoxic respiration. In order to better understand the role of soil microorganisms in Sb and As release in wetland soil, we investigated the mobility of Sb and As through the anaerobic incubation of a “sterilized” and “non-sterilized” hydromorphic soil. Sodium azide (5% (w/w)) was used as an inhibitor of microbial activity. Soil batch incubation experiments were conducted until Fe-reducing conditions were reached (36 days) and the evolution of dissolved As, Sb, Mn, Al, Fe(II), organic carbon (DOC) as well as pH and Eh were monitored.

During the non-sterilized soil incubation, we observed a rapid development of reducing conditions which was reflected by a decrease of redox potential (from 334 mV/ESH to -8 mV/ESH), a significant increase of dissolved Fe(II) (from 0.02 to 46.2 mg.L^{-1}), Mn (from 77 to 441 µg.L^{-1}) and pH (from 5.7 to 6.6) and a high mobilization of DOC (from 36 to 155 mgC.L^{-1}). Dissolved Sb concentration increased from 0.13 to 1.5 µg.L^{-1} during the first 11 days of incubation then decreased progressively by a factor of 3 suggesting Sb precipitation and/or resorption onto soil surfaces during soil reduction. In contrast, dissolved As strongly increased (from 2 to 359 µg.L^{-1}) over incubation time without decreasing.

In the “sterilized” soil incubation, the application of azide totally inhibited the development of reducing conditions (Eh > 250 mV/ESH; 5.7 < pH < 5.9; Fe(II) < 1 mg.L^{-1}; Mn < 200 µg.L^{-1}). The sterilizing treatment however significantly increased the release of DOM (up to 206 mgC.L^{-1}) probably due to the alteration of soil physical and chemical properties or cell lysis. Despite the inhibited development of reducing conditions, dissolved Sb was progressively released into solution and reached a final incubation concentration twice higher than that reached at the end of the non-sterilized incubation. These results indicated that Sb mobilization in the given system is not only related to microbial reductive dissolution of Fe-Mn (oxy)hydroxides but also to the release of organic matter. Moreover, azide application may have prevented the microbial antimonate Sb(V) reduction into antimonite Sb(III). Thus, Sb(V) which has been reported to be more mobile than Sb(III) was likely maintained in solution. Unlike Sb, As concentration remained low (below 8 µg.L^{-1}) during the “sterilized” incubation compared to the “non-sterilized” one highlighting that As mobilization from soil occurred through the microbially mediated reductive dissolution of As-bearing Fe-Mn (oxy)hydroxides and did not seem to be impacted by organic matter release.

References

[1] Mansfeldt, T., Overesch, M., 2013: Journal of Environmental Quality 42, 1130–1141;
[2] Nakamaru, Y.M., Altansuvd, J., 2014: Chemosphere 111, 366–271;

EXPERIMENTAL PILOT SCALE TREATMENT OF MINE WATER AFTER ANTIMONY MINING AT LOCALITY POPROC (SLOVAKIA)

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The abandoned Sb deposit Poproč represents a significant environmental burden in the Document MŽP SR and SAŽP "State program of environmental remediation of contaminated sites (2010-2015)". One of the most important sources of contamination at the site of Poproč is mining water flowing out of the adit Agnes, which includes several times elevated Sb and As compared to government regulations [1] as well as elevated levels of Pb, Zn, Fe, SO_4^{2-}. Other sources of contamination of environmental load at Poproč are the numerous ore heaps and tailing ponds which are not isolated from the surrounding environment.

The presented experimental work on the site of Poproč builds on the results of previous studies involving laboratory and field survey works [2, 3, 4]. Based on column experiments [2, 5], the best option for cleaning mine water with a high content of arsenic and antimony showed filling with zerovalent iron. Sorption of several potentially toxic elements on Fe0 have been described in many scientific studies [6, 7, 8]. We built the reaction barrier formed with zerovalent iron (ferrous waste chips) directly on the site in the effluent from the adit Agnes and for almost one year we took water samples and evaluated its effectiveness. The second remediation measure was the construction of a sedimentation tank in which precipitated contaminants from the mine water at the bottom of the tank and were not longer transported as slurry into surface water flow Olšava.

In the process of mine water purification from the adit Agnes was used zerovalent iron in the form of an iron fillings (waste of processing iron and steel) for the filling of the reaction barrier (tank 1). Iron fillings (about 150 kg) were cleaned of the waste and debris and were about 16 hours stored in plastic barrels in a solution of HCl in order to activate the iron chips. After the activation process were flushed with water. The plastic container on a volume of 1 m3 was placed in to the adit of portal Agnes and about one half of the volume was filled with activated iron fillings. Mining water from the adit is flown to the container through a PVC pipe with a diameter of 5 cm. To extend the contact between the water and the sorption container material does not pass through the entire discharge from the mine Agnes (390 l/min), but just a part (about 5 l/min - according to the conditions of the sources). The effluent from the tank was set to 5 l/min.

Second plastics tank (tank 2) was placed also in the portal of adit Agnes. It is filled with water, which flows directly from the adit Agnes and used for sedimentation of iron oxide-hydroxides from mine water, which absorbed Sb and As. The inflow and the outflow from the settling tank is similar to tank nr. 1.

Regularly every two or three weeks were sampled water flowing from the Agnes adit, from the both tanks and the creek Olšava above and below the spot where the contaminated water from Agnes flows into the creek. Water samples were analyzed in accredited labs EL, spol. s r.o., Spišská Nová Ves. In the water samples were determined physico-chemical parameters such as pH, Eh, temperature, specific electric conductivity, values of selected chemical parameters (Na, K, Mg, Ca, Al, Fe, Mn, As, Sb, Cd, Cu, Zn , Pb, chlorides, phosphates, hydrogen carbonates, carbonates, sulphates, fluorides).

The amount of antimony and arsenic in mining waters in the effluent from the adit Agnes during the year varies very significantly. The highest values were measured 15.08.2013, so in dry, summer period, when high levels of contaminating elements are not diluted by rainwater. The highest measured value in the mining water for antimony was 406 µg.l-1 and 1620 µg.l-1 for arsenic. The indicative levels (As = 50 µg.l-1, Sb = 25 µg.l-1) and intervention levels (As = 100 µg.l-1, Sb = 50 µg.l-1) for antimony and arsenic in surface waters are definite in directive of Ministry of Environment of the Slovak Republic [9]. Contaminants content have decreased rapidly during each sampling after passing reactive barriers filled with zerovalent iron.

The average efficiency of removal of antimony during the period reached 85%, arsenic removal efficiency significantly fluctuated but reached an average of 79%. The efficiency of removal of antimony, arsenic and zinc, in sampling dates is shown in fig. 4. The pH, electrical conductivity and the sulfate content is not substantially change, while the interesting is behavior of zinc, which in the second half of the experiment was removed from the water, with an average efficiency of 49%. The limit value for zinc in surface water is set at 100 µg.l-1 and all Zn values it several times exceeded. Sedimentation tank achieved better average results for arsenic (87%) than for antimony (66%), although the problems with the location and operation of tank there were not sampled in such timing as the tank no. 1 with iron fillings. In the second part of our work on site Poproč, in September 2014, we lined up individual containers in a row position so the water from the adit Agnes at first passed sedimentation tank and then simply flowed into the reaction barrier fill with zerovalent iron. This helped mainly to increase the efficiency of removal of antimony (in 3 cases above 97 %).

Effectiveness of removing contaminants from the mine water through passive remediation process is high enough during our pilot experiment. Iron fillings as a reaction material in geochemical barrier began to crumble and corrode after one year. This fact could result in limiting the use of technology, so it was necessary to replace the iron contents and used fillings store to hazardous waste because of sorption toxic elements on the surface of an iron fillings. Iron oxide-hydroxides which are products of precipitation and sedimentation in settlings tanks can be classified as mineral phases goethite eventually ferrihydrite. These solid substances adsorb contaminants from mine water to their structure. Our remediation system can effectively purify contaminated mine waters and with a combination of other appropriate actions, such as using natural absorbent materials based on bentonite [10] may further increase the final effect of passive water treatment. The Poproč village has long-term problems with drinking water, especially during the summer months. Therefore achievement of limits of groundwater at least for irrigation purposes will really helpful.

Acknowledgements: This study was financially supported by the Slovak Research and Development Agency under the contract No. APVV-0344-11 „Pilot scale remediation of mine waters on the selected abandoned Sb deposit“.

References

[1] Slovak Government Regulation no. 269/2010 Z.z. of 25 May 2010 establishing the requirements to achieve good water status.

[2] Chovan, M., Lalinská, B., Šottník, P., Jurkovič, Ľ., Ženišová, Z., Fľaková, R., Krčmář, D., Lintnerová, O., Hiller, E., Klimko, T., Jankulár, M., Hovorič, R., Jašová, I., Lux, A., Vaculík, M., Hudáček, M., Michňová, J., Petrák, M.,

Andráš, P., Milovská, S., Majzlan, J., 2010: Evaluation of the impact of mining operations on the surrounding abandoned Sb deposits in Slovakia with suggestions for remediation. Final report on project progress, Manuscript, Comenius University in Bratislava, Slovakia, 358 p

[3] Hiller, E., Lalinská, B., Chovan, M., Jurkovič, Ľ., Klimko, T., Jankulár, M., Hovorič, R., Šottník, P., Fľaková, R., Ženišová, Ž., Ondrejková, I., 2012: Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia. In: Applied Geochemistry 27, pp 598-614 p

[4] Lalinská–Voleková, B., Majzlan, J., Klimko, T., Chovan, M., Kučerová, G., Michňová, J., Hovorič, R., Gottlicher, J., Steininger, R., 2012: Mineralogy of weathering products of Fe–As–Sb mine wastes and soils at several sb deposits in Slovakia. In: The Canadian Mineralogist, Vol. 50, pp 1208-1226

[5] Tóth, R, Hiller, E., 2010: Sorption of antimony and arsenic on modified zeolites, the application of water affected by mining operations. In: Geochemistry 2010 State Geological Institute of Dionýz Štúr, Bratislava, Slovakia, 2010. pp 12-130

[6] Puls, R.W., Paul, C.J., Powell, R.M., 1999: The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate- contaminated groundwater. In: Applied Geochemistry 14, pp. 989-1000

[7] Farrell, J., Wang, J., O'Day, P., Conklin, M., 2001: Electrochemical and spectroscopic study of arsenate removal from water using zerovalent iron media. In: Environmental Science and Technology 35 (10) (2001), pp. 2026-2032.

[8] Lackovic, J.A., Nikolaidis, N.P., Dobbs, G.M., 2000: Inorganic arsenic removal by zero-valent iron. In: Environmental Engineering and Science 177 (2000), pp 29-39.

[9] Directive of Ministry of Environment of the Slovak Republic from 28. January 2015 number 1/2015 – 7 directive to carry out risk assessments of contaminated sites, Bratislava, pp 1 – 96, 2015

[10] Janotka, I., Frankovska, J., Baslik, R., Stresko, V., 1996: Bentonite-based materials for environmental protection. In: Geologica Carpathica - Clays, 1 (1-2), pp 43-48

CORRELATING MICROBIAL COMMUNITY PROFILES WITH ANTIMONY CONTAMINATION DATA IN A WATERSHED HEAVILY CONTAMINATED BY AN ANTIMONY TAILING MINE

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Mining activities have introduced contamination to surrounding aquatic and terrestrial environments, posing adverse effect to both anthropospere and biosphere. Indigenous microbial communities have a profound impact on the biogeochemical cycles, indicating the potential to remediate the contamination introduced by the mining activities. Antimony has been extensively mined in China and antimony contamination in mining areas has been frequently encountered. However, the microbial composition and structure in response to antimony contamination has remained overlooked. Here we selected a watershed heavily contaminated by an antimony tailing mine located upstream. We obtained comprehensive geochemical data of the sediments in different depth and the water taken from the watershed. More specifically, different antimony extraction fractions have been determined and this watershed was divided by heavily Sb-contaminated zone and moderate-contaminated zone. In addition, the indigenous microbial communities have been profiled by high-throughput sequencing from 16 sediment samples (535,390 valid reads). Canonical correspondence analysis (CCA) demonstrated that a suite of *in situ* geochemical and physical factors significantly structured the overall microbial community compositions. Further, we showed significant statistical relationship between different Sb extraction fractions and individual phylotypes (bacterial genera). Spearman rank correlations indicated that a number of microbial phylotypes including *Desulfurivibrio* and *Thiobacillus* were positively correlated with different fractions of Sb, suggesting potential roles of these phylotypes in microbial Sb cycling. The current study indicated that the overall microbial communities and individual phylotypes could be significantly shaped by the *in situ* geochemical conditions.