



# antimony 2011

2nd International Workshop  
on Antimony in the  
Environment  
Jena, 21-24 August 2011



Cover image: Tailing sediments in Poproč, Slovakia, contaminated by antimony and other elements. (Photo courtesy Dr. Bronislava Lalinská).

# TABLE OF CONTENTS

WELCOME BY THE CONVENORS.....	i
ADMINISTRATIVE COMMENTS.....	ii
MAP OF JENA.....	iii
PROGRAMME.....	1
ABSTRACTS – ORAL PRESENTATIONS.....	5
ABSTRACTS – POSTERS.....	39
AUTHOR INDEX.....	73



## Welcome to Jena

The convenors are delighted to welcome you in Jena. We wish you a pleasant stay and an inspiring meeting.

The Second International Workshop on Antimony in the Environment continues loosely on the First Workshop which took place in Heidelberg in May 2005. The workshop reflects the advances and the need for further work on the field of chemistry, ecotoxicology, geomicrobiology, mineralogy, and geochemistry of antimony. We are pleased to receive diverse contributions whose center remains the element antimony. Our goal to concentrate the researchers of antimony in our meeting and have them discuss all facets of their work was fulfilled. Otherwise, these scientists may have not met because they come from different disciplines.

We are pleased to express our gratitude to the Deutsche Forschungsgemeinschaft (German Funding Society) which supported the keynote speakers and the students who will help you during the meeting. The company Bruker kindly sponsored the Welcome reception.

Montserrat Filella, Juraj Majzlan



## ADMINISTRATIVE COMMENTS

### VENUE

All scientific conference activities will take place in the building of the Institute of Geosciences in Burgweg 11 in Jena.

### REGISTRATION/HELP-DESK/WELCOMING RECEPTION

All participants should register at the Registration/Help desk. It will be staffed on Sunday from 3 pm until the Welcome reception begins, and then during the conference hours, i.e., while the scientific sessions are running.

### PRESENTATIONS

All presentations will take place in the Lecture Hall (Hörsaal) of the Institute. There is only one session at each time, that is, no parallel sessions. All conference participants have the possibility to listen to and discuss all presentations.

### POSTERS

Posters will be on display on Monday and Tuesday. During these days, time slots are reserved for poster sessions (see Programme). Participants are asked to put them up in advance on Monday. By the end of the conference, participants are asked to remove the posters. Posters which will not be removed will be destroyed.

### NAME BADGES

Participants are required to display their name badges at all the scientific sessions and social events during the meeting, with the exception of the organ pipe concert in a church.

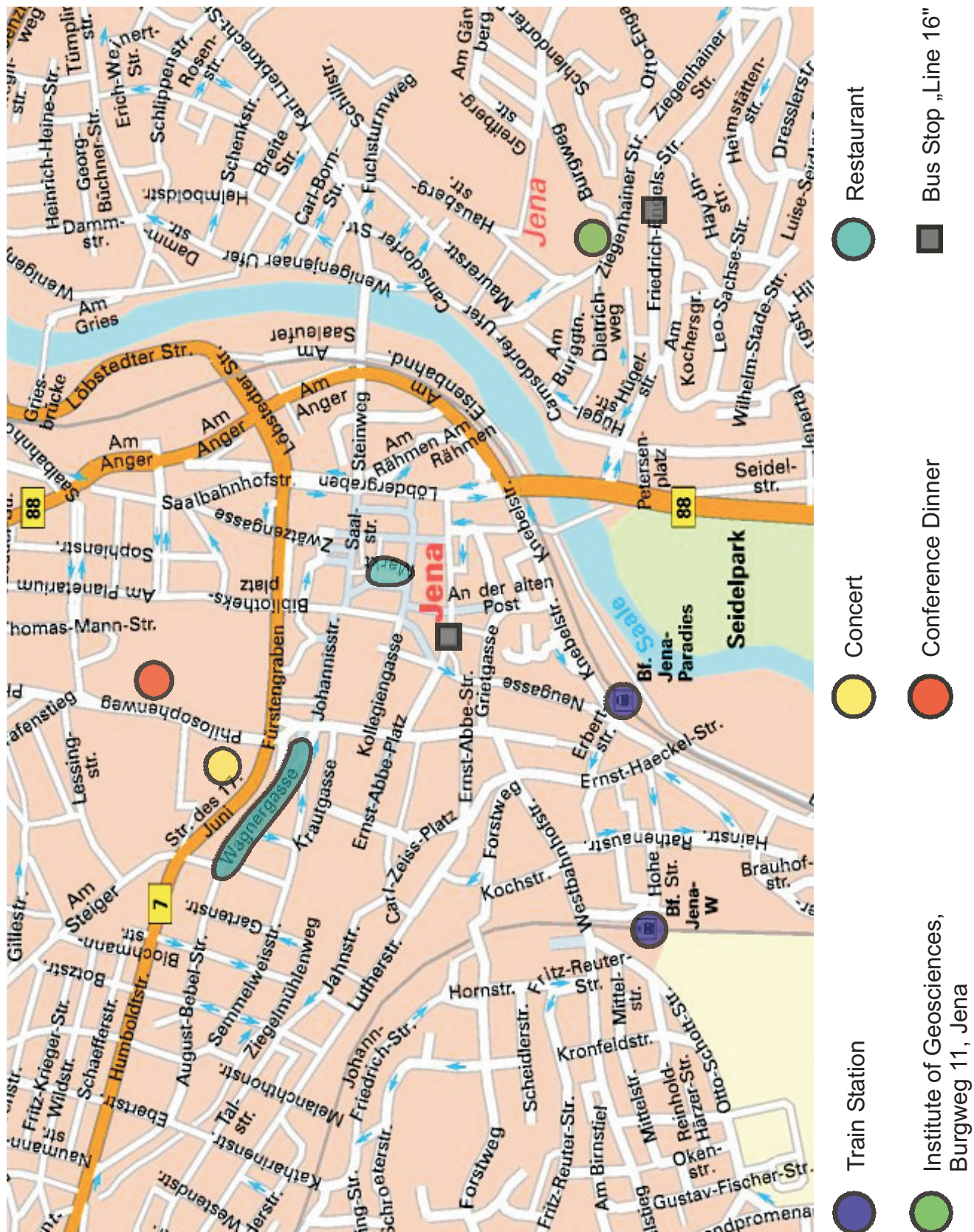
### CONFERENCE DINNER

Conference dinner will take place on Tuesday, August 22, at 8 pm at the Mensa im Studentenhaus, Philosophenweg 20 (see the map).

### CONCERT

A pipe-organ concert is planned for Monday, August 22, at 8 pm in the evangelic church at the Johannisfriedhof (Johannis cemetery). The address is Philosophenweg 1 (see the map).

# MAP OF JENA







# PROGRAMME

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## August 21, Sunday

15:00-18:00 Registration

18:00-18:10 Opening

18:10-19:00

### WELCOMING KEYNOTE LECTURE

**T01 Leishmaniasis, antimony and arsenic in India**

**Meghan Perry, University of Dundee, UK**

19:00-??? Welcome reception

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## August 22, Monday

9:00-9:30 Opening

### Session 1: ANTIMONY AND HUMAN AND ECOSYSTEM HEALTH

9:30-10:30

#### KEYNOTE LECTURE

**T02 Pathways of antimony uptake, efflux and detoxification**

**Barry Rosen, USA**

10:30-11:00 Coffee break

11:00-11:20

**T03 The environmental classification of Antimony and its compounds under REACH (EC 1907/2006) And EU CLP (EC 1272/2008)**

**Claire Massey, UK**

11:20-11:40

**T04 Differences in the biogeochemistry of antimony and arsenic**

**Irina Shtangeeva, Russia**

11:40-12:00

**T05 Uptake and bioaccumulation of antimony and arsenic species in plants by example of *Pteris Vittata***

**Rainer Wennrich, Germany**

12:00-12:20

**T06 Uptake and effect of antimony in Atlantic salmon (*Salmo salar*)**

**Lene S. Heier, Norway**

12:20-14:00 Lunch break

14:00-14:30

**T07 Human health effects of antimony – an update**

**Rüddiger Battersby, Germany**

14:30-14:50

**T08 Possible role of residual Sb(III) in the hepatotoxicity of pentavalent antimonial drugs**

**Frédéric Frézard, Brasil**

14:50-16:00

**POSTER SESSION**

16:00-16:30 **Coffee break**

**Session 2: ANTIMONY IN NATURAL WATERS**

16:30-16:50

**T09 Antimony mobilisation in a NSW catchment, Australia**  
**Susan Wilson, Australia**

16:50-17:10

**T10 Antimony release from man made construction materials in hydraulic engineering - a source of surface water contamination?**  
**Lars Duester, Germany**

17:10-17:30

**T11 Thioantimonates in geothermal waters**  
**Britta Planer-Friedrich, Germany**

17:30-17:50

**T12 Factors controlling the fate of antimony produced by a natural geothermal spring, Wai-O-tapu, New Zealand**  
**Nathaniel Wilson, New Zealand**

20:00 **Concert**

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**August 23, Tuesday**

**Session 3: ANALYTICAL CHEMISTRY OF ANTIMONY**

9:30-10:30

**KEYNOTE LECTURE**

**T13 Analytical challenges in antimony speciation**  
**Helle Hansen, UK**

10:00-10:20

**T14 New simplified voltammetric method for the sensitive speciation of inorganic antimony in marine and freshwaters**  
**Pascal Salaun, UK**

10:20-10:40

**T15 Analysis of Antimony species – pitfalls and problem solving**  
**Birgit Daus, Germany**

10:40-11:20

**POSTER SESSION** and **Coffee break**

**Session 4: ANTIMONY IN THE ATMOSPHERE**

11:20-11:50

**T16 Antimony: A traffic related element in size-fractionated road dust samples collected in Buenos Aires, Argentina**  
**Patricia Smichowski, Argentina**

11:50-12:10

**T17 Antimony deposition in Norway in time and space**  
**Eiliv Steinnes, Norway**

12:10-12:30

**T18 Speciation analysis of antimony in size-classified airborne particulate matter by HPLC-ICPMS**  
**Naoki Furuta, Japan**

12:30-14:00 **Lunch break**

**Session 5.1: ANTIMONY IN SOILS, MINES AND SHOOTING-RANGES: POLLUTION REMEDIATION AND SOLID PHASE INTERACTIONS**

14:00-14:20

**T19 Immobilization of Antimony (Sb) in shooting range soil by iron amendments**  
**Gudny Okkenhaug, Norway**

14:20-14:40

**T20 Phytomanagement of relocated shooting range soil**  
**Xiaoming Wan, Switzerland**

14:40-15:00

**T21 Use of sorbents for purification of lead, copper and antimony in runoff water from a small arms shooting range**  
**Espen Mariussen, Norway**

15:00-15:20

**T22 Antimony mobility and transport in mine dumps from the Dachang multi-metalliferous mine area, Guangxi, China**  
**Li Ling, China**

15:20-15:50 Coffee break

15:50-16:10

**T23 Adsorption of As(III) to paddy soils from irrigated rice fields in Bangladesh and potential interaction of Sb(III)**  
**Dominik Weiss, UK**

16:10-16:30

**T24 The sorption of antimony(V) by different solid phases, and the effects of sulfate and phosphate on the sorption of antimony(V)**  
**Matthew Tighe, Australia**

16:30-16:50

**T25 Effect of humic acids on antimony sorption to goethite**  
**Kerstin Hockmann, Switzerland**

16:50-17:10

**T26 The Transformation of ferrihydrite to goethite, hematite, and ferrioxhyte in the presence of Sb(V)**  
**Ralph Bolanz, Germany**

17:10-17:30

**T27 Solid phase speciation in Sb-rich mining residues**  
**Hubert Bril, France**

20:00 Banquet

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**August 24, Wednesday****Session 5.2: ANTIMONY IN SOILS, MINES AND SHOOTING-RANGES: POLLUTION REMEDIATION AND SOLID PHASE INTERACTIONS**

9:00-10:00

**KEYNOTE LECTURE**

**T28 Mineralogical control of the dispersion of antimony in the natural environment**  
**Peter Williams, Australia**

10:00-10:20

**T29 Mineralogy of the weathering products in mine wastes and soils at several abandoned Sb deposits in Slovakia**  
**Bronislava Lalinská, Slovakia**

10:20-10:40

**T30 Removal of antimonate from water – Sorption and leaching behaviour onto Akaganeite**  
**Falko Kolbe, Germany**



10:40-11:10 **Coffee break**

11:10-11:30

**T31 Antimonate removal by Zr-Fe binary oxide: performance and mechanism**

**Xiaomin Dou, China**

11:30-12:00

**CLOSING KEYNOTE LECTURE**

**T33 Priorities in antimony research**

**Montserrat Filella, Switzerland**

12:00 **Workshop closing**

## ABSTRACTS - ORAL PRESENTATIONS

Abstracts are organised according to the chronological order of the talks. In each abstract, the name of the lecturer is underlined.





## T01 KEYNOTE

## LEISHMANIASIS, ANTIMONY AND ARSENIC IN INDIA

Perry, M.R., Fairlamb, A.H.

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Antimony and arsenic are elements that have a long history of use as cosmetics, poisons, therapeutic agents. For over a century, compounds containing pentavalent antimony (antimonials) have formed the basis of treatment of the leishmaniasis worldwide. Antimonials remain first-line drugs for visceral leishmaniasis in Sub-Saharan Africa and Brazil but in the hyperendemic state of Bihar, India, the cure rate of antimonials has declined over the past 30 years from over 85% to less than 50%. This marked decrease in efficacy may be due to acquired parasite resistance secondary to long term, widespread misuse of antimonials, with patients undergoing inappropriate treatment courses often administered by the largely unregulated Indian private health care system. Our research focuses on an alternative theory – namely that the related element arsenic has contributed to the decline in antimonial efficacy in this area.

In the 1970s in Asia there was a large scale national programme of insertion of multiple shallow tubewells for provision of clean and safe drinking water. This had the unintended consequence of chronically exposing millions of the Asian population to naturally occurring arsenic from their daily drinking water. Antimony and arsenic share many structural and chemical properties and antimony resistance in *Leishmania* parasites can be induced experimentally by exposure to stepwise increasing concentrations of sublethal concentrations of trivalent arsenite in culture. If an individual who is chronically exposed to arsenic is infected with *Leishmania*, during the incubation period, the parasites would be exposed to arsenic due to its presence within organs of the lymphoreticular system. This could lead to the development of an arsenic-resistant *Leishmania* strain that would be cross-resistant to antimonial therapy.

This presentation will look at the history of antimony and arsenic use in medicine and expand on and discuss the hypothesis that arsenic has contributed to the development of decreased efficacy of antimonials in the treatment of visceral leishmaniasis in Bihar, India.

## T02 KEYNOTE

## MECHANISMS OF ANTIMONY UPTAKE, EFFLUX AND DETOXIFICATION

Rosen, B.P.

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One of the initial challenges of the earliest cells would have been the ability to detoxify heavy metal ions, transition metal ions and metalloids, including arsenic and antimony (3). In this presentation we will review the biology, biochemistry and structural biology of the transporters and enzymes involved in metalloid tolerance. We have identified the uptake systems for Sb(III) in most living cells to be aquaglyceroporins, which are channel proteins for neutral solutes such as glycerol and  $\text{Sb}(\text{OH})_3$  (2). The major uptake systems in humans are AQP9, the liver isoform, and AQP7, the adipose and kidney isoform. In prokaryotes Sb(III) induces transcription of *ars* operon genes by binding to the ArsR repressor, members of the ArsR/SmtB family of small metalloregulatory proteins (5). These homodimeric repressors bind to DNA in absence of inducing Sb(III) and dissociate from the DNA when metalloid is bound. A combination of data from Extended X-ray Absorption Fine Structure analysis and homology modeling, the nature of the metalloid binding site was elucidated. ArsR controls expression of *ars* genes that encode Sb(III) efflux systems and enzymes of antimony biotransformation. ArsA is the catalytic subunit of the ArsAB ATP-coupled Sb(III) efflux system. ArsA is an Sb(III)-activated ATPase, and ArsB is an  $\text{Sb}(\text{OH})_3/\text{H}^+$  antiporter. ArsD is an Sb(III) chaperone that ferries metalloid to the efflux pump. The crystal structures of ArsD and ArsA allow their interactions to be modeled. Finally, microorganisms methylate arsenic and antimony to a variety of species including volatile products such as trimethylarsine and trimethylstilbene (1). We have shown that the *arsM* gene encodes the ArsM As(III)/Sb(III) S-adenosylmethionine (SAM) methyltransferase, an enzyme that methylates Sb(III) (8). The *arsM* gene was cloned from the thermophilic eukaryotic alga *Cyanidioschyzon merolae*, which forms the major biomass in arsenic-rich hot springs in Yellowstone National Park (7), where volatile antimonials are generated (6). Purified CmArsM is active at 50-70 °C and produces volatile metalloid gases (9). CmArsM has been crystallized (4), and its crystal structure solved to 1.6 Å.

*Supported by NIH grant R37 GM52216.*

[1] Bentley, R., Chasteen, T. G., 2002: Microbiol Mol Biol Rev 66, 250-71. [2] Bhattacharjee, H., Mukhopadhyay, R., Thiagarajan, S., Rosen, B. P., 2008: J Biol 7, 33. [3] Bhattacharjee, H., Rosen, B. P., 2007: Arsenic metabolism in prokaryotic and eukaryotic microbes, p. 371-406. In D. H. S. Nies, Simon (ed.), Molecular microbiology of heavy metals, vol. 6. Springer-Verlag, Heidelberg/New York. [4] Marapakala, K., Ajees, A. A., Qin, J., Sankaran, B., Rosen, B. P., 2010: Acta Crystallogr Sect F Struct Biol Cryst Commun 66, 1050-2. [5] Ordóñez, E., Thiagarajan, S., Cook, J. D., Stemmler, T. L., Gil, J. A., Mateos, L. M., Rosen, B. P., 2008: J Biol Chem 283, 25706-14. [6] Planer-Friedrich, B., Lehr, C., Matschullat, J., Merkel, B. J., Nordstrom, D. K., Sandstrom, M. W., 2006: Geochimica et Cosmochimica Acta 70, 2480-91. [7] Qin, J., Lehr, C. R., Yuan, C., Le, X. C., McDermott, T. R., Rosen, B. P., 2009: Proc Natl Acad Sci U S A 106, 5213-7. [8] Qin, J., Rosen, B. P., Zhang, Y., Wang, G., Franke, S., Rensing, C., 2006: Proc Natl Acad Sci U S A 103, 2075-80. [9] Yuan, C., Lu, X., Qin, J., Rosen, B. P., Le, X. C., 2008: Environ Sci Technol 42, 3201-6.

T03

**THE ENVIRONMENTAL CLASSIFICATION OF ANTIMONY AND ITS COMPOUNDS UNDER REACH (EC 1907/2006) AND EU CLP (EC 1272/2008)**Massey, C.<sup>1</sup>, Peters, A.<sup>1</sup>, Van de Velde, K.<sup>2</sup><sup>1</sup>wca environment ltd, Brunel House, Volunteer Way, Faringdon, SN7 7YR, UK<sup>2</sup>International Antimony Association (i2a), Avenue de Broqueville 12, 1150 Brussels, Belgium  
e-mail: [claire.massey@wca-environment.com](mailto:claire.massey@wca-environment.com)

The first deadlines for two major pieces of European Chemical legislation have recently passed. The Registration, Evaluation and Authorisation of Chemicals (REACH) requires that manufacturers and importers of chemicals in the EU submit registration dossiers to the European Chemicals Agency (ECHA) containing data on various hazard endpoints and, if certain criteria are met, a risk assessment. The data requirements are based on the tonnage of the chemical, and the first deadline for substances produced or imported by a single entity at >1000 tpa was the 30th November 2010. The Classification, Labelling and Packaging Regulation (CLP) required that all manufacturers and importers of chemicals in the EU at >1 tpa submit a proposal for the classification and labelling of the substance to ECHA by the 3rd January 2011. Submission of a REACH registration dossier fulfilled the requirements of the CLP. This talk will give a brief introduction to these two pieces of EU legislation and describe the approach used to determine the appropriate environmental classification for antimony and several antimony compounds.

In the EU, the environmental classification of a substance is based on its acute aquatic ecotoxicity, although chronic ecotoxicity data can be used to remove certain classifications. The data set collated for the purposes of REACH registration contained an acute and chronic ecotoxicity dataset for algae, invertebrates and fish. For metals and metal compounds, which are often of low solubility, an alternative set of classification criteria can be used which also takes into account the amount of dissolved metal ion that is released over time. The UN Transformation/Dissolution Protocol (T/D) for Metals and Sparingly Soluble Metal Compounds is used to generate these data.

The T/D characteristics of Sb metal and several Sb compounds were investigated at pH 6 and pH 8.5, at loadings of 1, 10 and 100 mg/L. Antimony trisulphide, Sodium antimonate, Antimony tris(ethylene glycolate), Antimony trichloride, Antimony triacetate, Antimony pentoxide, Antimony trioxide, Sodium hexahydroxoantimonate and Antimony metal were studied.

We will demonstrate how the T/D and ecotoxicity data have been used to derive the appropriate environmental classification for Antimony and several of its compounds. On the basis of these data, none of the antimony compounds considered as part of this work would have an environmental classification for either acute or chronic hazard. These classifications have been submitted to ECHA to ensure compliance with REACH and the CLP Regulations.



## T04

**DIFFERENCES IN THE BIOGEOCHEMISTRY OF ANTIMONY AND ARSENIC**Shtangeeva, I.

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The understanding of the mechanisms of uptake of trace elements by different plant species is of critical importance for the environmental ecotoxicology. The toxic effects from metal bioaccumulation may take place even at very low concentration levels. Although there is a great interest in the metal uptake from soil and metal accumulation in different plants, list of the elements that have attracted attention of researchers is rather short.

Arsenic and antimony are similar chemical elements. They are found in trace quantities in various environmental samples. Arsenic is mainly distributed in the environment as an anion (negatively charged ion). This is different from most metals, which form cations (positively charged ions). Antimony is a naturally occurring mineral component. Antimony is considered by some researchers to be more toxic than arsenic [1], but others say it is less toxic [2]. As was recently reported [3], almost nothing is known about the mechanisms of Sb uptake by plants. Moreover, so far the data on the biogeochemistry of As and Sb are quite contradictory.

The aims of the present research were to estimate an ability of cereal crops grown in soil enriched with Sb and As to accumulate these trace elements and evaluate the potential of the plants to remove Sb and As from contaminated soils.

Seedlings of wheat, rye, and oat were grown in soil spiked with either Sb, or As, or Sb+As. Plants and soil were collected several times after planting and then analysed by ICP-MS.

Despite botanical similarity of the crops, their elemental compositions differed significantly. The biggest differences were observed between leaves of the different plant species. Concentrations of many elements in roots were higher than in leaves, thus suggesting that roots serve as a natural barrier preventing transfer of certain metals to upper plant parts.

Growth of seedlings in soil spiked with Sb and/or As influenced the plant development. Oat and rye were more affected by the treatments than wheat. Significant increase of concentrations of Sb and As in the plant roots was registered when the plants were grown in soil enriched with these metalloids. The accumulation of Sb and As in leaves was not so marked. Uptake and translocation of Sb and As were different when the elements were added to soil separately or together. All plants accumulated more As in roots and leaves when it was added to soil as single element. On the other hand, Sb uptake by roots as well as translocation of the element to leaves were more significant when Sb was added to soil together with As. Thus, bioaccumulation of Sb was positively affected by As, while Sb negatively influenced on As uptake.

The significant accumulation of Sb in plants resulted in a decrease of Sb concentration in the rhizosphere soil of wheat, rye, and oat. Meanwhile, the increase of As concentration in plants did not lead to significant decrease of As level in soil.

Although Sb and As are chemical analogues and thus, similar behaviour of the elements in plants could be expected, no correlation between Sb and As in plants and in the rhizosphere soil was found. Therefore, in spite of similar chemical properties, As and Sb demonstrated different biogeochemical behaviour. This indicates that in order to enter biological systems these elements probably form different metalloid-organic compounds.

[1] Pawlak, P.S. et al., 2010: Advanced Materials Res. 83-86, 553-562. [2] Duester, H.G. et al., 2011: Microchem. J. 97, 30-37. [3] Tschan, M. et al., 2009: Environ. Chem. 6, 106-115.

T05

## UPTAKE AND BIO-ACCUMULATION OF ANTIMONY AND ARSENIC SPECIES IN PLANTS BY EXAMPLE OF *PTERRIS VITTATA*

Müller, K.<sup>1,2</sup>, Daus, B.<sup>1</sup>, Mattusch, J.<sup>1</sup>, Vetterlein, D.<sup>1</sup>, Merbach, I.<sup>1</sup>, Wennrich, R.<sup>1</sup>

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Ten years ago Ma et al. [1] first reported ‘that *Pteris vittata* (brake fern) is extremely efficient in extracting arsenic from soils and translocating it into its above-ground biomass’. Since this first report a lot of work about hyperaccumulation of arsenic by this plant was published [2]. It was also shown that in areas, with high geogenic or anthropogenic arsenic pollution this element could be enriched by the fern plants.

The Mansfeld region (Germany) has been affected by non-ferrous ore mining and smelting activities for centuries. The waste of ore processing, characterized by elevated concentrations of arsenic and antimony (besides other metals) has been dumped and has adversely affected the environment. Little is known about the mobilization of these elements and the transfer into plants in general. Of particular interest was whether the arsenic hyperaccumulator *Pteris vittata* would be able to take up and translocate antimony to a similar extent as arsenic.

The bio-accumulation of antimony (and arsenic) by the fern was investigated by the admission of the two elements separately and in the mixtures with different mass ratios of Sb and As under greenhouse conditions.

The total concentration of Sb and As in different parts of the plants (roots, old and new fronds) was determined by using the ICP mass spectrometry. A different pattern of accumulation was found: high concentrations of Sb were in the roots and high concentration of As in the leaves, respectively, indicating differences in root-shoot transport for the two elements.

In aqueous extracts of the plant material (stored in liquid N<sub>2</sub>) speciation analysis (IC-ICP-MS) was carried out. The separation was performed using anion chromatography on a strong anion exchange column (IonPac AS15/AG15). Based on isocratic optimizations for the separation of Sb(III) and Sb(V) as well as Sb(V) and trimethylated Sb(V) - (TMSb(V)), a chromatographic method with an eluent gradient was developed [3].

Besides Sb(III) and Sb(V) as main components (CH<sub>3</sub>)<sub>3</sub>Sb(V) was identified and determined in the extracts. Additionally, two other Sb species (up to now being not identified) were found. The sum of the Sb species was found to be approx. 90 % of the total concentration of Sb in the aqueous extracts of the plant materials.

[1] Ma, L. Q., Komar, K. M., Tu, C., Zhang, W., Cai, Y., Kennelley, E. D., 2001: Nature 409, 579. [2] Vetterlein, D., Wesenberg, D., Nathan, P., Bräutigam, A., Schierhorn, A., Mattusch, J., Jahn, R., (2009: Environmental Pollution 157, 3016-3024. [3] Müller, K., Daus, B., Mattusch, J., Stärk, H.-J., Wennrich, R., 2009: Talanta 78, 820–826.

## T06

**UPTAKE AND EFFECT OF ANTIMONY IN ATLANTIC SALMON (*SALMO SALAR*)**

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Tollefsen K.E.<sup>1,3</sup>, Salbu, B.<sup>1</sup>

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<sup>2</sup>Norwegian Defence Research Establishment, P.O. Box 25, N-2027 Kjeller, Norway

<sup>3</sup>Norwegian Institute for Water Research, Gaustadalleen 21, N-0349 Oslo, Norway  
e-mail: lene.sorlie.heier@umb.no

The knowledge on uptake and effects of antimony (Sb) in aquatic organisms is scarce, and there is a great need for research within the field. The objective of the present work was to investigate the uptake of Sb in fish as a function of time using a radioactive tracer technique, and secondly investigate sub lethal effects in fish exposed to different concentrations and oxidation states of Sb in a chronic exposure study. Atlantic salmon (*Salmo salar*) were used as a model organism. The raw water quality used in the experiments is relevant for Scandinavian recipients (low ionic strength, low calcium).

The first experiment studied the uptake of <sup>125</sup>SbCl<sub>3</sub> as a function of time. Fish were sacrificed after 1, 3, 7 and 14 days of exposure, and gills, liver, spleen, kidney and brain were dissected out and the activity of <sup>125</sup>Sb was determined. In the second experiment fish were exposed for 72 hours to K[Sb(OH)<sub>6</sub>] (5, 25, 50, 500 and 5000 µg Sb/L) and SbCl<sub>3</sub> (5, 25 and 50 µg Sb/L). A range of endpoints were investigated; the bioavailability/reactivity of Sb was determined by measuring gill and liver accumulation of Sb, effects on ion-regulatory mechanisms were determined by analysing plasma ions (sodium, chloride and potassium), general stress were determined by analysing plasma glucose and the gill gene expression of heat shock protein (HSP70). Also, the gill gene expression of NaK-ATPase (ion regulation), gamma-glutamylcysteine synthetase (oxidative stress), growth arrest and DNA damage (Gadd45) ubiquitin (protein degradation) and metallothionein (metal exposure and oxidative stress) were determined. The exposure waters were characterized with respect to size and charge distribution of Sb as well as determination of oxidation state of Sb by HG-ICP-OES.

The radioactive tracer experiment showed that <sup>125</sup>Sb was accumulating on gills, liver and in the gastrointestinal tract, and the accumulation seemed to reach steady state after about 7 days of exposure.

Exposure to different concentrations of K[Sb(OH)<sub>6</sub>] resulted in changes in several of the endpoints. The gill accumulation of Sb clearly increased when the Sb concentrations in the water increased, and the accumulation of Sb(III) was higher than Sb(V). The highest concentrations of Sb had an immediate impact on the fish physiology, such as increased glucose levels (increased stress). The gene expression data is currently being analyzed and further work will be performed on the mechanisms of toxicity.



T07

**HUMAN HEALTH EFFECTS OF ANTIMONY – AN UPDATE**Battersby, R.V.<sup>1</sup>, Van de Velde, K.<sup>2</sup><sup>1</sup>EBRC Consulting GmbH, Raffaelstr. 4, 30177 Hannover, Germany<sup>2</sup>International Antimony Association (i2a), Avenue de Broqueville 12, 1150 Brussels, Belgium  
e-mail: rvb@ebrc.de

Antimony and several inorganic derivatives have been the subject of two major reviews recently: firstly, diantimony trioxide was comprehensively assessed under the Risk Assessment scheme of the Existing Substances Regulation of the EU (793/93), and secondly all antimony substances marketed at tonnages above 1,000 tpy required registration under the new chemicals legislation REACH.

Both legislations require a comprehensive hazard characterisation by the provision of a comprehensive set of toxicological data, covering all aspects of toxicokinetics, acute toxicity, irritation and sensitisation effects, repeated dose toxicity, carcinogenicity, mutagenicity and reproduction toxicity.

Further, all intended uses of the substance need to be addressed with so-called „Exposure Scenarios“ in which the description of technological processes, the associated exposures of workers, professional users and consumers are assessed quantitatively. In a subsequent risk characterisation, the comparison of hazard information with the exposure assessment allows the identification of sustainable, safe uses.

In the above context, all available information on human health aspects of antimony were collated and evaluated for quality and reliability. Any remaining data gaps were identified and subsequently addressed either by commissioning guideline-conform, state-of-the-art studies (under GLP) or by way of read-across between similar substances in order to minimise testing. Since only a very limited number of these recent studies have been made publicly available, it is the purpose of this presentation to provide an oversight of the conclusions that can be derived from these studies.

Together with its unique toxicokinetic profile, it will be shown that antimony is generally of a low order of toxicity, as reflected in the lack of classification for human health endpoints except for one. The current classification for inhalation carcinogenicity will be discussed in the context of the underlying mechanism, with a reflection on the current uses of antimony substances.

T08

**POSSIBLE ROLE OF RESIDUAL Sb(III) IN THE HEPATOTOXICITY OF PENTAVALENT ANTIMONIAL DRUGS**

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Pentavalent antimonial drugs, such as meglumine antimoniate (MA), are the first-line drugs for the treatment of leishmaniasis in several countries. These drugs are highly effective but, unfortunately, promote severe side effects, such as elevation of transaminase levels evidencing hepatotoxicity [1]. These side effects are often attributed to the *in situ* reduction of Sb(V) into more toxic Sb(III). On the other hand, *in vitro* studies gave support to the model that residual Sb(III) in pentavalent antimonial drugs is responsible for their cytotoxicity [2]. The aim of the present work was to investigate the hepatic histological features of mice experimentally infected with *Leishmania chagasi* after chronic treatment with MA from three different sources and containing different amounts of residual Sb(III). The drugs used were the commercial drug (Glucantime®) and the compounds obtained from different sources of Sb(V) (either SbCl<sub>5</sub> for MA or KSb(OH)<sub>6</sub> for MA1) and synthetic process [3]. Female BALB/c mice infected with *L. chagasi* were distributed in four groups (n=5/group) that received by intraperitoneal route 80 mg Sb/Kg/day for 20 days, as Glucantime® (Glu), MA or MA1. Control group received saline solution. Livers were processed for histology and stained with hematoxylin & eosin. Ten fields of each mice slide were randomly analyzed by microscopy at 40x and 10x objectives in order to determine the % of semi-quantitatively alterations, involving %necrosis, %peliosis and relative hepatocyte cytoplasmic characteristics [4]. Besides the Sb(III) determination was based on the specific interaction of Sb(III) with the chromogen bromopyrogallol red [2]. The amount of Sb(III) obtained for the compounds were: 0.118% (w/w) for MA, 0.015% for Glu and <0.002% for MA1. Animals submitted to Glu and MA showed predominantly swollen hepatocytes and the highest frequencies for necrosis and peliosis. On the other hand, animals treated with MA1 showed cytoplasm mainly granulous and lesions to a lesser extent. Typical normal features were observed in control animals. Interestingly, all drugs were equally effective in reducing the parasite load in the liver. In conclusion, all groups submitted to MA drugs showed histological alterations in the liver. However, the group treated with the MA compound containing the lowest amount of residual Sb(III) showed significantly reduced alterations, indicating a possible role of residual Sb(III) in the hepatotoxicity of pentavalent antimonial drugs. MA1 compound showed promise for the treatment of leishmaniasis. Financial support from the Brazilian agencies: FAPEMIG, CNPq and CAPES.

[1] Marsden, P. D., 1985: Rev. Soc. Bras. Med. Trop. 18,187-198. [2] Dzamitika, S.A., et al., 2006: Chem.-Biol. Inter. 160, 217-224. [3] Demicheli, C., et al., 2003: Appl. Organomet. Chem. 7, 226-231. [4] Huerre, M.R., et al., 2001: Virchows Arch. 438, 107-115.

T09

**ANTIMONY MOBILISATION IN A NSW CATCHMENT, AUSTRALIA**

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The Macleay River catchment in northern NSW is contaminated by antimony (Sb) and arsenic (As) as a result of historic mining operations in the upper catchment. Stream sediment concentrations in the upper catchment are high (80–438 ppm Sb, 86–329 ppm As) and a contaminated sediment dispersion plume extends to the coastal floodplain 300 km to the east, where Sb and As concentrations exceed background over 90% of the floodplain area [1, 2]. This is the largest known anthropogenic dispersion of Sb in Australia. The aims of this study were to understand Sb (and As) mobilisation processes as the enriched sediment moves through the catchment river system in terms of geochemical and mineralogical transformations, fluctuations in dissolved river water concentrations and sediment deposition.

A three year monitoring and research program showed that dissolved stream water concentrations in the upper catchment were consistently greater than Australian drinking water guidelines up to 100 km downstream of the source area. Water concentrations in the lower catchment were elevated only during flood conditions and also the load associated with suspended sediment was low or non detectable except when the river was flood conditions. Sequential leaching of stream sediments showed that the Sb water concentration was controlled by sorption to silicate clay minerals and iron and aluminium oxyhydroxides. Antimony (and As) was sorbed mainly to the 0.125–0.5 mm particle fraction which released the metalloids relatively slowly. Hyporheic water samples showed higher solution concentrations than adjacent stream water but results suggested Sb mobilisation under anoxic conditions was lower than that of As. Antimony (and As) concentrations in core samples from low and high flood terraces were significantly elevated above active streambed levels indicating the important role of flood sediment deposition in contamination dispersion.

[1] Ashley, P.M., Graham, B.P., Tighe, M.K., and Wolfenden, B.J. 2007. Australian Journal of Earth Sciences 54, 83–103. [2] Tighe, M., Ashley, P., Lockwood, P. and Wilson, S. 2005. Science of the Total Environment 347, 175–186.

## T10

**ANTIMONY RELEASE FROM MANMADE CONSTRUCTION MATERIALS IN  
HYDRAULIC ENGINEERING - A SOURCE OF SURFACE WATER  
CONTAMINATION?**

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Construction materials commonly used in hydraulic engineering may contain significant portions (e.g. fly ashes in concrete) or completely consist of materials from industrial processes (e.g. armour stones from slags). Even though it is well known that these water construction materials can contain significant amounts of metal(loid)s and hence have the potential to influence the water chemistry during weathering, as yet this topic seems to be under-represented in the scientific community.

For instance, copper slags contain - in addition to significant amounts of e.g. arsenic, copper or lead - between 100 and 600 mg/kg antimony (48 samples measured by X-ray fluorescence analyses). From 1970 to 1999, in Germany, twelve million tons of copper slags were built in rivers, channels and estuaries [1]. These slags, produced in Germany and merchandised as 'iron silicate stones', consist as main mineral phase of fayalite ( $\text{Fe}_2\text{SiO}_4$ ), and most of the antimony is embedded as fahlore micro spots [2]. According to our incubation and leaching experiments, up to several hundred  $\mu\text{g/kg}$  antimony can be leached within 24 h from the slags, depending among other things on the mineral phase composition, the available surface, the aging status of the material, the pH and the ionic strength of the media.

Today, the approval on the suitability of materials to be used in water construction is strongly driven by engineering and economic demands, including criteria like the density of the material or its resistance to weathering as well as by considerations about the transport distances or the production costs. In contrast the regulatory frameworks and the criteria for testing the suitability, from an environmental point of view, are much less elaborated. Often only simple elution scenarios are used and long term influences towards the chemical water quality or biomagnification effects of pollutants are not considered at all. In addition, for elements like Sb, European or national quality standards are missing and threshold values have to be defined, due to this lack of regulation, case by case.

Based on the experiences from field studies, laboratory incubation experiments and leaching experiments, supported by analyses from inductively coupled plasma with atomic emission spectrometry and sector field mass spectrometry as well as from X-ray fluorescence analysis, the following topics will be elucidated in the presentation:

(i) Which construction materials are used in relevant quantities in surface water bodies? (ii) Compared to the surface water concentrations in Germany: Which materials have the potential to release antimony in significant amounts? (iii) The antimony release of natural vs. artificial materials. (iv) Which weathering processes are crucial for the antimony release: chemical $\leftrightarrow$ physical $\leftrightarrow$ biological? (iv) Which key factors and mechanisms govern the Sb release from copper slag armour stones?

[1] Larm, A., Rospunt, J., Blum, U., Schwedt, G. and Bertram, H., 2000: Nachhaltiges Niedersachsen 9. [2] Khorasani, R., 1995: Investigation report - mineralogical-petrographical examination of iron silica rocks of the Norddeutschen Affinerie Hamburg.

T11

## THIOANTIMONATES IN GEOTHERMAL WATERS

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The formation of aqueous antimony sulfide complexes upon dissolution of stibnite ( $\text{Sb}_2\text{S}_3$ ) and their importance for geothermal antimony transport has often been stressed. All the more surprising, up to date only laboratory studies and theoretical calculations support the existence of these thioantimony species<sup>1-5</sup>. We successfully applied alkaline chromatographic separation and detection by inductively coupled plasma mass spectrometry (AEC-ICP-MS) previously used for thioarsenates<sup>6</sup>, for the determination of two antimony-sulfur species in synthetic solutions and natural geothermal waters. Based on their S/Sb ratios of  $3.08 \pm 0.28$  and  $4.05 \pm 0.32$  they were provisionally assigned as tri- and tetrathioantimonate. Using X-ray absorption spectroscopy (XAS), the identity of tetrathioantimonate was confirmed based on shell fits by about 4 Sb-S paths (CN 4.2-4.3) and the characteristic pentavalent Sb-S binding length of 2.33-2.34 Å. Aqueous trithioantimonate concentrations were too low for structural characterization.

XAS analyses further confirmed that the initial species formed from antimonite in the presence of excess sulfide under anoxic conditions is not a pentavalent thioantimonate, but the trivalent trithioantimonite (CN 3.4-3.7, binding length 2.40-2.41 Å). However, this species is highly instable and rapidly transforms either to tetrathioantimonate in the presence of oxygen or antimonite at excess  $\text{OH}^-$  versus  $\text{SH}^-$  concentrations. Thioantimonites thus escape chromatographic detection even in complete absence of oxygen.

In natural geothermal waters from Yellowstone National Park, where oxygen concentrations  $> 0.2$  mg/L render the presence of thioantimonites highly unlikely, tri- and tetrathioantimonate were detected. In accordance with our own laboratory studies and previous observations<sup>1-5</sup> their share increased at increasingly alkaline pH and with increasing sulfide and decreasing oxygen concentrations to a maximum of 30 and 9% of total antimony, respectively. However, given the large S/Sb ratio (100 to 10,000) almost quantitative transformation of antimony to thioantimonates would have been expected based on results in synthetic pure antimony solutions. We postulate that the presence of arsenic and direct competition for a limited source of sulfide affects thioantimonate formation in natural waters. In the same samples, thioarsenate formation at S/As ratios of 2 to 4 is much higher ( $> 80\%$  of total arsenic) and corresponds to results from synthetic pure arsenic solutions. Sulfur might therefore be a key species in helping to resolve different results and an ongoing controversy on similar<sup>7,8</sup> or dissimilar<sup>9,10</sup> behavior of arsenic and antimony in the environment.

[1] Tossell, J.A., 1994: *Geochim. Cosmochim. Acta* **58**, 5093. [2] Wood, S.A., 1989: *Geochim. Cosmochim. Acta* **53**, 237. [3] Mosselmans, J. F. W. et al., 2000: *Appl. Geochem.* **15**, 879. [4] Helz, G. R. et al., 2002: *Environ. Sci. Technol.* **36**, 943. [5] Sherman, D. M. et al., 2000, *Chem. Geol.* **167**, 161. [6] Planer-Friedrich, B. et al., 2007: *Environ. Sci. Technol.* **41**, 5245. [7] Vink, B.W., 1996: *Chem. Geol.* **130**, 21. [8] Sakamoto, H. et al., 1988: *Bull. Chem. Soc. Japan* **61**, 3471. [9] Stauffer, R.E.; Thompson, J.M., 1984: *Geochim. Cosmochim. Acta* **48**, 2547. [10] Landrum, J.T. et al., 2009: *Appl. Geochem.* **24**, 664.



T12

## FACTORS CONTROLLING THE FATE OF ANTIMONY PRODUCED BY A NATURAL GEOTHERMAL SPRING, WAI-O-TAPU, NEW ZEALAND

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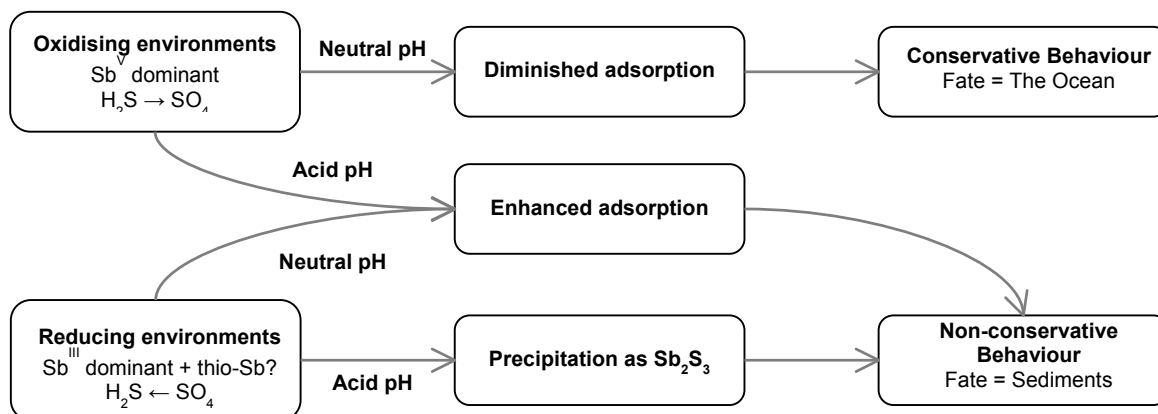
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The behaviour of antimony (Sb) has typically focussed on anthropogenic sources, such as mining<sup>1</sup>. In comparison, the behaviour of Sb in geothermal systems is rarely considered<sup>2</sup>. The Sb-enriched geothermal systems of New Zealand's central North Island provide an ideal environment to investigate the behaviour and fate of Sb produced from natural geothermal systems. Antimony concentrations in the deep, hot fluids used for geothermal power generation contain in excess of 1000 µg/L Sb<sup>3</sup>. Although most of this Sb will precipitate before the fluids reach the surface, geothermal springs in the Taupo Volcanic Zone are a significant source of Sb into freshwater systems.

Antimony concentrations in the discharge from Champagne Pool, the central feature of the Wai-O-Tapu geothermal field, are in the order of 10 µg/L, and are a mix of antimonite, antimonate, tri- and tetra-thioantimonate. Although Sb concentrations are relatively low in Champagne Pool itself, the discharge from the pool can contain up to 300 µg/L Sb, depending upon the time of day. Remarkably, Sb produced from Champagne Pool has the potential to be transported all the way to the Pacific Ocean, more than 300 km downstream, but the fate of the Sb in this discharge depends on a number of factors, including redox conditions, pH, the presence (or absence) of sulfide and exposure to Fe or Mn-bearing sediments. The influence of these factors are summarised in Figure 1.



At Wai-O-Tapu, another critical factor is wind direction. If the wind blows towards the north, then Sb can be transported out of the geothermal system, otherwise any Sb in the discharge from Champagne Pool will eventually be contained. Such a finding is a reminder that physical processes, as well as chemical processes, should always be considered when determining the fate of Sb in the environment.

[1] Telford, K. et al, 2009: Environmental Chemistry 6, 133-143. [2] Filella, M. et al, 2003: Earth-Science Reviews 57, 125-176. [3] Brown, K. and Simmons, S., 2003: Geothermics 32, 619-625.

## T13 KEYNOTE

## ANALYTICAL CHALLENGES IN ANTIMONY SPECIATION

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This presentation aims to give an overview of the state of the art in antimony speciation and addresses the analytical challenges and limitations associated with the applied methods.

Within the metal/metalloid speciation community, HPLC-ICP-MS and HPLC-ES-MS have the last decade proven highly successful tools in speciation studies: HPLC-ICP-MS is ruinously used for quantification of metals species, and a large number of new metal-containing species have been identified by using the two methods in combination. *For antimony, however, the success has been limited.*

The different oxidation states of antimony (+3/+5) can relatively easily be determined in dilute aqueous standard solutions or samples such as tap water, run-off waters or streams by anion exchange chromatography-ICP-MS. *However, antimony redox speciation in more complex environmental and biological samples is not a simple task:* Often low chromatographic recoveries and the occurrence of peaks with unknown identity and redox state occur. Recent work in our laboratory [1] suggests that part of the problem can be solved by using mobile phases of higher eluting strength than the “default” mobile phase of 20 mM EDTA and 2 mM phthalic acid. Results also suggest that the presence of macromolecules, presumably oligomeric and polymeric Sb(V) species, is the primary cause of low chromatographic recoveries. Full chromatographic recovery can in most cases be obtained if samples/polymers are hydrolyzed with acid (1 M HCl) prior analysis [1].

Identification of intact antimony complexes by HPLC-ICP/ES-MS have been successful for a few Sb(V) complexes [2], but no Sb(III)-complexes have been identified by this method. It appears that the complexes are too labile to survive chromatographic separation, and adsorbance of Sb(III) to stainless steel present in the HPLC system further disrupts the measurements. So far, Sb(III)-complexes have only been detected by direct infusion ES-MS and NMR analysis, restricting their detection to pure standard solutions.

[1] Hansen C, Schmidt B, Larsen EH, Gammelgaard B, Stürup S, Hansen HR, 2011: *Analyst* 136: 996-1002. [2] Hansen HR, Pergantis SA, 2008: *J. Anal. At. Spectrom.* 23:1328-1340.

T14

**NEW SIMPLIFIED VOLTAMMETRIC METHOD FOR THE SENSITIVE SPECIATION OF INORGANIC ANTIMONY IN MARINE AND FRESHWATERS**Salaün, P., Gibbon-Walsh, K., van den Berg, C.M.G.

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Voltammetric detection of trivalent antimony Sb(III) is routinely achieved by stripping analysis either on mercury or gold electrode material. The detection of the pentavalent antimonate Sb(V) is however more difficult due to a strongly hydrolysed state. In many cases, Sb(V) is considered as electroinactive and its voltammetric determination can only be achieved after a chemical reduction step, involving the addition of reducing agents and may also require heating of the solution. This reduction step limits sample throughput, is a source of contamination and may change the original speciation. Direct reduction of Sb(V) during the deposition step of an anodic stripping voltammetric (ASV) procedure is possible using low deposition potential in acidic media. Such experimental conditions however generate significant amount of hydrogen which interfere with the analytical determination. To overcome such H<sub>2</sub> evolution, the aqueous solution is made strongly acidic (e.g. 5.5 M HCl) allowing the use of a relatively positive deposition potential [1]. This is however problematic in terms of potential contamination from the acid, strong acidic waste and corrosion of the apparatus.

We report here a simple and robust procedure to perform sensitive voltammetric speciation of inorganic antimony. Sb(III) is solely determined at natural pH while Sb(III) + Sb(V) is measured by ASV in relatively low acidic conditions (~ pH 1) using low deposition potential [2] (Edep ≤ -1.8 V). Measurements are made at a vibrated gold microwire electrode which facilitates the removal of electro-generated H<sub>2</sub>. Using a 200 Hz vibrating frequency, enhanced mass transport over standard stirring occurs with thinning of the diffusion layer down to c.a. 0.7 μm (for 5 μm wire diameter) ensuring low detection limits (e.g. 5 pM / 0.7 ppt for Sb(V) – 300s deposition). Such LOD is two orders of magnitude lower than previously reported ASV method and compare well with the most sensitive analytical method. The common interference of arsenic on gold electrodes is dealt by appropriate choice of deposition potential. For instance, when depositing at -1.8 V in 0.1 M HCl, arsenic is reduced to arsine AsH<sub>3</sub> (which does not remain adsorbed at the electrode) and only Sb is analysed. Although thermodynamically predicted, the electrochemical hydride generation of Sb to stibine does not occur, possibly because of competitive recombination of nascent H<sup>0</sup> to H<sub>2</sub> rather than to SbH<sub>3</sub>. The method has been extensively tested on mineral, river, tap and coastal seawater. Good correlation was obtained with Certified Reference Materials data (NASS-4 and SLRS-3) and ICP-MS analysis.

[1] Santos, J. R.; Lima, J.; Quinaz, M. B.; Rodriguez, J. A.; Barrado, E., 2007, *Electroanalysis* 19, 723-730. [2] Salaün, P., Gibbon-Walsh, K., van den berg, C.M.G., 2011, *Analytical Chemistry*, accepted.

## T15

## ANALYSIS OF ANTIMONY SPECIES – PITFALLS AND PROBLEM SOLVING

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Coupled techniques based on the combination of a chromatographic separation with an element-selective detection method have become reliable in speciation analysis to discriminate different compounds (species) of an element. Species analysis of antimony seems to be a solved problem looking at the high number of published methods (e.g., review [1]). Most of the methods use a complexing agent (EDTA or tartrate) for the chromatographic separation of the various species, which are not very ICP-MS friendly due to their high concentrations of carbon necessary.

A method with a small column (Hamilton PRP-X100, 150 x 2.1 mm) was tested next and optimized to minimize the input of organic into the ICP-MS system. The final eluent is 10 mM EDTA and 10 mM  $\text{NH}_4\text{NO}_3$  with a flow rate of 0.4 mL/min using a Micromist nebuliser (Agilent) for an effective sample introduction into the ICP-MS (ICP-MS, Agilent Technologies 7700 Series). A separation of Sb(V) and Sb(III) was achieved within 6 minutes.

While testing this method, an influence of the sample matrix was recognized. The response of Sb(III) is decreased significantly using acids (e.g., 10 mM  $\text{HNO}_3$ ) or pure water standards. Only the matrix of 10 mM EDTA in the samples yield to a response factor similar to Sb(V). The addition of EDTA to each sample as well as to the standard solutions was found to be necessary to avoid such matrix influences.

Additionally, experiments to preserve Sb(III) in iron rich water samples were carried out. Samples containing 20  $\mu\text{g/l}$  Sb(III) and 10  $\text{mg/l}$   $\text{Fe}^{2+}$  and different stabilisation agents (10 mM HCl, 10 mM  $\text{H}_3\text{PO}_4$ , 10 mM  $\text{HNO}_3$ , 10 mM EDTA, and 20 mM EDTA) were analysed over 3 weeks. Without preservation a fast oxidation of Sb(III) to Sb(V) is observed.

This aim of Sb(III) preservation is difficult to achieve, but essential to do species analysis in such water samples. The addition of acids only partially prevented the oxidation. The best results were obtained using EDTA for sample preservation.

[1] Miravet, R., Hernández-Nataren, E., Sahuquillo, A., Rubio, R., López-Sánchez, 2010: Trends in Analytical Chemistry 29, 28 - 39

## T16

**ANTIMONY: A TRAFFIC RELATED ELEMENT IN SIZE-FRACTIONATED ROAD DUST SAMPLES COLLECTED IN BUENOS AIRES, ARGENTINA**

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The growing interest of public opinion in environmental problems directed us to investigate the levels of a toxic traffic-related element (TRE) such as antimony in 19 size-fractionated street dust samples. Samples were collected in the megacity of Buenos Aires during two months at 20 sites with different urban characteristics and traffic profile. Samples were sieved in four fractions (F1 < 37  $\mu\text{m}$ , F2: 37-55  $\mu\text{m}$ , F3: 55-75  $\mu\text{m}$  and F4: 55-100  $\mu\text{m}$ ) before elemental analysis. A mixture of aqua regia and hydrofluoric acid was used to digest all samples. Antimony concentrations were quantified by inductively coupled plasma optical emission spectrometry (ICP OES) or flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS).

Twenty four out of 73 sub-samples analyzed showed Sb levels < 0.05  $\mu\text{g g}^{-1}$  while in the rest of the samples mean Sb concentrations varied from 1.40 to 20.35  $\mu\text{g g}^{-1}$ . Maximum and minimum concentrations (in  $\mu\text{g g}^{-1}$ ) found in individual samples in the four fractions were: Fraction 1, < 0.05-20.35; Fraction 2, < 0.05-18.37; Fraction 3, < 0.05-6.33; Fraction 4, < 0.05-7.68.

In addition to Sb, major, minor and trace elements (Al, As, Ca, Cd, Cu, Fe, Mg, Mn, Mo, Ni, Pb, S, Sn, and Zn) content was quantified in the four particle size ranges. The set of measured concentrations was independently classified by cluster analysis. Our results identified two distinct clusters, one composed by elements of both geological and anthropogenic origin (Cu, Fe, Ni and Sn) and another one composed by typical traffic-related elements (Cd, Mn, Pb, S, Sb and Zn). The cluster of traffic-related elements (TREs) can be further divided into two sub-groups, the first group composed by Cd, S, and Sb exhibited the closest distances consistent with the highest correlations among the three pairs of these elements. In addition, the concentrations in the finer fractions were higher than those in the coarser fractions in practically all regions under consideration. For the particular case of antimony, it was found to be enriched in the smallest size fraction of road dust, with mean enrichment factors varying between 27 (F3) and 272 (F1).



T17

## ANTIMONY DEPOSITION IN NORWAY IN TIME AND SPACE

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Antimony is one of the most typical components of long-range transported aerosols to Norway from other parts of Europe. Antimony generally shows highly positive correlations with lead, zinc, cadmium, arsenic and some other elements in aerosols [1], precipitation [2], moss samples from six nationwide surveys 1977-2010 [3-5], and corresponding surveys of organic-rich natural surface soils [6] and peat cores [7]. The atmospheric deposition is 5-10 times higher in the far south of the country than in areas in the middle and northern part of the country, but is currently 20% or less of the levels around 1980, cfr. Fig. 1. A slight change in geographic distribution with time indicates a greater relative contribution from domestic automobile traffic in recent years.

Unpublished data from peat cores sampled at six ombrotrophic bogs in different parts of Norway will be presented, showing a dramatic increase all over the country from pre-industrial time until the 20<sup>th</sup> century. The relative increase over time is almost as great in the middle and northern parts of the country as in the south where the impact of transboundary pollution is greatest.

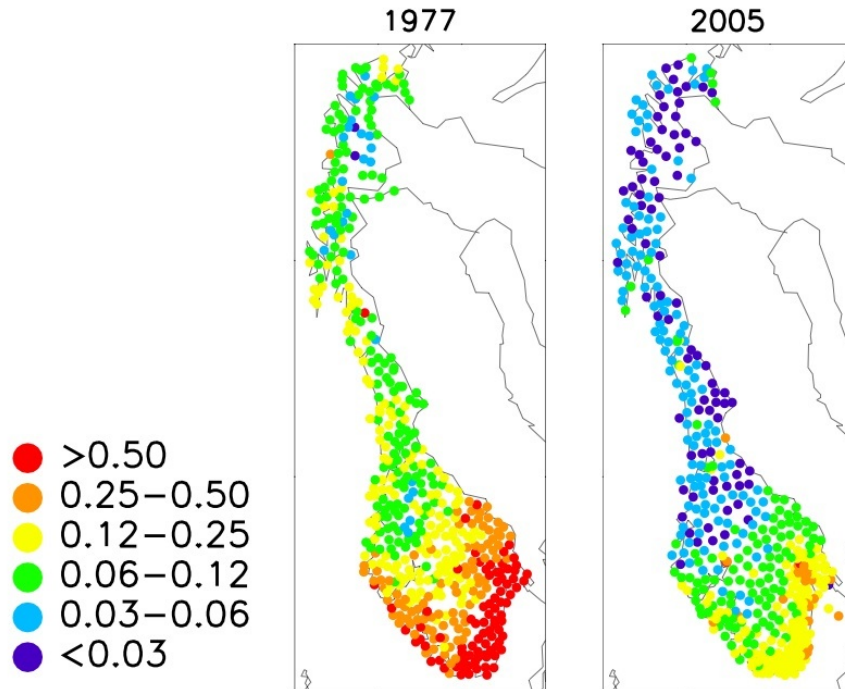


Fig. 1. Distribution of Sb in moss in Norway 1977 and 2005 [ppm]

[1] Amundsen C.E. et al. 1992: Atmos Environ 26A, 1309-1324; [2] Berg T. et al. 2008: Atmos Environ 42, 7494-7501; [3] Schaug J. et al. 1990: Atmos Environ 24A, 2625-2631; [4] Steinnes E. et al. 1992: Chemosphere 25, 735-752; [5] Berg T. et al. 1995: Atmos Environ 28, 3519-3536; [6] Steinnes E. et al.: Sci Total Environ 1997: 205, 255-266; [7] Steinnes E. et al. 2005: J Environ Qual 34, 192-197.

T18

## SPECIATION ANALYSIS OF ANTIMONY IN SIZE-CLASSIFIED AIRBORNE PARTICULATE MATTER BY HPLC-ICPMS

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Speciation analysis is required to understand the transformation cycling of elements in environmental systems. In this paper, speciation analysis will be presented as examples of Sb in water extract of airborne particulate matter (APM).

We have been monitoring trace elements in size classified APM in Tokyo for 16 years since 1995 [1]. From the monitoring results, it was found that toxic elements such as Sb, Se, Cd, Pb, and As are enriched in smaller particles (less than 2  $\mu\text{m}$ ) and Sb is the most enriched element in comparison with the crust concentration. Since smaller APM is deposited deep inside the lung, human effect is anticipated.

Thirteen fractions of size-classified APM (<0.06, 0.06-0.12, 0.12-0.20, 0.20-0.30, 0.30-0.50, 0.50-0.70, 0.70-1.2, 1.2-2.1, 2.1-3.6, 3.6-5.2, 5.2-7.9, 7.9-11, and >11  $\mu\text{m}$ ) were collected on quartz fiber filters by using an Andersen-type low-pressure-impactor (LPI) air sampler. The sample-loaded filters were digested by using a microwave oven and the concentration of trace elements in the solutions were measured by ICP-MS.

Size distribution patterns for trace elements in APM were obtained. Sb had two peaks at 0.6  $\mu\text{m}$  and 4  $\mu\text{m}$ . At 0.6  $\mu\text{m}$ , Pb and Cd had a peak, and at 4  $\mu\text{m}$ , Cu and Ba had a peak. From these experimental results, we concluded that APM at 0.6  $\mu\text{m}$  was caused by fly ash of incinerator and APM at 4  $\mu\text{m}$  was caused by brake pads of automobiles. Sb is used as flame retardant of plastics and chemical fibers as a chemical form of  $\text{Sb}_2\text{O}_3$  and Sb is used as solid lubricant in brake pads as a chemical form of  $\text{Sb}_2\text{S}_3$ . Sb used in industrial materials has an oxidation state of Sb(III).

In order to clarify the chemical form of Sb, speciation analysis was conducted by citric acid extraction of APM [2, 3]. Using citric acid prevented from oxidation of Sb(III) and Sb(III) could be retained during extraction. The extraction efficiency of Sb in APM was from 20 to 30 %. Speciation analysis was performed by HPLC-ICP-MS. In the citric acid extract of APM, inorganic antimonate,  $[\text{SbO}_4]^{3-}$  (Sb(V)), inorganic antimonite,  $[\text{SbO}_3]^{3-}$  (Sb(III)), and trimethyl antimonyl hydroxide ion,  $[(\text{CH}_3)_3\text{SbOH}]^+$  (TMSb) were detected. The amount of Sb in APM was in the order of Sb(V) > Sb(III) > TMSb. In smaller APM (0.1-0.60  $\mu\text{m}$ ), Sb(V) was a major species. It can be explained by oxidation of Sb(III) during combustion process of incinerator. In larger APM (3.0-6.0  $\mu\text{m}$ ), both Sb(III) and Sb(V) were observed. It implies that some parts of brake pads are oxidized during braking of automobiles. TMSb was produced by microbiology in the atmosphere and the produced TMSb is adsorbed on the surface of APM. Therefore, TMSb was observed both smaller APM (0.1-0.60  $\mu\text{m}$ ) and larger APM (3.0-6.0  $\mu\text{m}$ ).

[1] Furuta, N., Iijima, A., Kambe, A., Sakai, K., Sato, K., 2005: J. Environ. Monit. 7, 1155-1161. [2] Zheng, J., Iijima, A., Furuta, N., 2001: J. Anal. At. Spectrom. 16, 812-818. [3] Iijima, A., Sato, K., Ikeda, T., Sato, H., Kozawa, K., Furuta, N., 2010: J. Anal. At. Spectrom. 25, 356-363.

T19

## IMMOBILIZATION OF ANTIMONY (Sb) IN SHOOTING RANGE SOIL BY IRON AMENDMENTS

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Iron (Fe) (hydr)oxides are important sorbents for heavy metals and Sb in soil [1]. Thereby, Fe based amendments represent potential stabilizing agents for Sb, lead (Pb), copper (Cu) and zinc (Zn) in contaminated shooting range soils [2]. In this study we (i) identified Fe based materials effective for Sb sorption and (ii) added selected materials to contaminated shooting range soils both in laboratory and field tests to investigate the stabilization effect. 4 materials were identified as effective Sb sorbents:  $\text{Fe}(\text{OH})_3$  powder and granulate,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Fe}^0$  granulate. The sorption could be described well by Freundlich sorption isotherms. Batch tests with soil from a shooting range butt material mixed with the selected sorbents (0.5 and 2% sorbent w/w) showed an overall excellent sorption of Sb. For  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Fe}(\text{OH})_3$  granulate a pH regulation was necessary to prevent a mobilization of Pb, Cu and Zn. Based on the laboratory results, a field test was established in July 2010 at a closed military shooting range (Steinssjøen, Norway). Butt soil material was mixed with sorbents ( $\text{Fe}(\text{OH})_3$  powder mixed with limestone and  $\text{Fe}^0$  granulate) in 2 different concentrations (2 and 4%). Porewater was sampled and analyzed for Sb, Cu, Pb, Zn, Fe, DOC, pH, and EC. Speciation analysis by hydride generation inductively coupled plasma optical emission spectrometry (HG ICP-OES) showed that Sb was exclusively present as Sb(V) in the porewater. Results from the sampling campaigns carried out in 2010 showed good retention efficiency of both sorption materials for Sb and Pb (Fig. 1), indicating their suitability for chemical stabilization under field conditions.

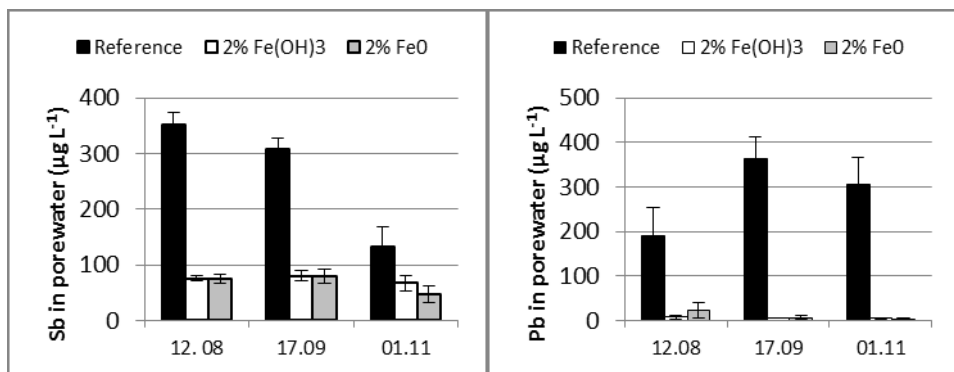


Fig. 1. Concentrations of Sb (A) and Pb (B) in reference soil (black columns), soil with 2% Ferrihydrite + 1% Limestone (white columns) and 2%  $\text{Fe}^0$  granulate (grey columns). The values are average values of replicates. The error bars show standard deviation.

[1] Wilson, S.C., Lockwood, P.V., Ashley, P.M., Tighe, M., 2010: Environmental Pollution 158, 1169-1181. [2] Kumpiene, J., Lagerkvist, A., Maurice, C., 2008: Waste Management 28, 215-225.

T20

**PHYTOMANAGEMENT OF RELOCATED SHOOTING RANGE SOIL**Wan, X., Evangelou, M.W.H., Hockmann, K., Tandy, S., Schulin, R.

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There is an increasing demand for reuse strategies of decommissioned military shooting range (MSR) soils with moderate concentrations of Sb and Pb. In this study, the feasibility of phytomanaging MSR soils was investigated. Their use for the production of green fodder and the risks were assessed.

In this study, we analysed the vegetation spontaneously growing on two relocated MSR soils, a calcareous soil from Chur and a weakly acidic soil from Losone, (Table 1), for species composition and trace element concentrations. Grasses were predominant on both soils, covering more than 80% of the soil surface area. The main plant species on the Chur soil were *Trifolium sp.* and *Polygonum aviculare*, while *Persicaria lapatifolia* and *Persicaria lapatifolia spp.* dominated on the Losone soil. Plants on Chur soil had 1.5-26 fold higher Sb concentration but lower Pb concentrations than plants on Losone soil. The highest Pb concentration was found to be 323  $\mu\text{g}\cdot\text{kg}^{-1}$  in *Chenopodium album* on the Losone soil, and the highest Sb concentration was 62  $\text{mg}\cdot\text{kg}^{-1}$  in *Rumex acetosa* shoots on Chur soil. All concentrations of trace elements found in the collected plants were lower than the respective tolerance values for fodder, except for Pb in *Chenopodium album* on Losone soil. This work indicates that with proper phytomanagement producing fodder can be a potential use of former MSR soils.

Table 1. Properties of the two study soils

	Chur	Losone
pH H <sub>2</sub> O	8.5±0.1	6.35±0.2
CaCO <sub>3</sub> (%)	20±2	<2
Total Sb ( $\text{mg}\cdot\text{kg}^{-1}$ )	19.7±4.1	19±3.9
Total Pb ( $\text{mg}\cdot\text{kg}^{-1}$ )	466±126	644±46

T21

## USE OF SORBENTS FOR PURIFICATION OF LEAD, COPPER AND ANTIMONY IN RUNOFF WATER FROM A SMALL ARMS SHOOTING RANGE

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Small arm shooting ranges accumulate large amount of metals such as lead (Pb), copper (Cu), and antimony (Sb) from use of ammunition. In Norway, there has been estimated a mean annual deposition of approximately 111, 68 and 13 metric tons of Pb, Cu and Sb respectively in military small arm shooting ranges for the years 2004-2008. The ammunition residues comprise a major source of environmental contamination and humans, as well as wildlife and domestic animals drinking or grazing on the contaminated area, may be exposed to hazardous amount of these elements. Leaching of elements from the berms to stream water may pose a threat to aquatic organisms. To reduce impact of metal runoff from a shooting range it was performed a study with different sorbents to evaluate their capacity to reduce the metal concentration in drainage water from a shooting range. The tests were performed *in situ* with water from a polluted drainage creek, which receives contaminated water from three shooting ranges. Mean concentrations of Cu, Sb and Pb in the creek were 46µg/l, 8.9µg/l and 22µg/l respectively.

The sorbents were added to columns with dimension of 13dm<sup>3</sup> and tested for at least four weeks. A total of approximately 10000 L of water passed through the columns with a residential time of approximately 30 minutes. The sorbents tested were: A) brimac charcoal; B) magnetite; C) Kemira iron hydroxide; olivine mixed with D) 2.5% elemental iron powder, E) 5% elemental iron powder and F) 2.5% elemental iron powder of which the iron was oxidized into the olivine beforehand.. For all three elements Brimac charcoal and Kemira iron hydroxide had the best effect with a mean sorption of 84%, 66%, 85% and 58%, 78% and 69% for Cu, Sb and Pb respectively. Olivine with 5% elemental Fe-powder showed good sorption for Cu and Pb, with 81% and 87% reduction respectively. The Fe-olivine filters were less efficient in reducing the Sb-concentration, but it appeared that by increasing the Fe-content one can achieve better results also for Sb. Fe expands when oxidized, which is followed by reduced flow rate and clogging. The Fe should therefore be oxidized into the filter beforehand. In periods with high elemental concentrations in the creek, the sorption Pb, Cu and Sb improved. This is probably due to a proportional higher contact time with the sorbent, increased reactivity of the metal species or an increased amount of particular or colloidal bound elements. To increase the selectivity and capacity of a filter one should consider combining different sorbents.

T22

## ANTIMONY MOBILITY AND TRANSPORT IN MINE DUMPS FROM THE DACHANG MULTI-METALLIFEROUS MINE AREA, GUANGXI, CHINA

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Antimony (Sb) is a toxic element and a global environmental contaminant [1] that is found throughout the environment as a result of natural processes and human activities [2]. Mine exploitation is as an important source of Sb and other heavy metal contamination, and lead to the release of particularly high Sb concentrations in the environment [3]. The distribution of Sb in tailings, topsoils and plants (*Pteris vittata*, *Saccharum arundinaceum*, *Miscanthus floridulus* and *Thysanolaena maxima*) in the Dachang multi-metalliferous mine area, one of the largest antimony deposit in China, was investigated, so as to discuss the mobility and transport of Sb in mine soil-plant systems.

Antimony and other metals mobility in the topsoils and tailings was estimated by measuring the soluble fraction. Sb appears to have a higher mobility than As and other metals (Fig. 1). The percentage for the soluble fraction of metals shows the following order: Sb > (Zn, Cu, As) > Pb. The pH value is usually considered as a crucial role for the mobilization of metals. According to our study results, the mobility of Sb and As shows a positive correlation with soil pH. In contrast, Pb, Cu and Zn could be more mobilized in a acid condition.

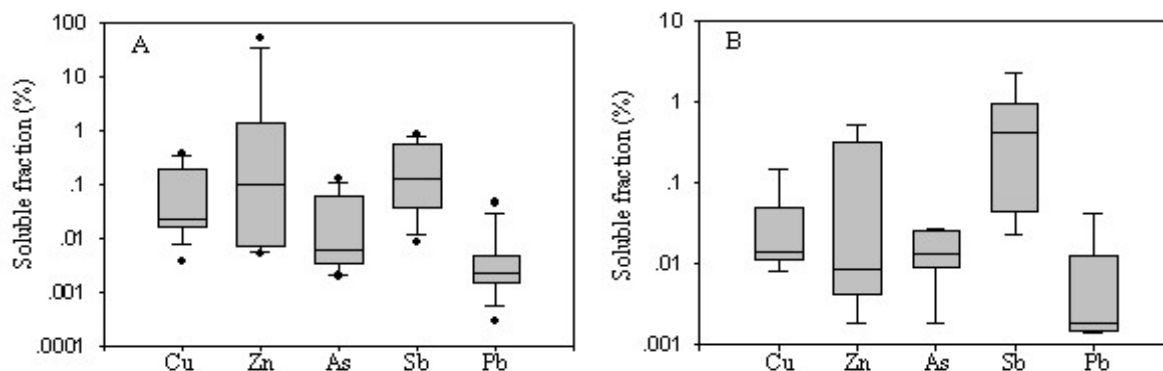


Fig. 1 The percentage of soluble metals in topsoils(A) and tailings(B) from mine area

Regarding the metalloid enrichment in plants, Sb and As only appears to accumulate in *Pteris vittata*, and the concentrations of Sb and As in plant parts are in the order of roots > leaves > shoots. Regarding the element translocation from roots to the epigeal parts, plant samples have a lower ability to transport Sb than As from the roots to the epigeal parts. Moreover, a positive correlation ( $r = 0.91$ ) between As content in the epigeal parts and roots in plants but a poor correlation ( $r = 0.19$ ) between Sb content in the epigeal parts and roots in plants might suggest arsenic content in epigeal parts associated with plant roots.

[1] Shotyk, W., Krachler, M., Chen, B., 2005: Journal of Environmental Monitoring 7, 1135-1136. [2] Filella, M., Belzile, N., Chen, Y.-W., 2002: Earth-Science Reviews 57, 125-176. [3] Tschan, M., Robinson, B., Schulin, R., 2009: Environmental Chemistry 6, 106-115.



T23

**ADSORPTION OF As(III) TO PADDY SOILS FROM IRRIGATED RICE FIELDS IN BANGLADESH AND POTENTIAL INTERACTION OF Sb(III)**Weiss, D., Khondoker, R.

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Paddy soil is copious in South East Asia and exerts a major control on the arsenic (As) cycle in rice ecosystems through its adsorption from the aqueous phase. However, prolonged irrigation with groundwater enriched in As and other trace metals might affect its adsorption capacity. Consequently, we conducted a preliminary study assessing the adsorption of arsenite, As(III), the more toxic form of As prevalent under anoxic conditions, onto paddy soil collected from an extensively irrigated rice field in Bangladesh. Furthermore, we investigated the adsorption of antimony (Sb) in its reduced form as Sb(III). This equally toxic element has been proposed as potential confounding factor in the environmental toxicology of arsenic. One potential effect is the competitive adsorption with As on the paddy soils, leading to higher mobility in groundwater and to higher As concentrations in water wells. We used batch experiments to quantify ion adsorption in the presence of 0.1 M KNO<sub>3</sub> background electrolyte solutions. As(III) and Sb(III) concentrations between 2 to 20 µg/ml and As:Sb weight ratios of 5:1 and 2:1 were tested to mimic natural conditions of irrigation waters. The As(III) and Sb(III) adsorption isotherms fit well Langmuir and Freundlich models and the adsorption capacity were reached at approximately 0.4 mg As(III)/g and at 3.3 mg Sb(III)/g of paddy soil, respectively. We found no strong evidence for competitive behaviour between Sb(III) and As(III). Due to the low absorption capacity, prolonged irrigation with contaminated groundwater could affect As mobility in paddy rice ecosystem. Furthermore our data suggest that Sb(III) adsorption on paddy soils is stronger than As(III) which likely explains the low Sb concentrations found in well waters in Bangladesh.

T24

**THE SORPTION OF ANTIMONY(V) BY DIFFERENT SOLID PHASES, AND THE EFFECTS OF SULFATE AND PHOSPHATE ON THE SORPTION OF ANTIMONY(V)**Tighe, M., Wilson, S.C., Lockwood, P.V.

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Previously we examined the sorption of Sb(V) by two organic rich soils, goethite (amorphous iron hydroxide), and humic acid [1]. We found high sorption on all phases, and in particular goethite sorbed greater than 95% of Sb(V) in all instances. To further explore the characteristics of Sb(V) sorption, we examined the relationship between Sb(V) sorption by common soil constituents including gibbsite (amorphous aluminium hydroxide), montmorillonite and kaolinite, and the point of zero charge ( $\text{pH}_{\text{zero}}$ ) of each phase. We found a general decrease in Sb(V) sorption above the  $\text{pH}_{\text{zero}}$  in gibbsite and montmorillonite, but for both the previously examined goethite and the kaolinite maximum Sb(V) sorption occurred at higher pH than the  $\text{pH}_{\text{zero}}$ . Additional experiments provided further evidence for chemisorption on these two soil constituents. Replicating the Sb(V) goethite and Sb(V) kaolinite sorption experiments in the presence of low (4  $\mu\text{M}$ ) and high (1 mM) sulfate concentrations did not change the Sb(V) – pH sorption curve. However, replicating the same experiments in the presence of low (4  $\mu\text{M}$ ) and high (1 mM) phosphate produced a significant decrease in the sorption – pH curves at the high phosphate concentration. For both goethite and kaolinite, this shift appeared most strongly once the pH corresponding to the first  $\text{pK}_a$  value of phosphoric acid was exceeded. We conclude that while the sorption mechanisms of different soil phases are different, and the effect of a competing anion such as phosphate is evident, significant desorption of Sb(V) from these phases under field conditions would be limited to specific circumstances.

[1] Tighe, M., Lockwood, P., Wilson, S., 2005: Journal of Environmental Monitoring 7, 1177-1185.

T25

**EFFECT OF HUMIC ACIDS ON ANTIMONY SORPTION TO GOETHITE**Hockmann, K.<sup>1</sup>, Tandy, S.<sup>1</sup>, Lenz, M.<sup>2</sup>, Schulin, R.<sup>1</sup><sup>1</sup>Institute of Terrestrial Ecosystems, Swiss Federal Institute of Technology (ETH), Universitätsstrasse 16,  
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Several studies have shown the affinity of antimony (Sb) for iron (Fe), aluminium (Al) and manganese (Mn) (hydr)oxides in natural systems [1, 2]. An important factor that may influence Sb sorption to these mineral surfaces is the presence of dissolved organic matter (DOM). DOM components, such as humic acids, are ubiquitous in soils. They strongly sorb to (hydr)oxide minerals and might therefore compete with Sb for the same binding sites.

In this study, equilibrium batch and dialysis experiments were performed with pure goethite and humic acids in order to identify the effect of DOM on Sb sorption to an Fe hydroxide. Goethite was chosen as a sorbent because it is the most abundant Fe (hydr)oxide in well-aerated soils in humid climates and is known to play a key role in the sorption behavior of Sb. Purified and pre-dialyzed commercial humic acid (PAHA; Sigma Aldrich, tech.) was used as a model compound for DOM due to its low cost and prevalent use in environmental studies. Antimony species were measured using liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS). In order to compare PAHA with a natural humic acid, the experiments were repeated using Suwannee River humic acid standard II (IHSS). Particular attention was given to the influence of pH on the ternary systems containing goethite, Sb and humic acids.

Results of the dialysis experiment at pH 7 showed that sorption of Sb(V) to PAHA, which are both negatively charged in the pH range studied, was negligible at Sb concentrations up to 5  $\mu\text{M}$ . Antimony sorption to goethite was drastically reduced in the presence of 40  $\text{mg l}^{-1}$  PAHA at neutral pH when Sb(V) was added at the same time as humic acid. When Sb was allowed to equilibrate for 24 hours before PAHA was added, the effect was far less pronounced (Figure 1).

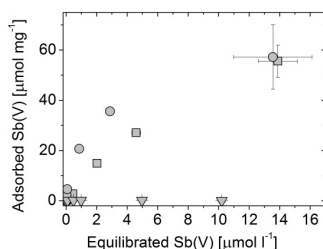


Fig. 1. Sorption of Sb to goethite in the absence (circles) and presence of humic acid. Antimony and PAHA were either added at the same time (triangles), or PAHA was added after 24 hours of equilibration between Sb(V) and goethite (squares). Error bars (S.E.,  $n=3$ ) that are not visible are smaller than the symbols.

[1] Johnson et al., 2005: J. Environ. Qual. 34, 248-254. [2] Scheinost et al. 2006: Geochim. Cosmochim. Acta 70, 3299–3312.

T26

## THE TRANSFORMATION OF FERRIHYDRITE TO GOETHITE, HEMATITE, AND FERROXYHYTE IN THE PRESENCE OF Sb(V)

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During the weathering process of iron minerals, poorly crystalline ferrihydrite (an ferric oxyhydroxide) is formed and later transforms into other iron oxides like goethite ( $\alpha$ -FeOOH) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The rate of transformation depends on pH, temperature and ions and molecules present during the transformation process [1]. In this work, we decided to focus on the transformation of synthetic ferrihydrite to crystalline iron oxides in the presence of Sb(V). Transformations were performed at pH 4, 7, and 12 with different Sb concentrations (0.00, 0.23, 0.75, 2.25, and 6.00 mM Sb). The doped ferrihydrite was aged at 70°C for 1-16 days, during which nine samples were taken, washed, dried, and characterized by X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS). At pH 12 goethite (Sb concentrations up to 3.7 mg g<sup>-1</sup>) is favored and the transformation was completed after 24 h of aging at 70 °C. However, concentrations of 6 mM Sb(V) retarded the transformation. Even after eight days of aging only 50 % of ferrihydrite was transformed into goethite. In neutral conditions (pH 7) a mixture of 75 % hematite and 25 % goethite (4.3 mg Sb g<sup>-1</sup>) occurred. Yet, concentrations of 6 mM Sb led to the formation of feroxyhyte ( $\delta$ -FeOOH) (9.1 mg Sb g<sup>-1</sup>) (Fig. 1). At pH 4, the elevated temperature favored hematite (32.3 mg Sb g<sup>-1</sup>), except for concentrations of 6 mM Sb, which led again to the formation of feroxyhyte (141.1 mg Sb g<sup>-1</sup>). We assume that increased Sb concentrations favor feroxyhyte and indicate the incorporation of Sb into the structure of feroxyhyte.

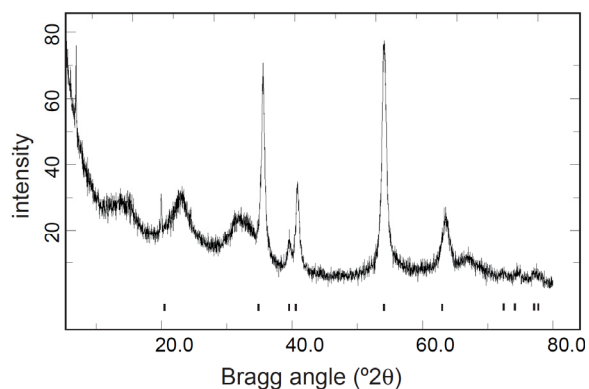


Fig. 1. XRD pattern ( $\lambda = 1.54056 \text{ \AA}$ ) of feroxyhyte formed at concentrations of 6 mM Sb. The ticks below the pattern mark the calculated positions of diffraction peaks of feroxyhyte.

[1] Cornell (1987) Pflanzenern Boden 150, 304-307.

## SOLID PHASE SPECIATION IN Sb-RICH MINING RESIDUES

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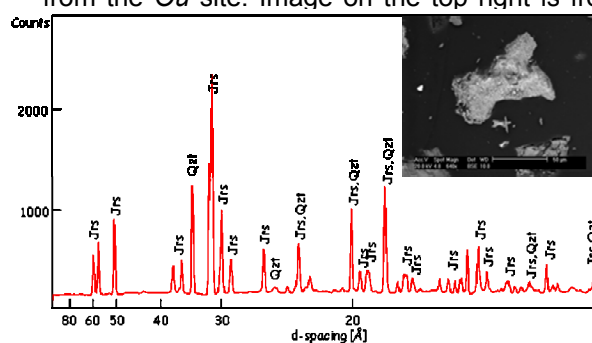
Most of the previous Sb speciation studies concerned ores and mineralized veins [1] and seem to indicate a relationship between Sb(V) and Fe(III) hydroxide [e.g., 2,3]. However mineralogy of solid mining residues was barely studied [4]. One goal of this study is to determine the solid speciation of As and Sb and the main factors controlling the fate of these elements in altered host phases during the solid and dissolved transport at a basin scale.

The Massif Central is one of the largest metallogenic areas of France, where U, Au, W, Sb, F, Ba, Pb-Zn were exploited during the middle 18<sup>th</sup> through the 20<sup>th</sup> century, and include the second largest nationwide district for Sb, Brioude-Massiac. This mining district consists of several extraction sites of various size, which produced altogether around 40 000 t of Sb over a century period (1830-1930). Several mining sites have been studied in this area, with mining residues leftover as mill tailings and slags. Two sites are presented here: *La Chassagne - LC* (1901-1916; 2 000 t of Sb) and *Ouche - Ou* (1810-1977; 8 300 t of Sb). Both types of residues still contain high amounts of As and Sb, with mill tailings showing the highest concentrations (Tab. 1).

Table 1. Chemical composition of solid residues at LC and Ou mining sites (ICP-MS/OES)

	LC		Ou	
<i>Mill tailings</i>	Sb <sub>max</sub> (%)	As <sub>max</sub> (mg/kg)	Sb <sub>max</sub> (%)	As <sub>max</sub> (mg/kg)
	1.237	67.1	1.156	1641.7
<i>Slags</i>	Sb <sub>max</sub> (mg/kg)	As <sub>max</sub> (mg/kg)	Sb <sub>max</sub> (%)	As <sub>max</sub> (mg/kg)
	324.4	8	0.566	47.9

Figure 1. Integrated diffraction pattern obtained on Sb-rich jarosite (Jrs: jarosite; Qtz: quartz) from the *Ou* site. Image on the top right is from



Mineralogical investigations of both mill tailings and slags showed that few sulfides (stibnite and berthierite) remain at the two locations, and rare alteration features were observed. In secondary products, Sb was observed in association with Fe (and possibly Mn). Synchrotron X-ray Micro-diffraction (beamline 12.3.2, Advanced Light Source, USA) showed that Sb is trapped in jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  suggesting a substitution of  $\text{Fe}^{3+}$  by  $\text{Sb}^{5+}$  which has never been reported at this level (c.a. up to 3% Sb) (only minor integration of Sb in jarosite has been observed [5]) (Fig. 1). Usually this kind of substitution is mentioned for dussertite  $\text{Ba}(\text{FeSb})_3(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$  but not for jarosite [6]. Furthermore complex Fe-Sb mixing phases have been identified as Sb-rich iron (oxy-)hydroxides, mainly goethite and lepidocrocite.

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## T28 KEYNOTE

MINERALOGICAL CONTROL OF THE DISPERSION OF ANTIMONY IN THE  
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Oxidation of primary Sb-rich or discrete Sb minerals in the supergene zone gives rise to the formation of some 40 secondary Sb phases that have so far been described [1]. Each of these exerts a control on the solubility and dispersion of Sb in ground waters. Just what this control might be and what its significance is have remained matters of some conjecture during the last few decades. This has been, in part, due to simplistic evaluations of the geochemistry of Sb in the supergene zone, based on Pourbaix diagrams that have used  $\text{Sb}_2\text{O}_5(\text{s})$  as a proxy for species formed under more oxidizing conditions.  $\text{Sb}_2\text{O}_5(\text{s})$  is not stable in Nature and an erroneous view of the solubility of Sb at ambient temperatures has been promulgated in the literature [2]. Only over the last few years has a different picture emerged [3, 4].

Both Sb(III) and Sb(V) species result from the oxidation of primary Sb minerals, the most common of which is stibnite,  $\text{Sb}_2\text{S}_3$ . The most frequently reported secondary phases are senarmontite and valentinite, dimorphs of  $\text{Sb}_2\text{O}_3$ , cervantite,  $\text{Sb}_2\text{O}_4$ , and pyrochlore minerals of the romeite group (oxycalcioromeite is  $\text{Ca}_2\text{Sb}_2\text{O}_7$ ). The latter species are cation-exchanged members of “antimonic acid”, stabilized by cations such as  $\text{Bi}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sb}^{3+}$  and  $\text{H}_3\text{O}^+$ . Senarmontite and valentinite limit solution Sb concentrations to a couple of ppm at ambient temperatures and are stable under moderately oxidizing conditions. Nearer the surface, and with time, secondary Sb(V) minerals dominate the oxidized zone and dissolved Sb levels are limited to a few ppb with respect to the romeite group. The solubilities of salts containing smaller cations such as  $\text{Na}^+$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  and the  $\text{Sb}(\text{OH})_6^-$  ion are somewhat higher [3]. Other “simple” oxides even more important roles in this regard. Thermochemical data for tripuhyite,  $\text{FeSbO}_4$ , and schafarzikite,  $\text{FeSb}_2\text{O}_4$ , have been determined recently at 25°C [4]. Both phases have “anomalously” high stabilities, so much so that goethite,  $\text{FeOOH}$ , is thermodynamically unstable with respect to them. Activities of  $\text{Sb}(\text{OH})_5(\text{aq})$  as low as  $10^{-11}$  are sufficient to transform goethite to tripuhyite. Although tripuhyite has been reported from about 50 localities, it is much more common than previously thought and has certainly been overlooked because of its physical similarities to goethite and other secondary Fe(III) minerals; this has been noted elsewhere [5].

It is now apparent that Sb is not very mobile in the supergene environment at all, leaving aside physical dispersion. This is illustrated by reference to a number of soil geochemical surveys over undisturbed, oxidized, Sb-rich ore bodies.

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T29

## MINERALOGY OF THE WEATHERING PRODUCTS IN MINE WASTES AND SOILS AT SEVERAL ABANDONED Sb DEPOSITS IN SLOVAKIA

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Distribution and mobility of elements in mine wastes strongly depend on mineralogical composition of the material. Previously, Sb was suggested to be quite mobile in the supergene environment, but recently this hypothesis has been refuted. The reason of the earlier assumptions might be insufficient knowledge of the occurrence and stability of secondary Sb minerals.

In this work, we have summarized results from detailed mineralogical studies of the weathering products in tailing impoundments and soils rich in Fe, As and Sb, from five Sb deposits in Slovakia. Our results based on 250 samples of tailing material and soil, 2500 microprobe analyses and 500  $\mu$  - XRD analyses is also supporting the second theory.

All studied bulk samples are rich in Fe (24.2–181 g/kg), As (0.1–13.5 g/kg), and Sb (1.2–15.7 g/kg). The most frequent sulphides in the flotation wastes are pyrite (FeS<sub>2</sub>) and arsenopyrite (FeAsS); stibnite (Sb<sub>2</sub>S<sub>3</sub>) is rare owing to its rapid oxidation.

The most common Sb-bearing secondary oxide is tripuhyite (FeSbO<sub>4</sub>) with variable Sb (15.94 - 50.83 wt. %) and Fe content (4.13 - 41.52 wt. %). Unit cell volume is in the range from 64.70 Å<sup>3</sup> to 75.83 Å<sup>3</sup> and depends mostly on the Fe/(Fe+Sb) ratio of the tripuhyite grains. In the tailings and soils rich in Ca, secondary minerals with the pyrochlore structure have been identified. These phases are rich in Sb (25.17 – 52.90 wt. %), Fe (0.30 – 21.22 wt. %) and Ca (0.18 – 7.40 wt. %) and the  $\mu$ -XRD patterns fit well with the structural models of stibiconite (Sb<sup>3+</sup>Sb<sup>5+</sup><sub>2</sub>O<sub>6</sub>(OH)) and lewisite (Ca,Fe<sup>2+</sup>,Na)<sub>2</sub>(Sb,Ti)<sub>2</sub>O<sub>7</sub>).

The most frequent secondary mineral at all studied sites is goethite ( $\alpha$ -FeOOH), with high content of Sb (up to 14.49 wt. %) and As (up to 6.49 wt. %). Cell parameters depend on incorporation of foreign elements, in agreement with earlier studies. Frequent are also X-ray amorphous Fe oxides with variable amounts of adsorbed elements (up to 6.66 wt. % of Mg, 3.43 wt. % of Si, 2.27 wt. % of Ca, 2.94 wt. % of Pb, 13.91 wt. % of Sb and 10.64 wt. % of As). Simple secondary Sb oxides such as cervantite ( $\alpha$ -Sb<sub>2</sub>O<sub>4</sub>) and senarmontite (Sb<sub>2</sub>O<sub>3</sub>) were observed each just in one soil sample. As-containing hydrated Fe oxides are the most common products of arsenopyrite oxidation. Scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) occurs rarely and beudantite (PbFe<sub>3</sub>(AsO<sub>4</sub>)(SO<sub>4</sub>)(OH)<sub>6</sub>) was identified in a few samples with increased content of Pb. In one sample, a porous secondary oxide rich in Pb and As was identified by  $\mu$ -XRD as clinomimetite (Pb<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>Cl).

T30

## REMOVAL OF ANTIMONATE FROM WATER – SORPTION AND LEACHING BEHAVIOUR ONTO AKAGANEITE

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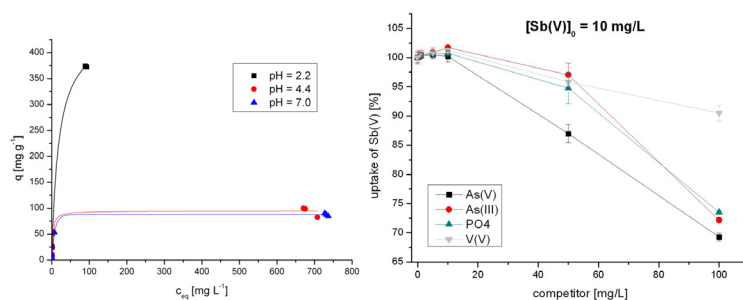
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Due to the harmful effects of antimony, the maximum contamination levels in drinking water is very low and vary slightly from  $5 \mu\text{g L}^{-1}$  (WHO 2003; European Communities 1998) to  $6 \mu\text{g L}^{-1}$  (US EPA, 2009). In water the two major antimony species exists, Sb(III) (under anoxic conditions) and Sb(V) in oxic milieu according to thermodynamic data [1]. In oxic water the ratio Sb(III)/Sb(V) is  $10^{-18.4}$  - nearly complete on the side of the oxygenated species [2].

In many areas of the world the content of antimony in the raw water exceeds these limits, and a water purification is required. Next to ion exchange, precipitation and coagulation, the sorption onto iron(hydr)oxides was tested successfully for the removal of the chemical similar species arsenate [3].

Akaganeite ( $\beta\text{-FeOOH}$ ) was tested for the removal of antimonate (and trimethyl antimonate) from water. Antimonate shows a high affinity to both iron materials resulting in a calculated maximum sorption capacity of  $450 \text{ mg g}^{-1}$ . The sorption is influenced mostly by pH and competitor oxyanions, which is shown in Fig.1 [4].

Fig. 1. Influence of pH (left) and competitors (right) on the sorption of antimonate onto akaganeite.



After breakthrough of the adsorber, the filter material can be changed easily in water treatment facilities. A risk assessment of the dumping material can be estimated by a sequential extraction of the material. Hence, a sequential leaching procedure for arsenic from soils [5] was applied with classical batch and new dynamic leaching systems (extraction cell and rotating coiled columns) to proof the remobilisation of antimonate and its kinetic [5].

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T31

## ANTIMONATE REMOVAL BY Zr-Fe BINARY OXIDE: PERFORMANCE AND MECHANISM

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Due to wide application of antimony-contained products and natural processes, large amount of Sb compounds are released into water environment. Considering its toxicity and no use in biological function, removal of Sb compounds from water has attracted more and more attention.

In this study, a Zr-Fe binary oxide adsorbent containing bulk- or surface-bound sulfate, was successfully synthesized for antimonate (Sb(V)) removal using a co-precipitation method. It showed a better performance than zirconium oxide or amorphous ferric oxide. Performance of this adsorbent for antimonate removal was further evaluated under various operating conditions such as initial Sb(V) concentration, temperature, solution pH, ion strength, reaction time and co-existing substances. The results showed that this adsorbent has a capacity of 51 mg/g at an initial Sb(V) concentration of 10 mg/L at pH 7.0. Sb(V) adsorption on the Fe-Zr bimetal oxide is an endothermic reaction in nature. Most of Sb(V) adsorption was found to be finished within 3 h and followed a pseudo-second-order rate law. A maximal removal was observed below pH 5.5. Co-existing ions of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  had no significant effects on Sb(V) removal, while  $\text{PO}_4^{3-}$  and HA showed considerable inhibition effects. Mechanism of Sb(V) adsorption on the adsorbent was investigated using a combination of zeta potential measurement, XPS, Raman, FTIR observation and  $\text{SO}_4^{2-}$  release determination. Ion strength dependence and zeta potential measurement indicated inner-sphere surface complexes formed after Sb(V) adsorption. Raman and XPS observations demonstrated that both Fe-OH and Zr-OH sites at the surface of the adsorbent interacted with Sb(V). FTIR analysis and  $\text{SO}_4^{2-}$  release determination further proved that exchange of  $\text{SO}_4^{2-}$  with Sb(V) also played a minor role in the adsorption process. Mechanism of Sb(V) removal using this adsorbent was investigated via a combination of zeta potential measurement, XPS analyses, FTIR observation and sulfate releasing test. It was indicated that both of Zr-OH and Fe-OH surface groups were involved in Sb(V) removal and formed Sb-O-Fe/Zr bonds at the adsorbent/ $\text{H}_2\text{O}$  surface. In addition, exchange of bulk- and surface-bound sulfate in the adsorbent with Sb(V) anions was also promoted the adsorption of Sb(V).

As a conclusion, this adsorbent showed high potential in future application for Sb(V) removal from contaminated water, and the removal mechanism was well understood.

[1] K.A. McComb, D. Craw and A.J. McQuillan, ATR-IR spectroscopic study of antimonate adsorption to iron oxide, *Langmuir*, 23 (2007) 12125-12130.



# ABSTRACTS - POSTER PRESENTATIONS

Abstracts are organised according to the name of the presenting author. In each abstract, the name of the lecturer is underlined.





P01

## VARIATION IN TOTAL ANTIMONY AND ITS INORGANIC SPECIES IN GRASS SAMPLES WITH DISTANCE FROM A MOTORWAY

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Road traffic has been identified as a source of Sb release into the environment. Known sources are compounds used as fire retardants in brake linings and from Sb-containing additives employed during the vulcanization of tyres [1]. Active biomonitoring at nineteen locations at varying distance to traffic suggested that antimony emissions seem to be closely associated with traffic impacts [2]. Correlation analysis revealed a positive linear dependency of antimony bioaccumulation vs. deposition, on grass samples near traffic lane which was found to be significant [3]. Since, there are no studies reporting species distribution of bioaccumulated Sb, grass samples that grew on the contaminated sites were studied in this work, where the distribution of antimony species concentrations in grass samples in a roadside profile were determined after a chromatographic separation using on-line isotope dilution. The extraction of Sb species from contaminated grass sample was carried out using 100 mmol L<sup>-1</sup> citric acid (pH 2.08). The Sb depositions on the grass surfaces are higher than the bioaccumulations of Sb in grass samples where it reaches two-fold concentrations at locations nearest to the traffic. Sb(V) concentration is at least two folds higher than Sb(III) in grass samples near the road edge. The total and bioaccumulated Sb(V) species concentrations sharply decreases with distance from the road edge, while Sb(III) concentration also decrease with distance but less pronounced as for Sb(V). Sb(III) species (more toxic), could be detected in all the grass samples. It was observed that the majority of inorganic Sb species can be washed out applying water to the grass samples. These results are summarized in Table 1

Table 1. Results of antimony speciation in grass samples (unwashed and washed) taken at different locations faraway from a traffic road (Knittelfeld-Austria).

Sample	Distance (m)	Sb(III) (ng g <sup>-1</sup> )	SD (ng g <sup>-1</sup> )	Sb(V) (ng g <sup>-1</sup> )	SD (ng g <sup>-1</sup> )
L1 (unwashed)	0.2	35.9	2.5	112.6	3.9
L2 (unwashed)	2.2	13.8	2.1	25.7	2.5
L3 (unwashed)	10.2	14.1	1.8	15.3	2.1
LW1 (washed)	0.2	10.4	2.7	60.7	4.2
LW2 (washed)	2.2	8.0	1.3	18.4	1.6
LW3 (washed)	10.2	2.8	1.2	3.9	0.9

[1] Krachler, M., Burow, M., Emons, H., 1999. Journal of Environmental Monitoring, 1, 477-481. [2] Peichl, L., Wäber, M., Reifenhäuser, W., 1994. UWSFZ Umweltchem Ökotox, 6, 63-69. [3] Dietl, C., Wäber, M., Peichl, L., Vierle, O., 1996. Chemosphere, 33, 2101-2111.

P02

**THE METALLURGY OF ANTIMONY**Anderson, C.G.

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Antimony is an essential rare element for flame retardants, catalysts and alloys. This presentation will cover the global resources available and metallurgical processes employed in the production of antimony metal and compounds. Flowsheets will be illustrated along with pertinent economics associated where applicable.

P03

**STUDY OF STRESS PROTEIN EXPRESSION IN SOME INVERTEBRATES LIVING  
IN THE PRESA RIVER (CORSICA) SUBJECTED TO AN ARSENIC AND  
ANTIMONY CONTAMINATION**

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In Corsica, waters of the Presa River exhibit high concentrations of arsenic and antimony due to a past mining activity. If this chronic pollution has led to the disappearance of many benthic invertebrate species, others such as the *Leuctra budzti* have managed to survive while accumulating large amounts of pollutants.

The understanding of adaptive mechanisms is a key stage to assess the environmental consequences of a pollutant chronic exposure in population of one given species. Different cellular and molecular processes involved in resistance to toxic elements: setting up barriers prohibiting entry of the toxic compound into the cell, sequestration, conversion into less toxic kinds or less bio-available (by oxido-reduction reactions, for example). Thus contact with pollutants creates a cascade of reactions whose consequences in a more or less long time may differ according to the detoxification mechanism used.

In this study, we have undertaken in *Leuctra budzti*, a shredder species that tends to accumulate more metalloids than other benthic invertebrates, to investigate the expression of the stress proteins, such as metallothionein (MT), which consist of low molecular weight, cysteine-rich, metal-binding proteins, and the heat shock proteins (Hsp), ubiquitous chaperone proteins, whose the expression level increases in response to multiple stress, which can thus be seen as a marker of cell suffering. Our first results of immunofluorescence experiments using antibodies against MT and Hsp70 do not seem to show an overexpression of these stress proteins. However, other experiments are underway on other species and using other antibodies.

P04

# **HEALTH RISK ASSOCIATED WITH DIETARY CO-EXPOSURE TO HIGH LEVELS OF ANTIMONY AND ARSENIC IN THE WORLD'S LARGEST ANTIMONY MINE AREA**

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Like arsenic (As), antimony (Sb) is known to be a genotoxic element in vitro and in vivo. Antimony is now recognized as a global contaminant and has aroused the global concerns recently. However, knowledge is scarce concerning the transfer of Sb from the environment to humans and the related hazards to human health. In this study, the health risk and main pathway of long-term human exposure to Sb and As for residents around Chinese Xikuangshan (XKS) Sb mine, the world's largest Sb mine, were evaluated by dietary exposure and hair accumulations survey. The concentrations and species of Sb and As in food samples ( $n=209$ ) from three main categories and six subcategories, and in hair samples ( $n=89$ ) were determined. Residents in the vicinity of XKS had an estimated dietary intake of Sb (554  $\mu\text{g/day}$ ) which was 1.5 times higher than the TDI (Sb, 360  $\mu\text{g/day}$ ), whereas their dietary intake of inorganic As (107  $\mu\text{g/day}$ ) was slightly lower than the provisional tolerable weekly intake (PTWI) of 15  $\mu\text{g/Kg BW/week}$  (equal to 129  $\mu\text{g As/day}$ ). Hair Sb and As concentrations (Sb, 15.7  $\text{mg/kg,DW}$ ; As, 3.99  $\text{mg/kg,DW}$ ) in XKS residents are both above the normal/toxic level. Rice, vegetables (especially leafy vegetable), drinking water, and meat/poultry were the dominant dietary intake sources of Sb for the residents. In contrast, rice was the uniquely dominant dietary intake source of As. Antimonate (Sb(V)) was the dominant Sb species in vegetables, drinking water and residents' hairs. This study highlighted the difference of exposure characteristics between Sb and As. Antimony levels, not As, can adversely affect the health of residents via dietary exposure in such large Sb mine area.

P05

**ANTIMONY SPECIATION IN SWEETENERS USING LIQUID  
CHROMATOGRAPHY HYDRIDE GENERATION ATOMIC FLUORESCENCE  
SPECTROMETRY (HPLC-HGAFS)**

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Antimony and its compounds have no known biological role, are nearly as toxic as lead and have been listed as priority pollutants by the US EPA, Council of the European Union (EU) and German Research Community (DFG). Elevated level of Sb was found in various brands of sweeteners in the market which again raise the concern of its impact on human health. Total antimony and its speciation in sweeteners have been carried out using atomic fluorescence spectrometry. Antimony (III) and (V) was separated and quantified by an anion exchange column with a mobile phase containing 200mM ammonium tartrate at pH 5. The majority of Sb in sweeteners was found to be the more toxic Sb(III).

P06

**ANTIMONY IN HYDROTHERMAL MINERALIZATIONS IN THE WESTERN CARPATHIANS (SLOVAKIA)**Chovan, M.<sup>1</sup>, Lalinská, B.<sup>1</sup>, Majzlan, J.<sup>2</sup><sup>1</sup>Department of Mineralogy and Petrology, Comenius University, 842 15 Bratislava, Slovakia<sup>2</sup>Institute of Geosciences, Friedrich-Schiller University, Jena, Germany

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Western Carpathians are an antimony-rich metallogenic province. Stibnite-bearing hydrothermal veins occur in granitoid and metamorphic rocks of the Variscan basement. Stibnite exploitation in the Gemeric tectonic unit and in the Nízke Tatry Mts peaked in the middle of the 19<sup>th</sup> century. The Čučma and Magurka deposits have been probably the largest European producers of antimony at those times. In 1913, Slovak Sb deposits were on the third place, behind China France, among the world producers of Sb ores. After the World War II, mining concentrated at the Dúbrava deposit which ranked among the largest producers in the world. Recently, all Slovak Sb deposits have been closed.

Antimony is distributed in several types of hydrothermal mineralizations and to various minerals. The most important are **stibnite ores**. In the Gemeric tectonic unit, the larger deposit was Čučma. Major Sb mineral there is stibnite, minor berthierite and zinkenite. Sulphosalts Pb/Sb, Bi/Pb/Sb, Cu/Pb/Sb contain some amounts of antimony. Other ore minerals are pyrite, arsenopyrite, sphalerite, chalcopyrite, pyrrhotite, galena, gold. Gangue - quartz and dolomite. We can distinguish two types of stibnite ores in the Tatric tectonic unit. In the Nízke Tatry Mts (type locality Dúbrava), the dominant Sb mineral is stibnite; zinkenite and tetrahedrite are minor. Rare Sb minerals are Pb/Sb sulphosalts and Cu/Sb/Bi phases. Other ore minerals are pyrite, arsenopyrite, sphalerite, chalcopyrite, galena, gold, gangue – quartz, dolomite. Sb mineral assemblage in the Malé Karpaty Mts is characteristic by a Sb-Fe-S-O system. The major mineral is stibnite, however, berthierite, gudmundite, primary Sb oxides (valentinite, kermesite), and antimony are frequently present too. Other ore minerals are pyrite, Au-bearing arsenopyrite, pyrrhotite, löllingite, gangue - quartz and ankerite. Sb mineralization in the Veporic unit (Ozdín deposit) is similar, with dominant stibnite and subordinate berthierite, jamesonite. Stibnite ores were in a short period exploited also on the Kremnica deposit, a very simple mineralization with stibnite and rare cinnabar connected with the Neogene volcanic activity. Similar mineralization occurs in the Zlatá Baňa deposit.

**Tetrahedrite ores** occurs on siderite hydrothermal veins, that were exploited as Fe, Ba, less Hg, Ag, Cu ores (Rudňany, Rožňava deposits). Principal part of veins are developed in the Variscan metamorphic rocks. The most important tetrahedrite ores from Strieborná žila vein (Rožňava deposit) contains Cu 34 wt.%, Sb 0.68 wt.%, Hg 0.01 wt.%, and Ag 195 g.t<sup>-1</sup>. Major Sb mineral is tetrahedrite and its varieties. Rare ore minerals with Sb are Pb/Sb and Bi/Cu/Pb/Sb sulphosalts, stibnite, and antimony. Other ore minerals – chalcopyrite, pyrite, arsenopyrite, gangue are quartz, siderite, barite, ankerite. Similar mineral assemblages are developed on siderite – quartz-sulphide veins in the Tatric tectonic unit (type locality Boca).

**Silver ores** in neovolcanites (Banská Štiavnica, Hodruša) contain antimony-bearing sulphosalts polybasite and stefanite. Pyrargyrite was more abundant than proustite.

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P07

**DIFFERENCE IN ANTIMONY AND ARSENIC RELEASE FROM LEAD SMELTER FLY ASH IN SOIL ENVIRONMENTS: EXPERIMENTAL APPROACH**Ettler, V.<sup>1</sup>, Mihaljevič, M.<sup>1</sup>, Šebek, O.<sup>2</sup>, Valigurová, R.<sup>1</sup>

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Emissions from lead (Pb) smelting have been recognized to be one of the most important local sources of pollution by metals/metalloids with antimony (Sb) concentrations in soils attaining 2058 mg/kg [1, 2]. However, our previous investigation of the leaching behaviour of secondary Pb smelter fly ash indicated that Sb release in an aqueous environment was significantly lower than that of another metalloid, arsenic (As) [3].

To understand the dynamics and fate of Sb and As originating from smelter-derived contamination, we studied the reactivity of secondary Pb smelter fly ash in acidic soils with special emphasis on the release and mobility of Sb and As. The polyamide bags (mean mesh size 1 µm, 2 x 4 cm) were loaded with 0.5 g of fly ash and sealed by welding. Testing bags were placed in contrasting soils in two experiments: (i) a short-term (21-day) laboratory pot experiment using two different soils (forest/agricultural) and soil pore-water sampling (Rhizon suction cups) and (ii) a long-term (1-year) *in situ* experiment in soils developed under different vegetation cover (spruce, beech, meadow). After each experiment, the bags were weighted to determine the mass loss and the weathered fly ash was studied by XRD and TEM/EDS. The total concentrations of metalloids and their chemical fractionation (BCR sequential extraction procedure) in the soils were determined by ICP-MS.

The mass losses indicated that more than 60% of fly ash was dissolved during both experiments. Although no Sb- and As-bearing phases were detected by XRD, the TEM observations indicated primary Sb<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>, presumably present in the original fly ash [2, 3] transformed to an unidentified Pb-As nanocrystalline phase and Pb antimonate. In agreement with the fly ash leaching results [3], significantly higher release of As in soil water was observed during the pot experiment (30-40 µg/L, stabilized after 48 h). In contrast, low concentrations of Sb, close to the blank incubations were reported in soil water (0.5-1.5 µg/L). No significant changes in the Sb concentrations and chemical fractionation were detected in the soil after exposure. A slight concentration gradient was observed for As towards the bottom of the pot, indicating its mobilization. An increase in the Sb concentration was observed in the soil after 1 year of the *in situ* experiment, in particular in litter and organic soil horizons under the tree stand (up to 1.8 x). Interestingly, the expected increase in the As concentration in the soil after the exposure was observed only in the litter horizons. This phenomenon may be related to more significant changes in the soil hydraulic properties in the mineral soil horizons, caused by soil probe excavating and subsequent faster flushing of As from the mobile soil fractions [4].

[1] Ettler, V., Mihaljevič, M., Šebek, O., Nechutný, Z., 2007: Chemosphere 68, 455-463. [2] Ettler, V., Tejnecký, V., Mihaljevič, M., Šebek, O., Zuna, M., Vaněk, A., 2010: Geoderma 155, 409-418. [3] Ettler, V., Mihaljevič, M., Šebek, O., 2010: Waste Manag. Res. 28, 587-595. [4] Mihaljevič, M., Ettler, V., Šebek, O., Drahot, P., Strnad, L., Procházka, R., Zeman, J., Sracek, O., 2010: Sci. Total Environ. 408, 1286-1294.

P08

**ANTIMONY MASS BALANCES IN TWO SWISS PERIALPINE LAKES**Filella, M., Carrard, F., Loizeau, J.-L.

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Antimony behaviour in open oceans is not considered to be highly reactive: some authors report that antimony behaves conservatively while for others antimony shows a pattern corresponding to a mildly scavenged element with surface atmospheric input [1]. Antimony behaviour in freshwater systems is not well-known; very few antimony concentration profiles have been published for lakes and no long-term studies have been reported. We have followed total dissolved antimony concentrations in two Swiss prealpine lakes: Lake Brienz and Lake Geneva. Lake Brienz is a ultra-oligotrophic lake, extremely rich in suspended glacial flour and poor in natural organic matter. It stratifies in summer but its bottom never gets anoxic. Lake Geneva is one of the largest lakes in Western Europe and one of the most studied. It is a mesotrophic lake with a seasonally hypoxic hypolimnion. Antimony concentrations were followed in Lake Brienz and its main tributaries over a year. Mean total dissolved ( $0.45\ \mu\text{m}$  filtered) concentrations in the lake, determined by ICP-MS, ranged from  $0.059 \pm 0.023$  to  $0.090 \pm 0.028\ \mu\text{g/L}$ . Concentrations were close to the detection limit of the technique but were confirmed by parallel determinations by DPASV in some samples. The lake mass stocks remained constant over the studied year with a mean value of  $376 \pm 42\ \text{kg}$ , suggesting conservative behaviour of this element in this lake. Negligible sedimentation of antimony seems to take place. Antimony concentrations were determined in Lake Geneva and in its seven main tributaries in two campaigns, in spring and autumn of the same year. Measured concentrations in the lake ranged from  $0.118 \pm 0.026$  to  $0.157 \pm 0.027\ \mu\text{g/L}$  and were constant with depth. The stock of antimony in Lake Geneva for the two campaigns gave similar values:  $11.1 \pm 1.7\ \text{tonnes}$  (March) and  $11.6 \pm 1.1\ \text{tonnes}$  (October). Mass balance calculations showed a significantly higher input through the tributaries than exit through the only outlet, the Rhone River in Geneva. Estimations of sedimentation rates using sediment core data did not explain the observed differences. They seem to be due to the dependence of antimony concentrations with flow in the main tributary, the Rhone River, that leads to an overestimation of antimony input in the lake in our mass balance calculations.

[1] 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.

P09

**ANTIMONY INTERACTIONS WITH HETEROGENEOUS COMPLEXANTS IN WATERS, SEDIMENTS AND SOILS: A REVIEW OF BINDING DATA FOR HOMOLOGOUS COMPOUNDS**Filella, M.

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Any chemical element, such as antimony, can exist in an aquatic system in different forms at the same time: free, complexed with 'simple' or low molecular weight (l.m.w.) organic or inorganic ligands, complexed with macromolecular or colloidal ligands, adsorbed on or incorporated in suspended organic or inorganic particles, adsorbed or assimilated by living organisms. All these different types of species in which an element can participate may significantly influence their biogeochemical behaviour and their bioavailability. In the case of antimony, the binding by macromolecular or colloidal ligands and particles remains little known compared to other elements of environmental concern (e.g., cadmium, lead, mercury, arsenic).

Published studies on antimony binding by NOM (natural organic matter) and inorganic colloids are reviewed. Concerning NOM, only complexation by humic-type substances has been studied. Existing data are very limited. Antimony complexation by these substances does not seem to be significant at the pH and concentration levels of surface waters but it might be more important locally in soils where there are higher acidic pH conditions and higher humic concentrations. Binding parameters describing antimony interactions with a variety of inorganic compounds, mainly different types of iron oxides, have been published. Binding is significant at acidic pH values both for Sb(III) and Sb(V) but it decreases abruptly above pH 6-8 in the case of Sb(V). The variety of solid phases, experimental conditions and binding models used so far preclude any comparison between different binders and the use of binding data for accurate quantitative predictions. Different techniques (e.g. Mössbauer spectroscopy, ATR-IR (attenuated total reflection infrared spectroscopy) and XAS (X-ray absorption spectroscopy)) have shown that adsorption of Sb by iron oxides in acidic media takes place via an inner-sphere surface interaction, with the formation of Fe-O-Sb bonds. NOM and mineral surfaces not only binds metal ions but can also accelerate Sb redox reactions in aqueous systems.

P10

## ANTIMONY AND ARSENIC BEHAVIOUR UPON MICROBIAL DISSOLUTION OF MINING WASTE

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In surface and sub-surface environment, microorganisms mediate dissolution and precipitation processes of minerals, and thus affect geochemical cycling of elements. Antimony (Sb) and arsenic (As) are considered to have comparable geochemical behavior and toxicity, both are redox sensible and toxic even at low concentrations. In natural environment, weathering of mining waste is one of the major source of contamination by metal(oid)s including Sb and As. Determination of biotic factors influencing Sb and As mobility is crucial to understand geochemical behaviour of these elements in environment.

In this study, we performed controlled incubations of mine tailings containing > 0.2% and 0.06% of Sb and As respectively under abiotic and biotic (phylogenetically diverse heterotrophic bacteria) conditions to assess the role of bacteria on As and Sb release upon dissolution process. Role of microbes (biotic factor) was evaluated by comparing the amount of a given element released during biotic incubation to the amount of the same element released during abiotic incubation at the same pH value.

The results shown that all used bacteria were able to weather highly contaminated solids. For a given pH value, the amount of released Sb and As varied between the strains and was from half-fold less to three-fold greater than under abiotic conditions. This indicates that complexing metabolites produced by bacteria play an important role in the overall dissolution process and may have accelerating or inhibiting effect on Sb and As release. Positive correlation coefficients of biotic factors between Sb and Fe ( $R^2 = 1$ ), Ca ( $R^2 = 0.58$ ), and Al ( $R^2 = 0.999$ ) as well as negative correlation coefficients of biotic factors between As and Fe ( $R^2 = 0.58$ ), Ca ( $R^2 = 0.98$ ), and Al ( $R^2 = 0.57$ ) suggest its different behaviour upon microbial dissolution.

In conclusion, heterotrophic bacteria influence Sb and As geochemical pathway and mobility in environment.

## P11

## ANTIMONY SORPTION AND OXIDATION AT MANGANITE SURFACES

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Antimony (Sb) is a toxic element commonly occurring in the environment via natural processes and anthropogenic activities. In natural water, Sb is primarily present in inorganic forms and exists mainly as Sb(III) and Sb(V) species [1]. Antimonite is more toxic than antimonate. In this study, Sb(III) oxidation by manganese oxide- pyrolusite was studied over a wide range of initial mineral concentration, pH, temperature and competitive cation conditons.

The oxidation of Sb(III) by pyrolusite occurs on the time scale of minutes. The increase of initial mineral concentration will increase the oxidation rate. A more rapid rate was found at lower pH than at higher pH and the amount of oxidized Sb(III) decreased with the increasing pH values (Fig. 1.), which indicated that the oxidation rate may be directly influenced by the surface charge of the solid. A more rapid oxidation rate was found at lower temperature, the examination of thermodynamic parameters showed that the reaction between Sb(III) and pyrolusite was an exthermin process spontaneously. In the  $Mn^{2+}$  treated pyrolusite system, little decrease occurred in the rate of Sb(III) oxidation and sorption onto the solid. This suggested that  $Mn^{2+}$  added caused a surface conprotonation with Mn(IV) onto the pyrolusite, creating fresh reaction sites for Sb(III) on it.

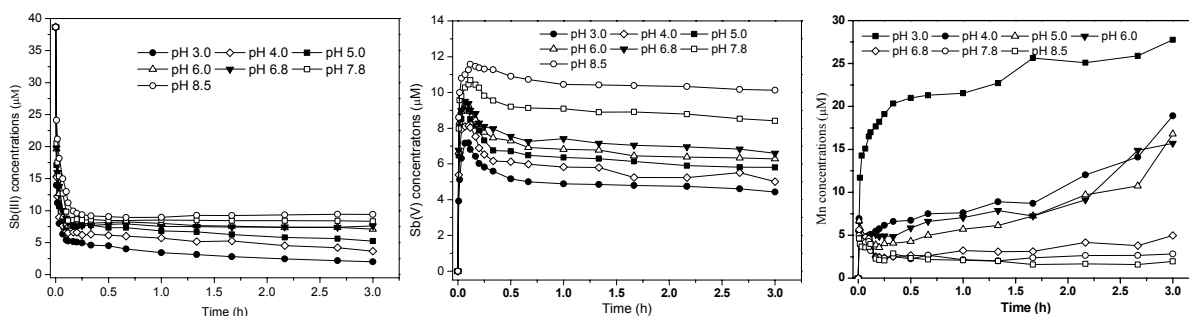


Fig. 1. Concentrations of Sb species and Mn(II) in aqueous solution as a function of time at different pH values. Conditions:  $T=25\text{ }^{\circ}\text{C}$ ,  $[\text{NaNO}_3]=0.01\text{M}$ ,  $[\text{CH}_3\text{COONa}]=0.05\text{mM}$ , and  $[\text{Sb}]_{\text{total}}=38.89\text{ }\mu\text{M}$ , adsorbent=600mg/L

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

P12

## MOBILITY OF ANTIMONY (Sb) IN SHOOTING RANGE SOIL: ROLE OF WATER SATURATION ON FE-STABILIZED SOIL

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Shooting range soil is potentially contaminated by Sb, copper (Cu), lead (Pb) and zinc (Zn). These elements are released due to weathering of spent bullets. The bullet core consists of 2-5 wt% Sb for getting hard lead alloys. A potential soil remediation method is to add Fe-based sorbents, which are good sorbents for Antimony and other metals. This may represent a feasible stabilization of shooting range soil prior landfilling. However, common anoxic bottom condition in the landfill may interfere with the stability of iron oxides, and a possible subsequent release of Sb and other metals.

In our experiments the impact of different water saturation, and thus the redox conditions, on shooting range soil stabilized with two different Fe-based sorbents was studied. Two different water saturation levels (half and fully water saturation) were simulated for stabilized shooting range soil from Steinsjøen in southern Norway. The soils with both 1 and 5 wt% TOC, were treated by 2 wt% iron hydroxide and 2 wt% zero-valent iron granulate (Fe<sup>0</sup>) respectively. The soil pore water for these different treatments is sampled at week 1, 3, 5, 8, 12 and 16 analyzed by ICP-OES (Fe, Cu, Pb and Zn) and hydride generation ICP-OES (Sb).

During the first 5 weeks of monitoring high Fe release in the iron-granulate sorbent treated soil was observed due to incompletely oxidizing of Fe<sup>0</sup> presumably. Much higher Fe release in the organic rich soil under fully water saturated condition indicates reduced conditions. This was supported by redox potential measurements (ca 200 mV). Despite the increased Fe solubility, no increased release of Sb, Cu, Pb and Zn in any of the treatments could be observed after 5 weeks. The experiment is still running and will continue until 16 week of monitoring.

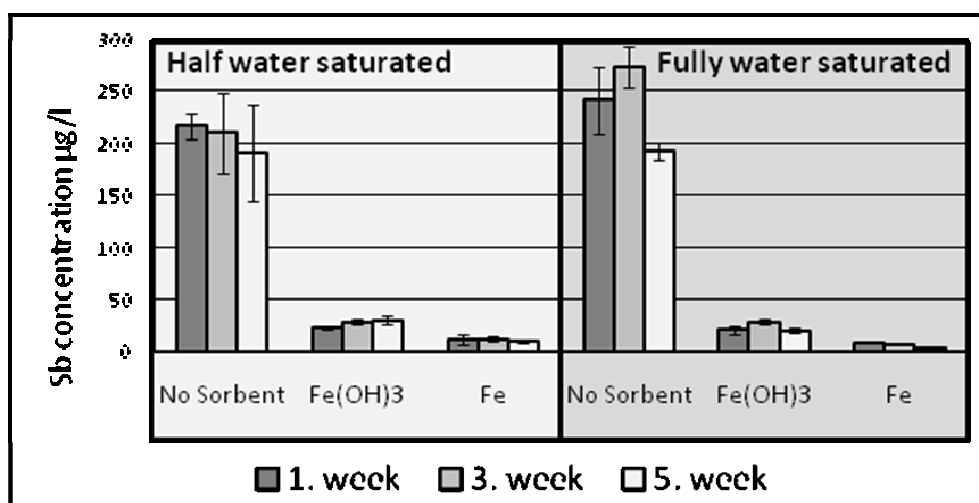


Fig. 1 Antimony concentration [µg/l] in pore water of organic rich shooting range soil (5 wt% organic matter) under half and fully water saturation; treated with iron hydroxide or zero-valent iron sorbent



## P13

**ADSORPTION AND CO-PRECIPITATION OF MN-OXIDES IN THE PRESENCE OF Sb(V)**Jahns, T., Bolanz, R.M., Majzlan, J.

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Due to the negative surface charge in many natural systems, manganese oxides are important sorbates for cations. However, several studies have shown that sorption to Mn-oxides is also possible for anionic species like arsenate [1] or selenite [2] as well. For environmental studies the sorption of heavy metals, which occur often as anionic complexes, is of special interest. In this work we studied the adsorption of the most common antimony specie in water  $[\text{Sb}(\text{OH})_6]^-$  [3] onto Mn-oxides, and the effects of Sb(V) on the precipitation of Mn-oxides from solution. Two series of sorption experiments were performed at pH 2.5 and 4, the former near the point of zero charge of K-birnessite ( $\text{K}_x\text{Mn}_2\text{O}_4 \cdot 1.5 \text{H}_2\text{O}$ ) [4], where attraction of anions to the birnessite surface should be observed. The potassium bearing birnessite used in our experiments was prepared after a modified version of McKenzie (1979) [5]. Sorption experiments were carried out for a maximum storage period of 10 days. In a second approach the incorporation of Sb(V) in K-birnessite was investigated. Therefore K-birnessite was precipitated from solutions at different concentrations of antimony (0.00, 0.37, 0.89, 2.50 and 6.69 mM Sb).

The Sb concentration of all samples was analysed via atomic absorption spectroscopy (AAS). X-ray diffraction (XRD) was performed for all samples precipitated in the presence of Sb, in order to investigate changes in crystallinity at different antimony concentrations. Additionally scanning electron microscopy was used to determine the chemical composition and grain size of selected samples. The chemical composition was obtained in energy-dispersive mode (EDX). During the investigations another occurring mineral was tentatively identified as cryptomelane.

The results show, that the Mn-oxides are able to take up Sb from solution in both cases; during adsorption and co-precipitation. The adsorption carried out at Sb concentrations of 6 mM display high Sb contents, depending on pH and storage time (Tab. 1). Co-precipitated samples show a max. of 0.17 mmol Sb/g, almost 100 % of available Sb(V) in solution. Although this study shows that Mn-oxides can have an impact on the sorption of anionic Sb-species, further investigations are necessary to identify the mechanisms of Sb uptake.

Table 1. Antimony content (mmol/g) of different birnessite samples from adsorption experiments.

pH of stocking solution	Sb concentration in stocking solution	storage time 2 hours	storage time 2 days	storage time 10 days
2.5	6 mM	0.23	0.48	0.62
4	6 mM	0.17	0.32	0.40

[1] Manning, B. A.; Fendorf, S. E.; Bostick, B.; Suarez, D. L., 2002: Environmental Science & Technology 36, 5, 976-981. [2] Saeki, K.; Matsumoto, S.; Tatsukawa, R., 1995: Soil Science 160, 4, 265-272. [3] Filella, M., Belzile, N., Chen, Y., 2002: Earth-Science Reviews 59, 265-285. [4] Kosmulski, M., 2009: Surfactant Science Series 145. [5] McKenzie, R. M., 1971: Mineralogical Magazine 38, 493-502.

P14

**ANTIMONY DISTRIBUTION IN SOILS FROM AREAS AFFECTED BY Sb MINING  
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Distribution of antimony in soils is a specific problem in Slovakia and till now a small attention was focused on study of contamination generated by Sb-mining, migration of this toxic element, binding on Fe-oxyhydroxides or other natural sorbents. Economically, the most important stibnite mineralizations are located in variscan basement - in the Tatric tectonic unit (Pernek, Dúbrava), and in the Gemeric tectonic unit (Poproč, Čučma). Soil contamination in case localities is result of several processes – mechanical redistribution of solid phases from spoil material, weathering of waste dump materials, occurrence of Fe-ochre layers, distribution of dissolved contaminants by surface waters from old adits and spoils, and their mobilization from waste material stored on impoundments.

In this work, we have summarized results from geochemical and mineralogical studies of contaminated soils from selected abandoned Sb deposits in Slovakia. Results of chemical analyses of soil samples showed large-scale contamination of soils by Sb, As, Pb and Zn. Extremely high concentrations of Sb and As were observed in fluvial soils in surrounding of Sb-deposits. Ranges of total contents for Sb in soils are for Pernek 120 – 1596 mg/kg, for Dúbrava 68 – 9619 mg/kg resp. Poproč 40 – 1989 mg/kg. Average concentration of Sb in Slovakian soils is 0.7 mg/kg in A-horizons, 0.5 mg/kg in C-horizons [1].

Sb and As occurs in the soils mainly in the secondary mineral phases which are products of sulphide oxidation. Main sulphides in the soils are pyrite, arsenopyrite and stibnite. Stibnite is the main source of Sb and it is very unstable and easy to dissolve in oxidation conditions. Secondary mineral phases are Fe, Sb(Fe) and Fe(Sb) oxides and oxyhydroxides. Furthermore, these mineral phases are relatively stable and they can reduce mobility of trace elements through the soils horizons. A pyrite identified in the soil samples from Dúbrava is suppressed by secondary oxide/oxyhydroxide Fe(Sb) minerals. They appear as a massive, often markedly zonal crystals with high content of Sb (from 13 to 20,49 wt.%), Fe (from 34,98 to 43,45 wt.%) and relatively low As content (to 1,49 wt.%). The most common products of sulphide oxidation, Sb(Fe) and Fe(Sb) oxides and oxyhydroxides, were on a locality Poproč, which probably originate in *in situ* precipitation of soil solutions, proven by the zonality of crystals and its coating character. The content of Sb in mineral phases of Fe(Sb) oxides is ranging from 5,47 to 23,93 wt.%, for As from 0,44 to 3,23 wt.%, for Fe from 14,62 to 47,26 wt.%. These mineral phases are very instable and can be easily destructed in the changing Eh and pH conditions.

Weathering and dissolution processes in environment significantly affect the mobility and bioavailability of Sb and may represent a risk to the surrounding ecosystem. To estimate the bioavailability of several certified extraction procedures (EDTA,  $\text{NH}_4\text{NO}_3$ , acetic acid) were used. The bioavailability was reached only at low level, the max. concentration in EDTA extract was only 37 mg.kg<sup>-1</sup>. Some plants such as *Veronica officinalis* contained up to 203,60 mg/kg Sb or *Fragaria vesca* (Poproč) high content of Sb up to 269.6 mg/kg.

[1] Čurlík J. & Šefčík P., 1999: Geochemical Atlas of Slovak Republic, Part V - Soils. VÚPOP Bratislava, 100p.

Acknowledgements: This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-0268-06 and No. APVV-VMSP-P-0115-09.

P15

## GEOCHEMICAL BASELINE OF ANTIMONY IN THE DALIAO RIVER ESTUARY SEDIMENT OF LIAODONG BAY, BOHAI SEA (CHINA)

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In recent years, Sb levels have become a matter of increasing concern due to the potential carcinogenic properties and ubiquitous presence of this element in the environment as a result of natural processes and human activities. We took surface sediment samples at 35 sites in the estuarine area of the Daliao river and analyzed total Sb and other elements (Table 1).

Table 1. Elemental contents in the Daliao River's estuarine sediment and world shale and sediment (n=35).

	Sb	Sc	Mn	Ti	Al	Fe	Ca	Mg	Na	K
	mg/kg	mg/kg	mg/kg	mg/kg	%	%	%	%	%	%
<b>Mean</b>	0.68	8.70	623.9	3186	6.72	2.61	1.20	1.24	2.39	2.46
<b>Standard deviation</b>	0.25	3.63	238.6	821	1.09	1.02	0.27	0.37	0.41	0.12
<b>Maximum</b>	1.12	14.38	1073	4052	7.97	4.19	2.02	1.67	3.22	2.87
<b>Minimum</b>	0.27	2.60	264.7	765	3.77	0.67	0.75	0.34	1.63	2.29
<b>Shale[2]</b>	1.5	13	850	4600	8.8	4.8	1.6	1.6	0.59	2.45
<b>Sediment[2]</b>	1.2	10	770	3800	7.2	4.1	6.6	1.4	0.57	2.00

The level of Sb in the estuarine surface sediments ranged from 0.27 to 1.12 mg/kg, with a mean level of 0.68 mg/kg. Mean contents of Sc, Mn, Ti, Al, Fe, Ca, Mg and Na were 8.70 mg/kg, 623.9 mg/kg, 3186 mg/kg, 6.72%, 2.61%, 1.20%, 1.24%, 2.39% and 2.46%, respectively. Mean content in the world sediment and median content in the world soil of Sb were 1.2 and 1.0 (0.2-10) mg/kg, respectively [1]. The Daliao River's estuarine sediment contained lower Sb, Sc, Mn, Ti, Al, Fe, Ca and Mn but higher Na and K than world shale and sediment. This might show that Sb in the sediment originated from natural processes.

Based on covariation of elemental contents in uncontaminated sediments, geochemical baselines of various trace elements for sediments were developed to identity their anthropogenic vs. lithogenic origins. However, geochemical baseline of Sb for sediments was not reported up to now. We found that Sb was correlated to Fe and Sc in the Daliao River's estuarine sediment (Fig. 1). These linear regressions might be used as geochemical baseline models to estimate lithogenic Sb in the other sediments around Bohai bay.

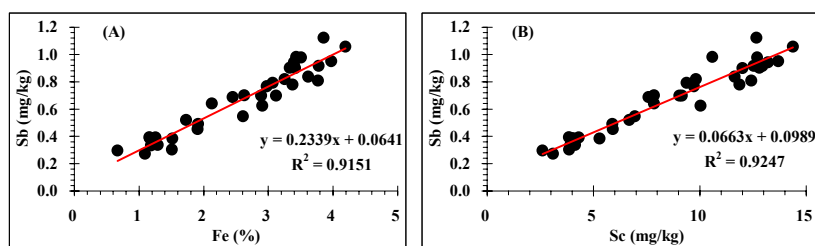


Fig. 1. Relationships between Sb and Fe (A) and Sc (B) in the estuarine sediment of the Daliao River.

[1] Bowen, H.J.M., 1979: Environmental Chemistry of the Elements, Academic Press.

Acknowledgments: Supported by NNSFC (40971058, 40873077) and PCSIRT (No.IRT0809).

P16

## THE DEPOSITION AND SUBSEQUENT MOBILITY OF Sb AND Pb IN SOILS AROUND A SMELTER, GUANGXI, CHINA

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The heavy metal contamination caused by smelters is usually a great environmental concern. The atmospheric deposition of heavy metals around an antimony-lead smelter as well as the subsequent mobility of heavy metals in soil profile have been addressed in this study, so as to understand the transport and fate of contaminants (antimony and lead) that originate from smelters.

The soil shows a high level of Sb and Pb contamination and a medium level of As contamination (Sb: 195-2034 mg/kg, Pb: 259-2261 mg/kg, As: 40-473 mg/kg). The heavy metal content in soil attenuates very rapidly in the area adjacent to smelter chimney, and then much mildly at a far distance. Within a distance of 400 m, Sb, Pb and As contents decrease 92.5%, 93.7% and 95%, whereas between 400-2400 m, Sb, Pb and As contents only decrease 64.4%, 52.1% and 80.9%. Antimony and Pb show a highly similar attenuation trend ( $r=0.998$ ), favoring the opinion that Pb and Sb usually present a similar behavior during their global migration. In addition, As shows a more rapid attenuation than Sb and Pb, possibly because As has a high affinity to iron minerals that usually have a higher density and is accordingly easier to deposit onto the ground.

Regarding the mobility of heavy metals in profile, an intensive variation of Sb and Pb concentrations in both soil and pore water is observed at a depth of 0-20 cm, where Sb and Pb decrease sharply. Below 20 cm, Sb and Pb show a much stable variation. Concerning the heavy metal distribution between soil and pore water, Sb content in pore water is much higher (ca. 20-100 fold) than Pb, although in soil they have similar contents. This means Sb has a lower affinity to soil than Pb, and is more readily to be leached into pore water and migrate to a deeper level. Compared to Pb, Sb is more likely to form a threat to ground water.

Different soil utilization is found to have an impact on the mobility of heavy metals in soil profile, with vegetable field showing a low migration potential for Sb and Pb. Vegetable field soil has a higher Sb content than uncultivated field soil above 20 cm, but a lower Sb content below 20 cm. Similarly, vegetable field soil also has a higher Pb content than uncultivated field soil above 15 cm, but a lower Pb content below 15 cm. It can be seen that heavy metal migration is made difficult by a layer at 15-20 cm. This layer is possibly a water-retarding zone, which is composed of fine soil particles and has very small interspaces due to cultivation. This is also supported by the difficulty for collecting pore water samples in vegetable field soil.

P17

**THE RELEASE OF Sb AND As DURING THE COMBUSTION OF TOXIC COAL IN SOUTHWEST GUIZHOU PROVINCE, CHINA**Zhang, G.<sup>1</sup>, Wei, X.<sup>1,2</sup>, Liu, H.<sup>1</sup>, Li, L.<sup>1</sup>, Xiang, M.<sup>1,2</sup><sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China<sup>2</sup>Graduate School, Chinese Academy of Sciences, Beijing 100049, China  
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Sever endemic poisoning has been reported in southwest Guizhou province, China, and more than 3000 patients have been diagnosed [1]. Coal combustion is regarded as the cause of the disease, since the coal for domestic use in this area usually has a high abundance of Sb and As (Sb-600 mg/kg, As-1000 mg/kg). To realize the release mechanism of Sb and As in coal combustion and to evaluate the threat of toxic elements in coal to human health, thermal decomposition (<1200°) and combustion experiments of the high toxic coal in this area were conducted in our research.

At the highest decomposition temperature of 1200°, the final coal weight loss, Sb and As releases are 66%, 46% and 75%, respectively. Three-stage weight loss of coal with temperature can be confirmed: <350°, 350-450°, >450°, which are mostly caused by volatile, organic carbon and mineral decomposition, respectively. Most weight loss of coal occurs at the T range of <450°, while Sb and As show a low release (Sb-7%, As-11%). This portion of Sb and As are mostly bound to organic phase. At 450-800°, the weight loss of coal as well as the release of Sb and As are very low (<3%). At 800-1200°, the weight loss of coal is only 3%, whereas Sb and As are largely released (Sb-35%, As-60%). This portion of Sb and As is considered mostly bound to sulfides.

In case coal is combusted at 900°, about 73-80% of toxic elements (Sb, As and Pb) remain in the bottom ash, while volatilized Sb, As and Pb enter dominantly into fly ash (19-26%), and poorly into gaseous phase (0.1-0.5%). Considering that the weight of fly ash is very low compared to bottom ash, the fly ash has a much high abundance of toxic elements. The high Sb, As and Pb contents in fine fly ash, more than 100 fold higher than those in coal, are considered to be caused by the adsorption on fly ash particles. Generally, the content of Sb, As and Pb increases in the order of coal, bottom ash, coarse fly ash and fine fly ash. The distribution of trace elements in the combustion products is correlated to the element volatility. Furthermore, Sb and Pb share a very similar distribution pattern in coal combustion products, which possibly favors the view that Sb and Pb show a similar behavior during their transport as a global contaminant.

[1] Ding, Z., Zheng, B., Long, J., Belkin, H.E., Finkelman, R.B., Chen, C., Zhou D., and Zhou, Y., 2001: Appl. Geochem. 16, 1353-1360.

P18

**SOURCES OF ANTIMONY IN AIRBORNE PARTICLES OF SHANGHAI, CHINA**Liu, W., Li, X.

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By analysis of antimony and the relative elemental composition in airborne particles and several potential sources, the predominant sources of antimony in airborne particles in Shanghai were discussed. Elemental ratios in coarse particles were found to be in good agreement with those of brake abrasion dust. However, in the fine airborne particle fractions, fly ash originating from waste incineration and coal combustion were identified as the most probable source of Sb. Chemical mass balance analysis was applied to determine the contributions of the emission sources of Sb. It was shown that brake abrasion dust and waste fly ash were the dominant sources of Sb in airborne particles in Shanghai, China. The present study provides important clues to understanding the cycles and fates of Sb in the atmospheric environment.



P19

**IMPACT OF AN ANTIMONY ENRICHMENT ON THE BENTHIC ECOSYSTEM IN A CORSICAN RIVER (FRANCE, MEDITERRANEAN REGION)**

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The chemical and biological characteristics of a Corsican river that drains contaminated waters from an abandoned realgar mine is studied here. The concentrations of antimony are found notably high (149.25  $\mu\text{g.L}^{-1}$  in water).

This contamination in the water falls with the disappearance leeches and the rarity of oligochaetes and mayflies populations. On the contrary, a large increase was noted within species belonging to stoneflies and gasteropods.

The concentration of antimony was measured in bryophytes and invertebrates. This concentration in bryophytes is 48.66  $\mu\text{g.g}^{-1}$ . For macroinvertebrates, the highest concentrations vary between 51.12  $\mu\text{g.g}^{-1}$  (*Leuctra budtzi*, Insect Plecoptera) and 197.60  $\mu\text{g.g}^{-1}$  (*Hydropsyche fumata*, Insecta Trichoptera).

Bioaccumulation factor of antimony is calculated. For bryophytes the mean value is 373.41. The value is of 1325.46 for the plecopteran *Leuctra budtzi* and of 1157.77 for the trichopteran *Silonella aurata*.

A ranking of invertebrates taxa is realized based on the bioaccumulation factor of antimony and is discussed.

The bioaccumulation factor of antimony in bryophytes and invertebrates is compared to the bioaccumulation factor of arsenic. Bioaccumulation of antimony in bryophytes is up to 3.14 times greater than for arsenic. Bioaccumulation of antimony from some benthic macroinvertebrates is 7 times greater than for arsenic.

The feeding and the current speed and the cuticle thickness play an important role in bioaccumulation processes of macroinvertebrates communities.

P20

## MOBILITY, SOLUBILITY AND UPTAKE OF ANTIMONY (Sb) AND ARSENIC (As) IN Sb MINING IMPACTED PADDY SOIL

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Mining of Sb is an important source for Sb contamination, with arsenic (As) often as a co-occurring contaminant with similar geochemical behavior. In the present study we investigated the behavior of Sb and As in flooded paddy soil sampled downstream an active Sb mining area in Xikuangshan, located in Hunan Province (China). Rice (*Oryza sativa* L. cv Jiahua) was grown under controlled conditions, and soil pore water concentrations of Sb and As were monitored during 7 weeks to study the effect of flooding, nutrient addition and rice plants.

Flooding the paddy soil (no rice plants) increased both the concentration of Sb (up to ca 2200  $\mu\text{g L}^{-1}$ ) and As (up to ca 1500  $\mu\text{g L}^{-1}$ ), most likely due to increased pH and subsequent decrease in positive charge on oxides and clay minerals and reduced anion sorption capacity (Fig. 1). Phosphate supply, in form of fertilizer, led to an initial increased Sb and As mobilization caused by the competition for the same sorption sites. Fe plaque developing on the rice roots acted as an effective scavenger for both Sb and As. The development of the As concentration with time suggests that the As solubility was governed by sorption. Sb occurred mainly as Sb(V) in the porewater, and a strong negative correlation between Sb(V) and calcium (Ca) concentrations in porewater indicated a Sb solubility governed by  $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ . After 6 weeks, the rice plants were harvested and both total and citric acid extractable (for speciation analysis: Sb(III) and Sb(V)) and total As in root and shoot were determined. High concentrations of Sb and As were found in rice roots, but concentrations were substantial lower in rice shoots. No significant difference in Bioaccumulation factor (BAF) (ratio of total shoot concentrations and concentration in porewater) and Translocation factor (TF) (ratio of total concentration in shoot to root) between Sb and As were found.

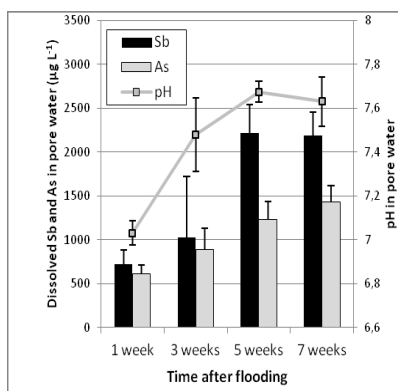


Fig. 1. Development of Sb and As concentration in porewater in soil with no nutrient addition and no rice.

## P21

**DETERMINATION OF THE ANTIMONY CONTENT AND ITS RELATION WITH THE MINERALOGICAL COMPOSITION IN DIFFERENT FRACTIONS OF THE SOIL**

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The study of antimony in soils is often hindered by the low levels that are usually present. However, moderately high concentrations of the element can be found in some zones due to natural geological reasons, or to the vicinity to mining sites, which facilitates reliable data to be obtained. This is the case of the zone here studied, which is placed in the surrounding of Sierra Minera (La Union, Murcia SE Spain) where mining activities, now abandoned, have been carried out for centuries. The area shows natural geogenic values of antimony several times greater than the background levels found in the SE Spain.

The purpose of this work was to study the possible relation between the level of antimony present in soil and the mineralogical composition in different soil fractions in the conviction that the knowledge of the main mineral phases present in the soils could help to clarify the fate of the elements present [1]. To this effect, a number of soil samples were collected, different fractions obtained, the level of antimony determined by hydride-based atomic fluorescence spectrometry, and the mineralogical composition of each fraction established by means of XRD.

The mineralogical analysis showed that the main minerals were quartz, muscovite, kaolinite, illite calcite and feldspars, while the minority minerals were products of mining influences (iron oxides and hydroxides, jarosite and gypsum). Some of the results for the levels of antimony found are shown in Table 1.

Table 1.- Total antimony content of soil samples (mg/kg).

Sample (soil fraction)	N	Mean	Maximum	Minimum	Range	Standard deviation
(<2mm)	10	16.80	35.68	4.54	4.54-35.68	8.06
(<2mm - >250µm)	10	15.88	25.83	4.38	4.38-25.83	6.57
(<250µm)	10	15.03	34.81	4.37	4.37-34.81	7.97
(<250µm - >63µm)	10	16.80	29.93	4.49	4.49-29.93	6.78
(<63µm)	10	17.74	28.34	4.42	4.42-28.34	7.14

A statistical analysis of the data was made with MINITAB 14 and SYSTAT V11 software. The Pearson product-moment correlation test and the Kruskal-Wallis test was used to establish possible relationships between the antimony content and the mineralogical composition of the soil samples. Results proving such relations exist are given in the full communication.

[1] Pérez-Sirvent, C., Martínez-Sánchez, M.J., Martínez-López, S., Hernández-Córdoba, M. Microchemical Journal 97 (2011) 52-56.

P22

**DEVELOPMENT AND VALIDATION OF AN ION CHROMATOGRAPHY  
SCREENING METHOD FOR ANTIMONY SPECIES ASSESSMENT IN  
ENVIRONMENTAL SAMPLES.**

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It is now recognised that assessment of antimony (Sb) (and chemically similar arsenic (As)) species in environmental samples is key to determining the real risk from these metalloids in ecosystems. Environmental and health studies have repeatedly shown that metalloid toxicity and bioavailability is related to the chemical species present. Species assessment, however, can be complex and highly variable and is significantly less well developed for Sb, due to analytical interferences and complications with species preservation [1]. Although progress has been achieved in recent years particularly for achieving the low detection limits required [2], access to techniques is often limited by funds, availability and expertise. The aim of this work was to develop and validate a robust routine ion exchange chromatography screening method for Sb species assessment in environmental samples with comparisons to As.

The method was developed using an anionic column (base model Ion Pac AS11-HC and AS20-HC) on a Dionex ICS2000 ion chromatograph. A general anionic separation method was validated for Sb(III) and Sb(V) species. The effect of matrix background, pH and co-occurring ions such as Ca and Fe which may function as redox catalysts on Sb species ratios was assessed [3]. Also determined was the effect of different field sample preservation additives (e.g. HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, EDTA).

The method was applied for screening a range of water samples collected from a northern NSW catchment, highly contaminated with Sb and As as a result of historical mining activities, and compared with field anionic samplers for Sb speciation [3, 4].

[1] Krachler, M. and H. Emons, 2001: Trends in Analytical Chemistry 20, 79-90. [2] Hoiki, A. 2008: Analytical Sciences 24, 1099-1103. [3] Watts, M. J., J. O'Reilly, A. L. Marcilla, R. A. Shaw and N. I. Ward 2010: Environmental Geochemistry and Health 32, 479-490. [4] Kim, Y.-T., H. Yoon, C. Yoon and N.-C. Woo 2007: Environmental Geochemistry and Health 29, 337-346

## P23

## ANTIMONY SPECIATION IN BLOOD FRACTIONS

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Brake pads systems are nowadays considered as one of the most important sources of antimony in airborne particulate matter (APM) [1]. 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. On the other hand total antimony distribution in blood fraction was found to be higher in the erythrocyte fractions specially in cytoplasm demonstrating that most of the antimony in human blood is able to permeate the erythrocyte membrane [2].

The mechanisms about cellular antimony uptake are still unknown. There are only few scientific studies that refer to the mechanisms of cellular transport of antimony species and most of them are mainly related to the cellular system of the Leishmania parasite [3]. In literature there is no study on the distribution neither of antimony in erythrocyte cells nor of analytical methodologies for the chemical speciation of antimony in these samples.

In this study we describe a suitable methodology for the antimony speciation in blood fractions (plasma and cytoplasm). A detailed study was carried out about plasma and cytoplasm treatment considering cleaning procedures as well as stabilization of species during the whole procedure. Preservation of species was better achieved by adding EDTA 0.1 M to both blood fraction before sampling cleaning procedure. C-18 cartridge was the best stationary phase for cleaning purposes. Treatment of the sample did not significantly affect the chromatographic figures of merit. Quantification limits under optimized conditions were 0.29 and 0.23  $\mu\text{g g}^{-1}$  for Sb(V) and Sb(III) respectively (considering a mass of 3 g of whole blood sample).

Recovery essays were performed under optimized conditions. For plasma 99% and 75% of recovery for Sb(V) and Sb(III) were obtained respectively. For cytoplasm 87% and 55% for Sb(V) and Sb(III) were obtained respectively.

The methodology was applied to whole blood culture experiment in which whole blood were put in contact for 20 minutes with Sb (V) and Sb (III) separately. Results showed that Sb(V) is able to permeate the erythrocyte cells reaching 60% to the cytoplasm fraction.

[1] Furuta, N., Iijima, A., Kambe, A., Sakai, K., Sato, K., 2005: J. Environ. Monit., 7, 1155-1161. [2] Quiroz, W., De Gregori, I., Basilio, P., Bravo, M., Pinto, M., Lobos, M.G., 2009: J. Environ. Monit., 11, 1051-1055. [3] Ulrich, N., Shaked, P., Zilberstein, D., 2000: Fresenius' J. Anal. Chem., 368, 62-66.

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P24

## ANTIMONY AND HEAVY METAL POLLUTION INDUCED DUE MINING ACTIVITIES IN GUANAJUATO, MEXICO

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Anthropogenic pressure has dramatically altered the geochemical cycles, a clear example is the imbalance created by the highly polluting mining industry. Mining tailing disposal has led to several environmental problems as soil pollution and contamination of streams and groundwater. Severity of the contamination by mining wastes lies in the complexity of mine tailing's composition.

This study focuses on determination of antimony (Sb) and heavy metals (Co, Cu, Mo and Tl) from mining tailings wastes which are considered as primary pollution source for their impact on environment. Samples were taken from mine tailings drainage (sludges) and parental rocks. Concentrations of Sb and heavy metals were determined by ICP-MS. The results are summarized in Table 1.

Table 1. Antimony and heavy metals values determined in a polluted mine site.

	Sb (mg <sup>-1</sup> )	Co (mg <sup>-1</sup> )	Cu (mg <sup>-1</sup> )	Mo (mg <sup>-1</sup> )	Tl (mg <sup>-1</sup> )
<b>La Valenciana mine</b>					
0 m	122.7	30.58	119.24	19.83	4.42
20 m	74.6	27.9	108.54	16.74	2.84
40 m	4.6	12.98	60.94	2.26	1.69
Mine drainage tunnel	4.2	18.59	41.30	0.94	2.63
Parental material	3.7	31.13	26.21	0.60	2.12
<b>Los Mexicanos mine</b>					
Material taken from a mine adit	3.0	10.84	318.61	1.66	0.50
Mine waste without process	1.8	1.36	16.39	0.04	2.43
Parental Material	0.74	2.70	32.25	0.09	4.04

Data of Table 1 shows a possible natural attenuation of elements analyzed in sludges from mine tailings drainage due to the decreased concentration of Sb and heavy metals according distance from the contaminant source. In general, data presented in this study indicate the potential risk of the mining tailings to liberate these elements to the natural environment.

P25

**ANTIMONY ACCUMULATION IN CEREAL CROPS GROWN IN MEDIA ENRICHED WITH  $\text{Sb}^{3+}$  AND  $\text{Sb}^{5+}$** Shtangeeva, I.<sup>1</sup>, Steinnes, E.<sup>2</sup>, Lierhagen, S.<sup>2</sup><sup>1</sup>St. Petersburg University, Universitetskaya nab., 7/9, St. Petersburg 199034 Russia<sup>2</sup>Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway  
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By now a lot of experimental data on environmental chemistry of many toxic metals has been collected. However, list of the toxicants is rather short. Information about many trace elements which always may be detected in all environmental samples is scarce. This resulted in a commonly accepted opinion that the trace elements presented in plants at rather low concentrations are non-necessary impurities which do not play any essential role in the biochemistry of the plants.

Antimony is widely distributed in the environment. In general, Sb exists in a variety of oxidation states, but in soils, it is mainly present as  $\text{Sb}^{3+}$  and  $\text{Sb}^{5+}$ . Till now, little is known about biogeochemistry and phytotoxicity of Sb. It is still a problem to accurately determine small amounts of Sb in solid matrices.

The commonly accepted opinion is that due to similar chemical parameters of As and Sb their biochemistry is also similar. However, despite similarities in the chemistry of the metalloids, there are many differences in their environmental behaviour, in particular, in uptake by plants. Therefore, it may hardly be possible to interpret experimental data on Sb plant uptake based only on the available information on biogeochemical behaviour of As.

The objectives of the research were (1) to study how the form in which Sb is present in the growth medium can affect uptake of Sb by plants, and (2) to estimate effects of different Sb species on 2 crop plants, wheat and rye and, in particular, to assess the variations in the concentrations of essential plant nutrients resulting from bioaccumulation of Sb.

Seedlings of wheat and rye were either germinated or grown in water spiked with either  $\text{Sb}^{3+}$  or  $\text{Sb}^{5+}$ . Plants were collected several times after planting and then analysed by ICP-MS.

When seedlings were germinated in the media enriched with Sb, its concentration increased significantly in all plant parts. However, there were certain differences between uptake of Sb by wheat and rye as well as plant uptake of different Sb species. Compared to control, the most significant increase of Sb concentration was observed for seeds, and the least for leaves. In most cases, rye was capable of accumulating larger amounts of Sb than wheat. Concentrations of Sb in rye seedlings were much higher when the seeds were germinated in the medium spiked with  $\text{Sb}^{5+}$  compared to Sb concentrations in the rye seedlings germinated in the medium spiked with  $\text{Sb}^{3+}$ . In wheat, concentrations of Sb were higher in the seedlings germinated in the medium spiked with  $\text{Sb}^{3+}$  compared to those in the seedlings germinated in the medium enriched with  $\text{Sb}^{5+}$ .

The accumulation of Sb in rye and wheat seedlings resulted in variations in concentrations of many elements in different plant parts. Such an essential unbalance in plant element concentrations provided certain variations in the physiological state of the seedlings. An enhanced uptake of Sb by rye seedlings caused necrosis of the plant leaves. The treatment with  $\text{Sb}^{5+}$  was probably more toxic for rye seedlings.

When seedlings germinated in Sb-spiked media were transferred to clean water, concentration of Sb both in roots and in leaves decreased with time. When seedlings germinated in Sb-free medium were transferred to water spiked with Sb, the plant concentrations of Sb increased significantly. However, with time saturation with Sb in leaves and partly in roots was observed.



## P26

**TAILING IMPOUNDMENTS WITH CONTENT OF Sb IN SLOVAKIA**

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Two types of tailing impoundment from Slovakia are presented in this contribution. Study of four mining area with tailing impoundments after Sb ore processing (Dúbrava, Medzibrod, Poproč, Čučma) and two tailing impoundments after siderite-sulphides vein mineralization (Rudňany, Slovinky) were the main objects of two scientific project realised from 2007 till now. These projects should contribute to the implementation of European Parliament and European Commission directive 2006/21/ES on the management of waste from extractive industries.

Samples for the study were obtained by sampling of drilling holes which were situated in the body of tailing impoundment and sampling points and nets on surface of tailing impoundments. Samples were stored in plastic bag to protect their contact with oxygen and transported to the laboratories.

Total chemical analyses of samples (Tab.1.) were used to determined basic chemical composition of tailing materials. Amounts of elements were analyzed by standard methods AAS-AMA, AES-ICP, FAAS, GA, HG-AAS in accredited laboratory. Determination of pH (active and exchangeable pH), conductivity (in soil paste), Eh, 3-step modification of sequence analyses, acidification [1] and neutralization potential [2] was used to obtain data for geochemical characterization of material.

We used 3-step sequence analyses [3] as main method to better understanding the physical-chemical processes of fixation, mobility and transportation of metals. We detected migration ability of elements in particular fractions of sequence analyses in chosen representative samples. The results of sequence analyses were consequently compared with total chemical analyses to detect potential amount of released elements to the environment.

Table 1. Content of Sb (in mg/kg) in material of studied tailing impoundment (n – number of analyzed samples).

	Poproč	Dúbrava	Čučma	Medzibrod	Slovinky	Rudňany
average	3897	1250	4594	3012	347	111
minimum	1509	444	87	2121	17	31
maximum	15831	3462	11736	3799	3791	191
median	3158	1093	2858	3064	71	113
n	20	21	6	5	21	58

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## ANTIMONY COORDINATION TO SOIL-DERIVED HUMIC ACID

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Antimony (Sb) is a non-essential element and toxic to most living organisms at elevated concentrations. It is released anthropogenically mainly to the terrestrial environment; therefore, it is crucial to investigate the fate of Sb in the soil system [1], including understanding of binding mechanisms of Sb to soil humic acid (HA). Sb forms complexes with natural organic matter both humic and non humic compounds, and a significant proportion of Sb is likely to be bound with HA via hydrocarboxylic moieties in the form of bidendate complexes [2]. The coordination chemistry of Sb to soil HA has a both theoretical and practical interests. For example, it may explain existence of reduced Sb form in oxic conditions, and Sb immobilization in soil organic layer; furthermore, this research may be essential to Sb detoxification process. Previous studies mainly focused on Sb binding to dissolved organic in aquatic environments [2] or its binding to soluble fraction of HA [3].

In the present study, HA-Sb (III) composite was obtained based on bulk soil-derived HA. The maximum concentration of Sb bound to HA was estimated to be  $253 \mu\text{mol}\cdot\text{g}^{-1}$  HA. Elemental composition, absorbance characteristics and Nuclear Magnetic Resonance (NMR) spectroscopy study on bulk HA and HA-Sb were conducted to elucidate Sb (III) coordination to natural organic ligands (Table 1).

Table 1. The elemental composition and aromaticity characteristics for soil-derived HA and HA-Sb.

Samples	Elements, % (ash free basis)					Ash, %	$E_4/E_6^{\dagger}$	Aromaticity $^{\ddagger}$	Sb, $\mu\text{mol}\cdot\text{g}^{-1}$
	C	H	N	S	O				
HA	48.4	5.9	3.0	0.7	42.1	8.8	5.1	66.9	0.18
HA-Sb (III)	47.2	6.3	2.6	0.6	43.3	35.6	5.4	63.4	253.3

 $^{\dagger}$  absorbance ratio at 465 nm and 665 nm;  $^{\ddagger}$   $^{13}\text{C}$  NMR data

$^1\text{H}$  NMR data showed that hydrogen for carboxyl and phenolic OH groups (these measured  $438.85 \text{ cmol}\cdot\text{kg}^{-1}$  and  $119.8 \text{ cmol}\cdot\text{kg}^{-1}$  in soil-derived HA, respectively) dramatically decreased in HA-Sb composite compared to HA. Also it was revealed that aliphatic protons possibly to contribute in this interaction. In solid-state  $^{13}\text{C}$  NMR, the general distributions of total aliphatic and aromatic carbon nuclear were similar independently if HA did not contain or contained Sb. Results suggested HA cyclic structure remained unchanged during Sb (III) association and data were consistent with  $E_4/E_6$  ratio. However, integrated areas of peaks for individual groups showed changes both increase and decrease (again in methyl and methylene) in HA-Sb composite compared to HA. Methyl and methylene groups in the aliphatic chain suggested Sb binding to HA. HA-Sb composite will be studied in detail using X-ray Absorption Fine Structure (XAFS). Selected Sb atom's coordination number and radial distance with its neighboring atoms will be determined; and also Sb valence states will be investigated to ascertain HA role in stabilization of trivalent form.

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P28

## **SUMMARY OF AVAILABLE SCIENTIFIC DATA ON ANTIMONY TRIOXIDE**

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The International Antimony Association (i2a) is a non-profit association whose mission is to study and disseminate information on the safe use of antimony and antimony compounds, especially with regard to the relevant environmental, health and safety regulations.

This poster will give a brief overview of the available scientific data on antimony trioxide (its uses, the environmental and health effects) after having studied this substance for 11 years (including peer review of the data by international experts of the EU, Canada and OECD).

P29

## **THE INTERNATIONAL ANTIMONY ASSOCIATION**

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The International Antimony Association (i2a) is a non-profit association whose mission is to conduct studies and to disseminate information concerning the safety and benefits of antimony and antimony compounds, by way of giving access to data, sharing and providing information on the content of data, for the benefit of producers and importers of antimony and antimony compounds world-wide regarding environmental, health and safety regulations of these antimony compounds.

This poster will give a brief overview of who i2a is, what its purpose is, which substances i2a works on and who the members are.

P30

**TRIPUHYITE AND SCHAFARZIKITE: TWO KEY PHASES THAT CONTROL THE SOLUBILITY OF ANTIMONY IN THE NATURAL ENVIRONMENT**Leverett, P., Reynolds, J.K., Roper, A.J., Williams, P.A.

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The behaviour of antimony in the natural environment is a matter of considerable concern and one of many questions that remain to be answered [1] is just what solid phases exert significant control on the solubility of Sb under oxidizing conditions. In some circumstances, Sb(III)/Sb(V) oxides and members of the stibiconite group are important sinks for the element [2]. As part of a study to answer the question, we have determined the stabilities of tripuhyite,  $\text{FeSbO}_4$ , and schafarzikite,  $\text{FeSb}_2\text{O}_4$ , using solution methods [3]. Derived  $\Delta G_f^\circ(\text{s}, 298.15 \text{ K})$  values for  $\text{FeSb}_2\text{O}_4$  and  $\text{FeSbO}_4$  are  $-959.4 \pm 4.3$  and  $-836.8 \pm 2.2 \text{ kJ mol}^{-1}$ , respectively [3]. These values compare favourably, and unexpectedly, with those in the literature, extrapolated from 771-981 K [4].

These results lead some rather startling conclusions. Except for quite acid conditions, schafarzikite and tripuhyite are dominant phases in terms of Sb solubility under oxidizing conditions. In particular, for the relation  $\text{FeSbO}_4(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{FeOOH}(\text{s}) + \text{Sb}(\text{OH})_5^\circ(\text{aq})$ ,  $\lg a(\text{Sb}(\text{OH})_5^\circ) = -11.0$  at 298.15 K. A calculated Pourbaix diagram for  $\lg a(\text{Fe}^{3+}) = -6$ , is dominated by the two phases except under very acid conditions. For tripuhyite the boundary is at *ca* pH 0.4. This explains in large part the fate of Sb in the supergene zone associated with Sb-rich ores and Sb-contaminated wastes exposed to ambient geochemical conditions [1, 2, 5]. The results, taken in conjunction with adsorption effects [6], may well have application in environments where total Sb concentrations are much lower than in the above cases. Both schafarzikite and tripuhyite are easily overlooked because of their physical properties [2, 3, 5]. It is virtually impossible to distinguish them visibly from goethite.

Further experiments have demonstrated that tripuhyite is easily formed when Fe- and Sb-bearing sulfides are oxidized under ambient conditions when the expected Fe-bearing phases are ferrihydrite, schwertmannite and goethite. Other simple Sb-bearing oxides have also been examined and these can be important for limiting the dispersion of Sb in special environments (oxidizing sulfide ores), depending upon the availability of cations such as Pb(II), Zn(II) and Mg(II) [7].

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P31

**ARSENIC, ANTIMONY AND BISMUTH IN VEGETABLES FROM AN ANTIMONY MINING AREA, CHINA**Liu, B.<sup>1</sup>, Li, X.<sup>1</sup>, Wu, F.<sup>2</sup>, Liao, H.<sup>2</sup>, Fu, Z.<sup>2</sup>, Mo, C.<sup>3</sup><sup>1</sup>Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621900, China<sup>2</sup>State Environmental Protection Key Laboratory for Lake Pollution Control, Chinese Research Academy of Environmental Sciences, Beijing 100012, China<sup>3</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China  
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A preliminary study was undertaken to monitor the exposure of environment and health of residents by heavy metals released by mining and smelting activities at Qinglong antimony mining area (in Guizhou Province, Southwest China). To this purpose, the edible parts of 14 vegetables from farmlands in Qinglong antimony mining area were collected, washed and digested. Hydride generation-atomic fluorescence spectrometry (HG-AFS) was employed for the determination of arsenic (As), antimony (Sb) and bismuth (Bi) in the vegetable samples. Results show that As, Sb and Bi concentrations in vegetables (dw) are ranging from 0.318 to 9.99 µg/g, from 0.06 to 57.8 µg/g, and from 0.0025 to 0.0976 µg/g respectively. Elevated levels of As, Sb and Bi were found in water convolvulus (*Herba Ipomoeae Aquaticae*), scallion (*Allium Fistulosum L.*) and mustard (*Brassica Juncea L.*), while lower levels of As, Sb and Bi were in eggplant (*Solanum melongena L.*), kidney bean (*Phaseolus vulgaris L.*). These results confirm that As, Sb and Bi contents in plant leaves are much higher than those in plant fruits and residents should be cautious to take vegetables whose edible parts are leaves in antimony mining area.





# AUTHOR INDEX

Ackermann, S. ....	34	Faggianelli, J. ....	61
Aguilar, L.F. ....	65	Fairlamb, A.H. ....	9
Amereih, S. ....	43	Filella, M. ....	50, 51
Amstätter, K. ....	27	Fouquoire, A. ....	61
Anderson, C.G. ....	44	Freitas, V.A. ....	16
Ashley, P.M. ....	17	Frézard, F. ....	16
Barria, M. ....	65	Fu, Z. ....	46, 73
Barthélémy, R.M. ....	45	Fujiwara, F. ....	24
Battersby, R.V. ....	15	Furuta, N. ....	26
Bolanz, R.M. ....	34, 55	García-Arreola, M.E. ....	66
Bravo, M. ....	65	Garrido, M. ....	61
Bril, H. ....	35, 52	Gibbon-Walsh, K. ....	22
Brown, K. ....	20	Gómez, D. ....	24
Calendini, S. ....	61	Göttlicher, J. ....	37
Carrard, F. ....	49	Grybos, M. ....	52
Chen, B. ....	46, 47	Hansen, C. ....	21
Chovan, M. ....	37, 48, 68	Hansen, H.R. ....	21
Corns, W. ....	46, 47	He, J. ....	62
Corrêa-Junior, J.D. ....	16	He, M.C. ....	53, 57
Courtin-Nomade, A. ....	35, 52	Heier, L.S. ....	14
Culioli, J.-L. ....	45	Heil, C. ....	18
Da Prato, J.-L. ....	45	Heininger, P. ....	18
Daus, B. ....	13, 23, 38	Hernández, E. ....	66
Demicheli, C. ....	16	Hernández-Córdoba, M. ....	63
Dou, X.M. ....	39	Herzel, H. ....	54
Duester, L. ....	18	Hockmann, K. ....	28, 33
Ecker, D. ....	18	Hovorič, R. ....	37
Ettler, V. ....	49	Iijima, A. ....	26
Evangelou, M.W.H. ....	28	Jahns, T. ....	55

Jankulár, M. ....	56	Ljønes, M. ....	29
Jiménez Rebagliati, R. ....	24	Lockwood, P.V. ....	17, 32
Jurkovič, L. ....	56, 68	Loizeau, J.-L. ....	50
Kato, K.C. ....	16	Maher, W. ....	17
Khondoker, R. ....	31	Majzlan, J. ....	34, 37, 48, 55
Kierczak, J. ....	52	Mariussen, E. ....	14, 27, 29
Kleiven, M. ....	14	Marrero, J. ....	24
Klimko, T. ....	37, 56	Martinez, D. ....	65
Kolbe, F. ....	23, 38	Martínez-López, S. ....	63
Krikowa, F. ....	17	Martínez-Martínez, L.B. ....	63
Kučerová, G. ....	37	Martínez-Sánchez, M.J. ....	63
Kunz, M. ....	35	Massey, C. ....	11
Lalinská, B. ....	37, 48, 68	Matejkovič, P. ....	56
Lassen Bue, H. ....	27	Mattusch, J. ....	13
Lenz, M. ....	33	Meisel, T. ....	43
Leverett, P. ....	36, 72	Merbach, I. ....	13
Liao, H. ....	46	Michňová, J. ....	37
Li, L. ....	30, 58, 59	Mihaljevič, M. ....	49
Li, X. ....	60, 73	Mo, C. ....	46, 73
Li, Y.X. ....	57	Morais-Teixeira, E. ....	16
Liang, W.Y. ....	39	Mori, C. ....	45, 61
Liao, H. ....	73	Morton-Bermea, O. ....	66
Lierhagen, S. ....	67	Mulder, J. ....	27, 62
Lin, C. ....	57	Müller, K. ....	13
Lin, C.Y. ....	53	Okkenhaug, G. ....	27, 54, 62
Liu, B. ....	46, 73	Orsini, A. ....	45, 61
Liu, C.Q. ....	30, 69	Pasqualini, V. ....	61
Liu, C.-Q. ....	30	Paterson, E. ....	17
Liu, H. ....	30, 58, 59	Pelzer, J. ....	18
Liu, W. ....	60	Pérez-Sirvent, C. ....	63
Liu, X.T. ....	57	Perry, M.R. ....	9

Peters, A. ....	11	Suzuki ,Y. ....	26
Petrák, M. ....	68	Tamura, N. ....	35
Picone, E. ....	64	Tandy, S. ....	28, 33
Planer-Friedrich, B. ....	19, 20	Teien, H.C. ....	14
Quiroz, W. ....	65	Ternes, T. ....	18
Rabello, A. ....	16	Tighe, M. ....	32, 64
Rakotoarisoa, O. ....	35, 52	Tollefsen K.E. ....	14
Ramos-Arroyo, Y. ....	66	Tserenpil, Sh. ....	69
Reynolds, J.K. ....	72	Valigurová, R. ....	49
Roper, A.J. ....	36, 72	Van de Velde, K. ....	11, 15, 70, 71
Rosen, B.P. ....	10	van den Berg, C.M.G. ....	22
Rosseland, B.O. ....	14	Vetterlein, D. ....	13
Salaün, P. ....	22	Wan, X. ....	28
Salbu, B. ....	14	Wang, X.Q. ....	53
Santos-del Angel, A.L. ....	66	Webster-Brown, J. ....	20
Sato, H. ....	26	Wegscheider, W. ....	43
Scheinost, A.C. ....	19	Wei, X. ....	30, 57, 58
Schmid, H. ....	18	Weiss, D. ....	31
Schmukat, A. ....	18	Weiss, H. ....	38
Schulin, R. ....	28, 33	Wennrich, R. ....	13, 23, 38
Šebek, O. ....	49	Williams, P.A. ....	36, 72
Segovia, N. ....	66	Wilson, N. ....	20
Shtangeeva, I. ....	12, 67	Wilson, S.C. ....	17, 32, 64
Smichowski, P. ....	24	Wu, F. ....	46, 73
Song, Y. ....	14	Xi, L. ....	62
Šottník, P. ....	56, 68	Xiang, M. ....	30, 58, 59
Steininger, R. ....	37	Zhang, G. ....	30, 58, 59
Steinnes, E. ....	25, 67	Zhang, Y.S. ....	39
Stockwell, P.B. ....	47	Zhu, Y.G. ....	62
Strømseng, A. ....	29		