



1st International Workshop on

Antimony in the Environment

May 16-19, 2005
Institute of Environmental Geochemistry
University of Heidelberg
Heidelberg (Germany)

THIRD CIRCULAR

re: THIRD CIRCULAR, Workshop on Antimony in the Environment

Dear Colleagues,

With sixty registered participants and a broad range of fascinating presentations on the horizon, the Workshop promises to be successful and we are very much looking forward to welcome you to Heidelberg. Our sincere thanks to each of you for helping to make this happen.

Please find attached the PROGRAM and the ABSTRACTS. We have done our best to organise the program such that Oraf Presentations with a common theme are in the same session. Please note that we suggest 20 minutes for the talk itself, and 10 min for discussion. We encourage all speakers to bring a Power Point Presentation, either on a USB stick (preferable) or CD. Speakers will not use their own Notebook computers, but rather we will transfer the files onto our PC/projector system. Of course an overhead projector will also be on hand for those of you who prefer that medium. All of the talks will be presented in the Lecture Hall of the Museum (INF 234).

The length of the coffee and lunch breaks are designed to allow discussions to continue beyond the lecture hall. The POSTERS will be available for viewing throughout the Workshop and we will have the necessary pins on hand for mounting them on display boards. The posters will be displayed in the Museum, adjacent to the Lecture Hall.

One rather urgent matter: REGISTRATION FEES. Some of you have paid, others have not. The deadline for the payment of fees has now passed. If you have not already paid, please do so immediately. These funds (100 EU) are essential for the Workshop to function as planned, and will be used to provide the refreshments, snacks, and lunches, in addition to help pay for student assistants. This Institute does not have sufficient funding to support the Workshop, so it has to pay for itself. We very much appreciate your understanding and look forward to receiving all overdue payments in the coming days.

Some of you have paid, but have not indicated to the University the reason for the payment. If you could please confirm that you have paid, we can try to get these funds transferred from the University to the Workshop. If the University is not informed that the reason for the payment is the Antimony Workshop, then the University will keep the funds, and not pass them along to us. The "reference number" (25124 / 7807141) is required for the University to pass along the funds to us. Please be sure to indicate your name, organization, and "Antimony Workshop".

Although we are willing to accept payments upon arrival, electronic bank transfer (see Second Circular) is preferable. We will have no means of accepting non-cash payments at the Registration. Again, if you have not yet done so, please submit the Registration Fees as soon as possible. If you cannot pay the Registration Fee in advance, we will request a <u>CASH</u> <u>payment of 150 EU</u> when you register.

Payments of late fees will not be accepted at the Registration Desk, but rather in our Main Office (Room 211 of INF 236) by Mr. Torsten Hoffmann.

Regarding the JEM Special Issue about Antimony in the Environment

The deadline for submission of manuscripts is 1. July

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with this deadline, we have a good chance of the Special Issue being published in the December Issue. Again, <u>all of the manuscripts should be submitted directly to the Journal</u>. All of the necessary instructions are posted on their web site. http://www.rsc.org/is/journals/current/jem/jempub.htm

Heidelberg is a beautiful, historic city, and well worth a visit. However, given the number of participants and the limited time available for the presentations, it was not possible to organise any sightseeing as part of the Workshop program. However, we do encourage you to enjoy your visit to Heidelberg, and suggest you allow some time to visit the Old City either before or after the meeting... it really is lovely and you will not be disappointed.

With warm regards from sunny Heidelberg.

Sincerely,

William Shotyk Michael Krachler Bin Chen

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REGISTRATION FEE PAYMENT

Confirmation of the Registration Fee For those who have already paid the registration fee, we kindly ask you to send us an email to confirm. If you have not yet done so, please submit the Registration Fees as soon as possible. If you cannot pay the Registration Fee in advance, we will request a CASH payment of **150 EUR** when you register.

Registration Fee The registration fee **EUR 100,-** (PhD students **EUR 50,-**) includes participation at the Workshop, the welcoming reception, lunches and refreshments during the breaks.

Payment All payments should be made in EURO (EUR) by bank transfer to the following account. Please address your bank transfer as follows:

Account holder

University of Heidelberg

Account number

530 278 7600

Bank code

672 200 20

Darik Code

072 200 20

Bank name

Baden-Württembergische Bank Heidelberg

SWIFT

BW BK DE 6 S 672

IBAN

DE 8867 2200 2053 0278 7600 Poststrasse 4, 69115 Heidelberg

Reference

Bank address

25124 / 7807141

(please make sure to mention this reference number in order to effect the

transfer of the registration fee)

Communication

Your name, organization and 'Antimony Workshop'

Cancellation Once an application/registration for the workshop has been accepted, the fee is NOT refundable.

CONFERENCE VENUE

Venue

Institute of Environmental Geochemistry University of Heidelberg
Im Neuenheimer Feld 234-236

Get there by tram

Tram line 1 or 4, station Technologiepark

Get there by bus

Bus line 12, station Technologiepark

THE DEMONSTRATION OF THE HG-AFS TECHNIQUE/INSTRUMENTATION

On the afternoon of May 18th there will be ongoing demonstrations of the HG-AFS (Hydride Generation - Atomic Fluorescence Spectrometry) technique/instrumentation. This will consist of a Hydride generation system with built in AFS detector and autosampler. A representative from the manufacturer will be present to discuss the theory and design of the instrumentation in addition to some applications. Discussion will be in English.

Demonstrations will be held in groups of up to 8 people and will last approximately 30 minutes each.

SCIENTIFIC AND SOCIAL PROGRAM

May 16th, Monday

15:00-18:00	Registration
18:00-18:05	Welcome
18:05-19:00	KEYNOTE LECTURE TO1 ANTIMONY: A METAL FOR THE 21ST CENTURY Nriagu Jerome, USA
19:00-20:00	Refreshments
20:00	Reception, BBQ

May 17th, Tuesday

9:00-10:00

Opening

Session 1: ANTIMONY AND ITS TRANSFORMATIONS IN CONTAMINATED SOILS

10:00-10:30

TO2 THE BEHAVIOUR AND DISTRIBUTION OF ANTIMONY IN AN HISTORIC MINING AREA, MARLBOROUGH, NEW ZEALAND Wilson Nathaniel, New Zealand

10:30-11:00

T03 MOBILISATION AND DISPERSAL OF ANTIMONY FROM Sb-Au MINERAL DEPOSITS IN CIRCUMNEUTRAL pH WATERS: ENVIRONMENTAL CONSEQUENCES IN AUSTRALASIA Ashley Paul, Australia

11:00-11:30 C

Coffee break

11:30-12:00

TO4 ANTIMONY MOBILITY ASSOCIATED WITH THE OXIDATION OF STIBNITE-BEARING WASTE ROCK IN HIGH LATITUDE SETTINGS: RESULTS FROM THE EASTERN TINTINA GOLD PROVINCE, ALASKA AND YUKON

Mueller Seth, Canada

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12:00-12:30

T05 AVAILABILITY OF ANTIMONY TO PASTURES IN FLOODED, ACID SULFATE SOILS, AND THE ROLE OF NON-CRYSTALLINE HYDROXIDES.

Tighe Matthew, Australia

12:30-15:00

Lunch break

15:00-15:30

T06 THE SOLUBILITY OF ANTIMONY IN CONTAMINATED SOILS Moench Hermann, Switzerland

15:30-16:00

T07 CHEMICAL FORMS OF ANTIMONY IN SHOOTING RANGE SOILS: AN X-RAY ABSORPTION SPECTROSCOPY STUDY

Scheinost Andreas C., Germany

16:00-16:30

T08 REDUCTION OF ANTIMONY LEACHABILITY OF MSWI-BOTTOM ASH BY CARBONATION Cornelis Geert, Belgium

16:30-17:00

T09 THE FREDERICK CHALLENGER CUP: ANTIMONY BIOMETHYLATION: METHANOGEN ARCHAEA VERSUS SULPHATE REDUCING BACTERIA.

Wehmeier Silvia, Scotland

17:00-17:30 Coffee break

Session 2: ANTIMONY AND ITS TRANSFORMATIONS IN NATURAL WATERS

17:30-18:00

T10 ANTIMONY SPECIATION IN AQUATIC SYSTEMS: CHALLENGES AND CONTROVERSIES Filella Montserrat, Switzerland

18:00-18:30

T11 PHOTOINDUCED OXIDATION OF ANTIMONY(III) IN THE PRESENCE OF HUMIC ACID Buschmann Johanna, Switzerland

18:30-19:00

T12 OXIDATION OF ANTIMONY IN THE ENVIRONMENT

Leuz Ann-Kathrin, Switzerland

19:00-19:30

T13 SURPRISING FINDINGS ON THE MARINE BIOGEOCHEMISTRY OF ANTIMONY: ANALYTICAL OVERSIGHTS, FAST PHOTOCHEMISTRY, AND STABLE METHYL ANTIMONY SPECIES Cutter Gregory, USA

May 18th, Wednesday

Session 3: ATMOSPHERIC EMISSIONS AND DEPOSITION OF ANTIMONY

9:00-9:30

T14 LONG-TERM MONITORING OF THE CONCENTRATIONS OF MAJOR AND TRACE ELEMENTS IN SIZE CLASSIFIED PARTICULATE MATTER COLLECTED IN THE MEGACITY OF TOKYO AND THE IDENTIFICATION OF SOURCES OF ANTIMONY

Furuta Naoki, Japan

9:30-10:00

T15 ANTIMONY IN ARCTIC SNOW AND ICE: ANALYTICAL IMPLICATIONS, LONG-TERM TRENDS, AND ENRICHMENTS

Krachler Michael, Germany

10:00-10:30

T16 A COMPARISON OF ANTIMONY AND LEAD PROFILES IN SCOTTISH OMBROTROPHIC PEAT BOGS Farmer John, Scotland

10:30-11:00 Coffee break

11:00-11:30

T17 ATMOSPHERIC SUPPLY OF ANTIMONY IN NORWAY: TEMPORAL AND SPATIAL TRENDS AND RELATION TO OTHER TRACE ELEMENTS

Steinnes Eiliv, Norway

11:30-12:00

T18 ASSESSMENT OF ATMOSPHERIC SB DEPOSITION FROM OCEANIC, LITHOGENIC, AND ANTHROPOGENIC SOURCES USING PEAT CORES FROM SWITZERLAND, SCOTLAND, SHETLAND, AND THE FAROE ISLANDS

Shotyk William, Germany

12:00-12:30

T19 ANTIMONY IN RECENT SEDIMENTS AND PORE WATER FROM LAKES IN THE VICINITY OF COAL-FIRED POWER PLANTS IN CENTRAL ALBERTA, CANADA

Sanei Hamed, Canada

12:30-13:30 Lunch break

13:30-14:00

THEORY AND PRACTISE OF ATOMIC FLUORESCENCE SPECTROSCOPY Barker Andrew, PSA, UK

14:00-15:30

DEMONSTRATION of HG-AFS

Session 4: ANTIMONY AND HUMAN HEALTH

15:30-16:00

T20 SUDDEN INFANT DEATH SYNDROME, SIDS, AND THE TOXIC GAS HYPOTHESIS Cullen William, Canada

16:00-16:30

T21 OCCUPATIONAL EXPOSURE TO ANTIMONY COMPOUNDS McCallum Ian, Scotland

16:30-17:00 Coffee break

17:00-17:30

T22 ANTIMONY IN BRAKE PADS —A CARCINOGENIC COMPONENT? Braungart Michael, Germany

17:30-18:00

T23 PROOF AND RISK OF ANTIMONY FROM BRAKE-LININGS Weckwerth Gerd, Germany

18:00-18:30

T24 FOOD FOR THOUGHT: ANTIMONY IN BEVERAGES Chen Bin, Germany

20:00 Banquet

May 19th, Thursday

Session 5: ANALYTICAL CHEMISTRY OF ANTIMONY

9:00-9:30

T25 BIOMETHYLATED ANTIMONY SPECIES IN SOILS, SEDIMENTS AND SEDIMENT ASSOCIATED ORGANISMS

Duester Lars, Germany

9:30-10:00

T26 USING ELECTROSPRAY IONISATION MASS SPECTROMETRY/TANDEM MASS SPECTROMETRY FOR THE CHARACTERISATION OF COMPLEXES BETWEEN ANTIMONY(V) AND BIOMOLECULES. Hansen Helle, Greece

10:00-10:30

T27 SPECIATION ANALYSIS OF INORGANIC ANTIMONY IN SOIL SAMPLE INCLUDING COMPENSATING FOR SPECIES TRANSFORMATION DURING ANALYSIS: FROM EXTRACTION TO DETECTION Amereih Sameer, Austria

10:30-11:00

T28 COMPARATIVE STUDIES ON EXTRACTION METHODS FOR ANTIMONY SPECIATION IN PLANTS Miravet Ricard, Spain

11:00-11:30 Coffee break

11:30-12:00

T29 TOTAL ANTIMONY AND ANTIMONY SPECIATION MEASUREMENTS IN ENVIRONMENTAL MATRICES BY ICP-MS, EAAS, HPLC-ICPMS AND SPME-GC Maher William, Australia

12:00-12:30

T30 ANTIMONY SPECIATION BY SELECTIVE BIOSORPTION ONTO SACCHAROMYCES CEREVISIAE: INFLUENCE OF DIFFERENT PARAMETERS AND POSSIBLE APPLICATION TO THE ANALYSIS OF ENVIRONMENTAL SAMPLES

Lagarde Florence, France

12:30-13:00

T31 ESTIMATION AND REMOVAL OF ANTIMONY FROM OTHER HEAVY METALS IN WATER SYSTEM BY USE OF SYNTHETIC INORGANIC ION EXCHANGERS

Deepak Pathania, India

13:00-13:30

T32 QUICK ANALYSIS OF ANTIMONY IN WATER - FIELD TESTS IN ABANDONED MINES IN AUSTRIA Holnsteiner Robert, Austria

13:30 Closing and lunch

POSTER PROGRAM

P-01 PHYTOAVAILABILITY AND PLANT UPTAKE OF ANTIMONY

Martin Tschan, and Rainer Schulin **Switzerland**

P-02 ANTIMONY IN AIRBORNE PARTICULATE MATTER EMITTED BY NATURAL AND ANTHROPOGENIC SOURCES. A CASE STUDY IN ARGENTINA

Patricia Smichowski, Dario Gómez, Maria Fernanda Giné, Ana Claudia Sánchez Bellato, and Susana Rosa **Argentina**

P-03 ASSOCIATION OF Sb IN CONTAMINATED SOILS, E.G. SHOOTING RANGES

Martin Schneider, Ann-Kathrin Leuz, Hermann Mönch and C.Annette Johnson **Switzerland**

P-04 MONITORING OF ANTIMONY IN THE ENVIRONMENT OF BAVARIA

M. Wegenke; M. Junge; J. Diemer; and J. Nittka **Germany**

P-05 MOBILIZATION OF ANTIMONY IN SEDIMENT AND SOIL SAMPLES BY LEACHING PROCESSES IN AN ABANDONED ORE MINING AREA, MANSFELD DISTRICT, GERMANY

Karsten Müller, Birgit Daus and Rainer Wennrich **Germany**

P-06 THE IMPORTANCE OF NON-CRYSTALLINE HYDROXIDE PHASES IN SEQUENTIAL EXTRACTIONS TO FRACTIONATE ANTIMONY IN ACID SOILS

Peter Lockwood, Matthew Tighe

Australia

SCHEDULE OVERVIEW

	16 th	17 th	18 th	19 th
09:00		opening	T14	T25
09:30		opening	T15	T26
10:00		T02	T16	T27
10:30		T03	coffee break	T28
11:00		coffee break	T17	coffee break
11:30		T04	T18	T29
12:00		T05	T19	T30
12:30		lunch	lunch	T31
13:00		tanen	turcii	T32
13:30				closing
14:00			HG-AFS	lunch
14:30			Demonstration	tunen
15:00		T06		
15:30		T07	T20	
16:00	Registration &	T08	T21	
16:30	Welcome	T09	coffee break	
17:00		coffee break	T22	
17:30	inka Prista Pilita	T10	T23	
18:00	Keynote	T11	T24	
18:30	Lecture	T12		
19:00	Refreshments	T13		8
20:00	Barbecue		Banquet	

SPONSORS











The munificent financial support of the German Science Foundation (DFG), for the costs of travel and accommodation, is sincerely appreciated. www.dfg.de

We are grateful to PS Analytical, Kent, England, for their generous support of the banquet supper. www.psanalytical.com

We wish to also thank the Environmental Office of the City of Heidelberg for their support. www.heidelberg.de

We are also grateful to LAMY (www.lamy.de) for kindly providing pens to each of the workshop participants, and to Capri Sonne (www.capri-sonne.com) for soft drinks

ABSTRACT OF ORAL PRESENTATIONS

ANTIMONY: A METAL FOR THE 21ST CENTURY

Jerome Nriagu

(Department of Environmental Health Sciences, School of Public Health, University of Michigan, Ann Arbor, MI 48109; E-mail: jnriagu@umich.edu)

Antimony occurs fairly widely in the natural environment with over 100 antimony-bearing minerals known. Stibnite (Sb_2S_3) , the most important ore of antimony, has been valued for metal alloys and used in removing gold and silver from base metal sulfides since the early Bronze Age. During the ancient Greek times, it was highly prized by women as a cosmetic (eyebrow paint) to increase the apparent size of the eye, hence they called it $\pi\lambda\alpha\tau\nu\delta\phi\theta\alpha\lambda\mu\sigma\nu$, from $\pi\lambda\alpha\tau\delta\varsigma$, wide, and $\delta\phi\theta\alpha\lambda\mu\delta\varsigma$, eye. The name of the metal itself, antimonium, seems to have been first used in the Latin editions of Geber's work republished in the latter part of the 15^{th} century. The classic book, Triumphal Chariot of Antimony written around 1470 by Basil Valentine, a Benedictine monk of Erfurt, described the preparations of metallic antimony from crude ore by roasting, deflagrating a mixture with nitre and saltpeter and fusing with metallic iron. The long record of antimony release into the regional and global environment from the production of the element, smelting of base metal sulfides, liquation of lead and silver and burning of coals that contain small amounts of antimony is well documented by the depositional profiles in an ombrotrophic in Switzerland (Shotyk et al., xxx). World production of antimony currently is about 140,000 tons per year and as the demand by the high-tech and biotech industries continues to grow, I predict that antimony will become a strategic metal to the world economy by the end of this century.

According to Eh-pH calculations, antimony occurs predominantly as oxy-anions with Sb(V) often present in oxic systems and as Sb(III) in anoxic environments. In antimonate ion, the Sb(V) is octahedrally coordinated with oxygen, unlike As(V) and P(V) which are tetrahedrally coordinated. In consequence, antimonic acid has been represented as H[Sb(OH)₆], or Sb(OH)₅. In the pH range of natural waters, Sb(V) occurs primarily as a negative species (as Sb(OH)₆⁻, also represented as SbO₃ while Sb(III) is found as a neutral species (Sb(OH)₃, also reported as HSbO₂). It should be emphasized that the preservation of samples for Sb speciation is far from being optimal in many studies. A recent study revealed that Sb(III) is easily oxidized within some hours to Sb(V), which raises the possibility that the concentrations of Sb(V) found as the major Sb species in extracts of various matrices may have been overestimated owing to oxidation of Sb(III) to Sb(V) during sample manipulation. In an anoxic sulfuretum, antimony forms insoluble stibnite, Sb₂S_{3(s)}, and soluble thiocomplexes SbS₂²⁻ and SbS₄³⁻, depending on pH. Formation of polymeric species (such as Sb₂S₄²⁻, Sb₂S₅⁴⁻, Sb₄S₇²⁻, etc) has been suggested but not confirmed in the natural environment. Limited information on antimony interactions with natural organic matter precludes any concrete inferences on the role of organoantimony species in the geochemistry of antimony in aquatic systems. Recent data on oceanographic distributions for dissolved antimony show that antimony occurs predominantly as antimonite and shows either conservative or mildly scavenged profiles (surface maxima of about 230 ng/L, decreasing in deep waters to about 135 ng/L). While the profiles are indicative of a passive, abiotic cycle (i.e. adsorption/desorption), the existence of low concentrations (6 ng/L) of Sb(III) and monomethyl antimony (24 ng/L) suggest biotic production pathways that may be similar to those of arsenic. Little is currently known about the environmental chemistry of the methylated antimony species that have been identified in some ecosystems. In fact, our understanding of the transformation, speciation and transport of antimony in the different environmental compartments is

Most humans are now being chronically exposed to low levels of antimony in their food, water and air. Antimony and its compounds are regarded as pollutants of priority interest by the U.S. Environmental Protection Agency (USEPA) and the Council of the European Communities and are on the list of hazardous substances under the Basel convention restricting the transfer of hazardous wastes across borders. In spite of these regulatory requirements, available data for estimating the environmental exposure and assessing the risks of antimony in the environment on human health remains very limited. In general, arsenic and antimony share some chemical and toxicological properties. For instance, both metalloids are nonessential to humans, act as clastogens in vitro and in vivo but do not have mutagenic properties, and their biological halflifes are relatively short in mammals, although there is evidence that certain parts are retained in the body for longer periods. The toxicological and physiological behavior of antimony depends on its oxidation state, the presence of binding partners and potential ligands, and on the solubility of the Sb compound. Elemental Sb is reported to be more toxic than its salts while Sb(III) compounds are said to be 10 times more toxic than Sb(V) species. Also, Sb(III) shows a high affinity for red blood cells and sulfhydryl groups of cell constituents, while erythrocytes are almost impermeable to Sb(V). There is evidence to suggest that antimony (in contrast to arsenic) is not detoxified via methylation in mammals, but the mechanism of antimony's carcinogenicity remains unclear. In spite of their toxicity, antimony compounds have been featured in the materia medica of human cultures since remote antiquity. Today, a major clinical use of antimony compounds is in the treatment of Leishmaniasis, although Sb₂O₃ is reported to offer therapeutic benefits to patients with acute promyelocytic leukaemia. The International Agency for Research on Cancer (IARC) has assigned antimony trioxide to the group of substances which are suspected of being carcinogenic in humans. On the other hand, recent studies increasingly show that some organoantimony compounds have anti-cancer properties. From the brief overview above, it is clear that antimony is a fascinating and enigmatic element in terms of its environmental chemistry and effects on human health.

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