



**PROCEEDINGS OF THE 24<sup>TH</sup>  
INTERNATIONAL APPLIED GEOCHEMISTRY SYMPOSIUM  
FREDERICTON, NEW BRUNSWICK, CANADA**



**JUNE 1<sup>ST</sup>-4<sup>TH</sup>, 2009**

**EDITED BY**

**DAVID R. LENTZ, KATHLEEN G. THORNE, & KRISTY-LEE BEAL**



**VOLUME II**



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ISBN 978-1-55131-137-1 (Volume 2)

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<b>APPLIED GEOCHEMISTRY OF GEOLOGICAL STORAGE OF CO<sub>2</sub></b> .....	<b>685</b>
Composition and levels of groundwater in the CO <sub>2</sub> CRC Otway Project area, Victoria, Australia: establishing a pre-injection baseline.....	687
<i>Patrice de Caritat<sup>1</sup>, Dirk Kirste<sup>2</sup>, &amp; Allison, Hortle<sup>3</sup></i> .....	687
Carbon mineralization in mine tailings and implications for carbon storage in ultramafic-hosted aquifers .....	691
<i>Gregory M. Dipple<sup>1</sup>, James M. Thom<sup>1</sup>, &amp; Siobhan A. Wilson<sup>1</sup></i> .....	691
Comparison of CO <sub>2</sub> -N <sub>2</sub> -enhanced coalbed methane recovery and CO <sub>2</sub> storage for low- & high-rank coals, Alberta, Canada and Shanxi, China.....	695
<i>William D. Gunter<sup>1</sup>, Xiaohui Deng<sup>1</sup>, &amp; Sam Wong<sup>1</sup></i> .....	695
Geochemical modelling and formation water monitoring at the CO <sub>2</sub> CRC Otway Project, Victoria, Australia.....	699
<i>Dirk Kirste<sup>1</sup>, Ernie Perkins<sup>2</sup>, Chris Boreham<sup>3</sup>, Barry Freifeld<sup>4</sup>, Linda Stalker<sup>5</sup>, Ulrike Schacht<sup>6</sup>, &amp; James Underschultz<sup>5</sup></i> .....	699
Pembina Cardium CO <sub>2</sub> Monitoring Project, Alberta Canada – geochemical evaluation and modelling of the geochemical monitoring data .....	703
<i>Ernie Perkins<sup>1</sup>, Stephen Talman<sup>1</sup>, &amp; Maurice Shevalier<sup>2</sup></i> .....	703
Numerical assessment of CO <sub>2</sub> enhanced CH <sub>4</sub> recovery from the Mallik gas hydrate field, Beaufort-Mackenzie Basin, Canada .....	707
<i>Mafiz Uddin<sup>1</sup>, J.F. Wright<sup>2</sup>, William D. Gunter<sup>3</sup>, &amp; D. Coombe<sup>4</sup></i> .....	707
Geochemical monitoring of chemical and isotopic compositions of CO <sub>2</sub> fluids and calcite precipitation during injection tests at Ogachi Hot-Dry Rock site, Japan.....	711
<i>Akira Ueda<sup>1</sup>, Yoshihiro Kuroda<sup>1</sup>, Kazunori Sugiyama<sup>2</sup>, Akiko Ozawa<sup>2</sup>, Hiroshi Wakahama<sup>3</sup>, Saeko Mito<sup>3</sup>, Yoshikazu Kajii<sup>4</sup>, &amp; Hideshi Kaieda<sup>5</sup></i> .....	711
<b>NORTH AMERICAN SOIL GEOCHEMICAL LANDSCAPES PROJECT</b> .....	<b>715</b>
The landscape geochemistry of the Sacramento Valley, California .....	717
<i>Martin B. Goldhaber<sup>1</sup>, Jean M. Morrison<sup>1</sup>, Richard B. Wanty<sup>1</sup>, Christopher T. Mills<sup>1</sup>, &amp; JoAnn M. Holloway<sup>1</sup></i> .....	717
The North American Soil Geochemical Landscapes Project: preliminary results from Nova Scotia .....	721
<i>Terry A. Goodwin<sup>1</sup>, Peter W. B. Friske<sup>2</sup>, Ken L. Ford<sup>2</sup>, &amp; Eric C. Grunsky<sup>2</sup></i> .....	721
Testing the variants of aqua regia digestion using certified reference materials.....	725
<i>E. C. Grunsky, R.G. Garrett, P.W. Friske, &amp; M. McCurdy<sup>1</sup></i> .....	725
Preliminary results of the North American Soil Geochemical Landscapes Project, northeast United States and Maritime Provinces of Canada.....	729
<i>Eric C. Grunsky<sup>1</sup>, David B. Smith<sup>2</sup>, Peter W.B. Friske<sup>1</sup>, &amp; Laurel G. Woodruff<sup>3</sup></i> .....	729
The North American Soil Geochemical Landscapes Project in New Brunswick .....	733
<i>Toon Pronk<sup>1</sup>, Michael A. Parkhill<sup>2</sup>, Rex Boldon<sup>1</sup>, Marc Desrosiers<sup>2</sup>, Peter Friske<sup>3</sup>, &amp; Andy Rencz<sup>3</sup></i> .....	733
The North American Soil Geochemical Landscapes Project: overview, goals, progress.....	737
<i>David B. Smith<sup>1</sup>, Laurel G. Woodruff<sup>2</sup>, Andy Rencz<sup>3</sup>, &amp; Alfredo de la Calleja<sup>4</sup></i> .....	737
Continental-scale patterns in soil geochemistry and mineralogy: results from two transects of the United States and Canada.....	741
<i>Laurel G. Woodruff<sup>1</sup>, David B. Smith<sup>2</sup>, D.D. Eber<sup>3</sup>, &amp; William F. Cannon<sup>4</sup></i> .....	741
<b>SOURCES, TRANSPORT, AND FATE OF TRACE AND TOXIC ELEMENTS IN THE ENVIRONMENT</b> .....	<b>745</b>

Sources of lead in soils and uptake by plants: Lower Guadiana River basin, south Portugal and Spain .....	747
<i>Maria J. Batista<sup>1</sup>, Maria M. Abreu<sup>2</sup>, J. Locutura<sup>3</sup>, T. Shepherd<sup>4</sup>, D. Oliveira<sup>1</sup>, J. Matos<sup>1</sup>, A. Bel-Lan<sup>3</sup>, &amp; L. Martins<sup>1</sup></i> .....	747
Risk assessment of arsenic mobility in groundwaters in Langley, British Columbia using geochemical indicators .....	751
<i>Rafael Cavalcanti de Albuquerque<sup>1</sup>, Dirk Kirste<sup>1</sup>, &amp; Diana Allen<sup>1</sup></i> .....	751
Spatial assessment of trace elements in Taylor Valley Antarctic Glaciers: Dominance of eolian deposition .....	755
<i>Sarah K. Fortner<sup>1,2*</sup>, Kathleen A. Welch<sup>1</sup>, W. Berry Lyons<sup>1,2</sup>, John Olesik<sup>2</sup> &amp; Rebecca A. Witherow<sup>1,2</sup></i> .....	755
Heavy metal loads in sediments influenced by Mežica Pb-Zn abandoned mine, Slovenia .....	759
<i>Mateja Gosar<sup>1</sup> &amp; Miloš Miler<sup>1</sup></i> .....	759
Relationship of heavy metals between rice and soils in Zhejiang, China .....	763
<i>Zhou Guohua, Wei Hualing, Sun Binbin &amp; Liu Zhanyuan</i> .....	763
Anthropogenic Gadolinium as a Micropollutant in Drinking Water .....	767
<i>Serkan Kulaksiz<sup>1</sup> &amp; Michael Bau<sup>1</sup></i> .....	767
Correlation of Atmospheric Soil and Atmospheric Lead in Three North American Cities: Can Re-suspension of Urban Lead Contaminated Soil be a Major Source of Urban Atmospheric Lead and Cause Seasonal Variations in Children's Blood Lead Levels? ...	771
<i>Mark Laidlaw<sup>1</sup></i> .....	771
Impact of Evolving Hypoxia on the Remobilization of As and Se in the Lower St. Lawrence Estuary (Québec).....	775
<i>Stelly Lefort<sup>1</sup>, Gwenaëlle Chaillou<sup>2</sup>, Nathalie Molnar<sup>1,3</sup>, Alfonso Mucci<sup>1</sup>, &amp; Bjorn Sundby<sup>1,2</sup></i> ..	775
Geochemistry of catchment outlet sediments: evaluation of Mobile Metal Ion™ analyses from the Thomson region, New South Wales, Australia .....	779
<i>Alan Mann<sup>1</sup>, Patrice de Carita<sup>2</sup>, and John Greenfield<sup>3</sup></i> .....	779
Five-Year History of a Biologically Based Treatment System that Treats High Concentrations of Effluent from an Industrial (Smelter Operation) Landfill .....	783
<i>Al Mattes<sup>1</sup>, Bill Duncan<sup>2</sup>, D.Gould<sup>3</sup>, Les Evans<sup>1</sup>, Susan Glasuaer<sup>1</sup></i> .....	783
Urban geochemistry and health in New Orleans: .....	789
Soil Pb, blood Pb and student achievement by 4 <sup>th</sup> graders .....	789
<i>Howard W. Mielke<sup>1,2</sup>, Christopher R. Gonzales<sup>3</sup>, &amp; Eric Powell<sup>4</sup></i> .....	789
Mercury concentrations in fungal tissues, as influenced by forest soil substrates and moss carpets .....	793
<i>Mina Nasr &amp; Paul A. Arp</i> .....	793
Hydrogeochemical processes governing the origin, transport, and fate of major and trace elements from mine wastes and mineralized rock.....	797
<i>D. Kirk Nordstrom<sup>1</sup></i> .....	797
Geological controls concerning mercury accumulations in stream sediments across Canada.....	803
<i>Jae Ogilvie<sup>1</sup>, Mina Nasr<sup>1</sup>, Andy Rencz<sup>2</sup>, Paul A. Arp<sup>1</sup></i> .....	803
Quantifying hydrothermal, groundwater, and crater lake contributions to the hyperacid Banyu Pahit stream, East-Java, Indonesia.....	809
<i>Stephanie Palmer<sup>1</sup>, Jeffrey M. McKenzie<sup>1</sup>, Vincent van Hinsberg<sup>1</sup>, &amp; A.E. Williams-Jones<sup>1</sup></i> .....	809

Land use/land cover influences on the estimated time to recovery of inland lakes from mercury enrichment .....	815
<i>Matthew J. Parsons<sup>1</sup> &amp; David T. Long<sup>1</sup></i> .....	815
Potential for contamination of deep aquifers in Bangladesh by pumping-induced migration of higher arsenic waters .....	819
<i>Kenneth G. Stollenwerk</i> .....	819
<b>CURRENT CAPABILITIES AND FUTURE PROSPECTS OF REAL-TIME, IN-FIELD GEOCHEMICAL ANALYSIS .....</b>	<b>823</b>
LIBS-based geochemical fingerprinting for the rapid analysis and discrimination of minerals – the example of garnet .....	825
<i>Daniel C. Alvey<sup>1</sup>, Jeremiah J. Remus<sup>2</sup>, Russell S. Harmon<sup>3</sup>, Jennifer L. Gottfried<sup>4</sup>, &amp; Kenneth Morton<sup>2</sup></i> .....	825
The U-tube sampling methodology and real-time analysis of geofluids .....	829
<i>Barry Freifeld<sup>1</sup>, Ernie Perkins<sup>2</sup>, James Underschultz<sup>3</sup>, &amp; Chris Boreham<sup>4</sup></i> .....	829
LIBS as an archaeological tool – example from Coso Volcanic Field, CA .....	833
<i>Jennifer L. Gottfried<sup>1</sup>, Russell S. Harmon<sup>2</sup>, Anne Draucker<sup>3</sup>, Dirk Baron<sup>3</sup>, &amp; Robert M. Yohe<sup>3</sup></i> ..	833
The application of visible/infrared spectrometry (VIRS) in economic geology research: Potential, pitfalls and practical procedures .....	837
<i>Andrew Kerr, Heather Rafuse, Greg Sparkes, John Hinchey, &amp; Hamish Sandeman</i> .....	837
Analysis of gem treatments: comparison of nano-second and pico-second laser-induced breakdown spectroscopy .....	841
<i>Nancy J. McMillan<sup>1</sup>, Patrick Montoya, Carlos Montoya, &amp; Lawrence Bothern</i> .....	841
Laser ablation chemical analysis LIBS and LA-ICP-MS for geochemical and mining applications .....	843
<i>R.E. Russo<sup>1,2,3</sup>, J. Yoo<sup>2</sup>, J. Plumer<sup>1</sup>, J. Gonzalez<sup>2</sup>, &amp; X. Mao<sup>3</sup></i> .....	843
In-situ Mössbauer spectroscopy on Earth, Mars, and beyond .....	847
<i>Christian Schröder<sup>1</sup>, Göstar Klingelhöfer<sup>1</sup>, Richard V. Morris<sup>2</sup>, Bodo Bernhardt<sup>3</sup>, Mathias Blumers<sup>1</sup>, Iris Fleischer<sup>1</sup>, Daniel S. Rodionov<sup>1,4</sup>, &amp; Jordi Gironés López<sup>1</sup></i> .....	847
Archaeometry in the House of the Vestals: analyzing construction mortar with portable infrared spectroscopy.....	851
<i>Jennifer Wehby<sup>1</sup> &amp; Samuel E. Swanson<sup>1</sup></i> .....	851
Fluorescence analysis of dissolved organic matter (DOM) in landfill leachates.....	853
<i>Caixiang Zhang<sup>1</sup>, Yanxin Wang<sup>1</sup>, &amp; Zhaonian Zhang<sup>2</sup></i> .....	853
Innovation for the CHIM method .....	857
<i>Liu Zhanyuan, Sun Binbin, Wei Hualing, Zeng Daoming, &amp; Zhou Guohua</i> .....	857
<b>GEOCHEMICAL ASPECTS OF MINE WASTES .....</b>	<b>861</b>
Geochemistry of the Lake George Antimony mine tailings, Lake George, New Brunswick, Canada: Understanding antimony mobility in a tailings environment.....	863
<i>Pride T. Abongwa<sup>1</sup> &amp; Tom A. Al<sup>1</sup></i> .....	863
Contribution of <i>Cistus ladanifer</i> L. to natural attenuation of Cu and Zn in some mine areas of the Iberian Pyrite Belt.....	867
<i>Maria J. Batista<sup>1</sup> &amp; Maria M. Abreu<sup>2</sup></i> .....	867
The Diavik Waste Rock Project: Design, construction and preliminary results .....	871
<i>D. W. Blowes<sup>1</sup>, L. Smith<sup>2</sup>, D. Segó<sup>3</sup>, L.D. Smith<sup>1,4</sup>, M. Neuner<sup>2</sup>, M. Gup-ton<sup>2</sup>, B.L. Bailey<sup>1</sup>, N. Pham<sup>3</sup>, R.T. Amos<sup>1</sup>, &amp; W.D. Gould<sup>1</sup></i> .....	871

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**SOURCES, TRANSPORT, AND FATE OF TRACE AND TOXIC ELEMENTS IN  
THE ENVIRONMENT**

EDITED BY:

**LEE ANN MUNK  
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## Sources of lead in soils and uptake by plants: Lower Guadiana River basin, south Portugal and Spain

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**ABSTRACT:** This study forms part of a larger multidisciplinary environmental study of the Lower Guadiana River basin carried out by a joint Portuguese-Spanish research team. It describes the mobility of lead in soil profiles taken over varied lithologies of the Iberian Pyrite Belt and the distribution of this metal with the root, stems and leaves of three plant species native to the area (*Cistus ladanifer* L., *Lavandula luisieri* and *Thymus vulgaris*). Results indicate that at all sample sites the mobility of lead is very low.

**KEYWORDS:** Lead, soils, plants; Guadiana River, Portugal, Spain

### INTRODUCTION AND SETTING

The purpose of this study was to identify and quantify the sources of heavy metals, especially lead, in soils and plants of the Lower Guadiana River basin and thereby model the potential mobility of lead. Other than direct pollution from mining, the main sources of heavy metal pollution in the environment are by diffuse pollution (Callender, 2004). In agricultural areas this can include lead from the use of pesticides, fertilizers and municipal sludge (Alloway, 1985). Metals can be attached or associated with different mineral phases in the soil, this along with environmental parameters determinesthe availability to plants.

The Guadiana Basin occupies a total area of 66,850 km<sup>2</sup> in Spain and Portugal, 8,350 km<sup>2</sup> of which comprises the Iberian Pyrite Belt (IPB); one of the world's largest concentrations of base metal sulphide deposits (Leistel et al., 1997; Ribeiro et al., 1990). Three plant species (*Cistus ladanifer*, *Lavandula luisieri* and *Thymus vulgaris*) were utilized in this study. The soils in which these plants were sampled are developed over varied geological formations. The oldest formation (PQ Group, Upper Devonian) consists of a thick sequence of arenites and shales

overlain by the Volcanic Sedimentary Complex (Upper Devonian). This unit hosts the IPB massive sulphide deposits and consists of volcanics and metal-rich shales. Both Devonian sequences are overlain by unmineralised, Carboniferous shales and sandstones of the Culm sequence that covers most of the southern part of the Lower Guadiana Basin.

### METHODOLOGY

Sampling of the superficial soils was carried out at 353 sites. At 66 of these sites, samples were collected at two depths: a near-surface sample at 0-20 cm and a sub-surface sample at 20-40 cm where the soil profile was deep enough to allow sampling. The plant species sampled were 136 *Cistus ladanifer* L., 9 *Lavandula luisieri* (Rozeira) Rivas-Martinez and 3 *Thymus vulgaris* L. To complete the understanding of bedrock control on soil lead concentrations, representative samples of the main IPB formations were sampled including sulphide ores from the main ore deposits (Sao Domingos in Portugal; Cabezas de Pasto, Romanera, Lagunazo, Isabel Mn, Cármen 1 and 2, Herrerias, Sierrencilla

Matutera and Vuelta Falsa-Trimpancho in Spain).

Chemical analysis of the soils and plants were made by INAA and ICP-OES following digestion by HCl+HNO<sub>3</sub>+HF+HClO<sub>4</sub>.

Soils were further characterized by the determination of pH in water and potassium chloride in the proportions 1:2.5, total organic carbon (TOC) and cation exchange capacity (CEC). Transfer coefficients between soil and plant and enrichment in soils were determined. The results for Pb were represented in the form of relative enrichments for soils (Kabata-Pendias, 1985) and transfer coefficients in plants (Kovalevskii, 1979).

A Principal Components Analysis (PCA) was performed on the data to determine the relationship of Pb to other chemical elements.

## RESULTS AND DISCUSSION

High concentrations of lead were detected in the wine-coloured and black shales of the Volcanic Sedimentary Complex with 96 mg kg<sup>-1</sup> and 52 mg kg<sup>-1</sup>, respectively. The highest concentrations were reported for the Cu-Pb-Zn massive sulphide ore samples from the abandoned mines of Cabezas del Pasto, Romanera and Serrencillas where concentrations of Pb exceeded 5000 mg kg<sup>-1</sup>.

The median value of Pb for the soils is 25 mg kg<sup>-1</sup> which is coincident with the world median concentration (Kabata-Pendias *et al.* 1985). However, the range of concentrations is between 5 and 25700 mg kg<sup>-1</sup>. In the sub-surface samples the mean value is 23 mg kg<sup>-1</sup> and a range of 9 to + 5000 mg kg<sup>-1</sup> (Table 1). In the Sao Domingos mine area, the enrichment in Pb is very significant probably due to wind dispersed mine wastes but the high concentrations are proportional as a function of depth in the surrounding soils. However, the sub-surface concentrations are significantly lower than the near - surface concentrations illustrating the

**Table 1-** Statistical parameters in soils

Parameters	N <sup>o</sup> samples	Average.
Pb Superficial	355	133,09
Pb_ sub-superficial	66	103,30
Ca	353	4,36
Mg	353	1,91
K	353	0,24
Na	353	0,14
CEC	353	9,81
V	353	66,78
pH (H2O)	353	5,55
pH (KCl)	353	4,36
Org. Carbon	353	13,37
Parameters	Minimum	Maximum
Pb Superficial	5,00	25700,00
Pb_ sub-superficial	9,00	5000,000*
Ca	0,21	17,97
Mg	0,16	13,59
K	0,00	1,54
Na	0,001	7,99
S	0,70	22,11
CEC	1,77	21,78
V	14,20	265,78
pH (H2O)	2,22	8,22
pH (KCl)	1,80	7,64
Org. Carbon	1,24	55,93

limited vertical mobility of Pb under the prevailing climatic conditions. From all the 66 soil profiles in the lower Guadiana basin, lead shows a low vertical mobility.

The factors that influence mobility and availability of lead are the mineralogy of clay fraction, pH, CEC and organic matter content. However, correlation coefficients indicate no clear relationship of lead to these parameters and are consistently low.

The PCA statistical treatment of both near-surface and sub-surface soil pairs shows that in general Pb is associated with the same group of elements irrespective of depth. This may be a

Parameters	Geom. Mean	Median
Pb Superficial	29,94	25,00
Pb_sub-superficial	24,78	23,00
Ca	3,58	3,60
Mg	1,57	1,52
K		0,19
Na	0,09	0,09
CEC	9,38	9,51
V	60,61	62,94
pH (H2O)	5,50	5,52
pH (KCl)	4,32	4,25
Org. Carbon	11,71	12,17
Parameters	Variance	St.Dev
Pb Superficial	189605	1376,97
Pb_sub-superficial	375046	612,41
Ca	8	2,91
Mg	2	1,46
K	0	0,18
Na	0	0,43
S	15	3,92
CEC	8	2,87
V	974	31,22
pH (H2O)	1	0,74
pH (KCl)	0	0,66
Org. Carbon	46	6,77

Org. carbon – Organic carbon; CEC cations exchange capacity

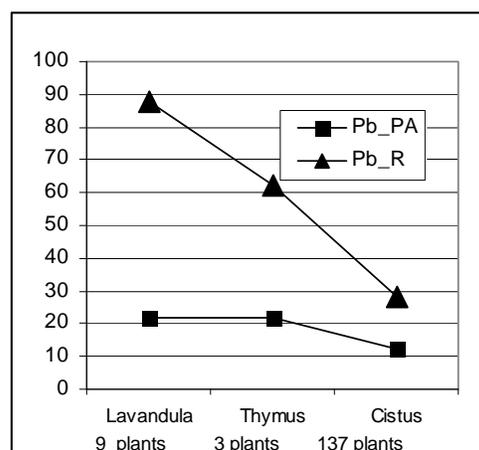
consequence of the shallow depth of these soils.

The concentrations of lead in plants are in general higher in the roots than in the aerial parts (stems and leaves), with 25 to + 5000 mg kg<sup>-1</sup> and 11 to 15 mg kg<sup>-1</sup>, respectively in *Lavandula luisieri* (Rozeira) Rivas-Martinez roots and aerial parts; 3 to 982 mg kg<sup>-1</sup> and 3 to 308 mg kg<sup>-1</sup>, respectively in *Cistus ladanifer* L. roots and aerial parts; and 35 to 70 mg kg<sup>-1</sup> and 8 to 29 mg kg<sup>-1</sup>, respectively in *Thymus vulgaris* L. roots and aerial parts.

Although the number of plant samples is not equally divided per species, due to availability it was nevertheless noted that

the highest concentrations of lead were determined in *Lavandula luisieri* (Rozeira) Rivas-Martinez (Figure 1).

Lead is known to have a very low transport within plants. It is absorbed by the roots but effectively immobilized there (Adriano, 1986). In fact, plants such as *Cistus ladanifer* L. present low transfer coefficients, consequently the animals that eat these plants have a very low risk of ingesting significant amounts of lead. The bi-plot diagram of soil lead/aerial part lead



PA –aerial part; R-roots

Fig. 1. Median results of leaves and roots for thr three plant species

versus soil lead/roots lead in the case of *Cistus ladanifer* L. shows that most of the individuals plot within a claw near the origin. The points that plot outside the claw are samples that were collected near roads or old mines.

## CONCLUSIONS

The low mobility of lead is reflected in the vertical concentrations of lead in the soil and the distribution of lead within the plant system. Lead seems to preferentially concentrate in roots rather than aerial parts of the sampled species. This is agreement with the frequent behaviour of most species in relation to this heavy metal.

### ACKNOWLEDGEMENTS

This study was part of a larger multi-disciplinary environmental project carried out in the framework of an INTERREG IIA Programme of the European Community between Portugal and Spain.

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## Risk assessment of arsenic mobility in groundwaters in Langley, British Columbia using geochemical indicators

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**ABSTRACT:** Arsenic is mobilized in groundwater under reducing and alkaline conditions as a result of its sorption properties. High arsenic concentrations have been associated with elevated concentrations of a number of specific anions and oxianions species, such as F, V, B, Mo, U, Be and Se, under alkaline conditions, and with redox sensitive species, as Fe, Mn and SO<sub>4</sub>, under reducing conditions. In this study, these species are used as indicators of arsenic mobility in a historical well water geochemistry dataset that contains sample entries with no arsenic data. The study area is the Township of Langley, British Columbia, where arsenic has been reported to be above the Canadian guideline (0.010 mg/l) in groundwater present in Quaternary sediments. A multi-proxy approach is used where a sample or well is only considered to potentially have high arsenic mobility if more than one indicator is observed. Sampling and laboratory analyses will take place during the summer of 2009 in order to test the results of the study.

**KEYWORDS:** *groundwater geochemistry, arsenic mobility, redox, sorption, Quaternary aquifers*

### INTRODUCTION

Arsenic is an element deleterious to human health. Although the World Health Organization guideline for drinking water is set at 0.010 mg/l, studies have shown that this guideline far exceeds tolerable cancer risks (Lindberg & Vahter 2006). Groundwater contamination by arsenic is commonly the result of factors influencing arsenic mobility rather than issues relating to arsenic sources (Smedley & Kinniburgh 2002). Due to sorption properties related to the charge of its dissolved species, arsenic is desorbed from solids and mobilized in water under specific groundwater conditions. The dissolved species formed by the oxidized form of arsenic, arsenate [As (V)], is negatively charged in the pH range typical of natural waters. This causes arsenate to be adsorbed to solids under acidic conditions, and to be released to solution at higher pH. Conversely, the dissolved species of the reduced form of arsenic, arsenite [As (III)], is uncharged. As a result, arsenite tends to be mobile in reducing environments regardless of water pH (Pierce & Moore 1982; Matsunaga *et al.* 1996; Howell 1994). Dissolution of arsenic

bearing minerals as a result of groundwater redox is also a recognized contributor to elevated arsenic levels in groundwater. Examples are the reduction of oxides and oxidation of sulphides containing arsenic (Smedley & Kinniburgh 2002).

In alkaline environments dissolved arsenic concentrations have been observed to correlate positively with other elements that occur in solution as anions and oxianions species, such as F, V, B, Mo, U, Be and Se (Smedley *et al.* 2002). In reducing environments, correlations have been observed between arsenic and redox sensitive species, such as dissolved organic carbon, Fe, Mn and SO<sub>4</sub> (Smedley *et al.* 2003).

The objective of the study is to carry out a risk assessment for arsenic mobility in groundwater on an aquifer system in a temperate climate region. The targeted region is the Township of Langley, British Columbia for which an extensive historical database of groundwater chemistry exists. However, as is typical for many groundwater systems, this database is variable in terms of the quality and extent of the hydrogeochemical and hydrogeological information. These

historical datasets will be evaluated to develop arsenic mobility risk maps for the different aquifer units and then tested by comparing the risk maps with arsenic data contained within more comprehensive datasets.

#### **HYDROGEOLOGICAL AND HYDROGEOCHEMICAL SETTING**

The Township of Langley is located in the Lower Fraser Valley of southern British Columbia, 40 kilometres to the southeast of downtown Vancouver. The groundwater system studied consists of aquifers in Quaternary surficial sediments that were deposited during and since the Fraser Glaciation. The Quaternary deposits are composed of a complex mixture of glacio-fluvial, glacial-marine and postglacial fluvial sediments (Armstrong 1976; Halstead 1986). The four major Quaternary units from oldest to youngest are: the deltaic, marine and glacial marine sediments of the Capilano Sediments; the stony clay and silty clay interbedded marine, glaciomarine and glacial sediments of the Fort Langley Formation; the Sumas Drift made up of till, glaciofluvial and glaciomarine sediments; and the postglacial fluvial, lacustrine and colluvial deposits of the Salish Sediments (Halstead 1986). The local bedrock geology is composed of sedimentary rocks deposited within the Tertiary Georgia Basin (Monger 1990).

Arsenic concentrations in drinking water from wells in Quaternary sediments in the Township of Langley have been reported to be above the Canadian guideline (0.010 mg/l) (Wilson *et al.* 2008a,b). In their studies of arsenic contamination of groundwater in the Langley/Surrey region, Wilson *et al.* (2008a,b) found that the highest arsenic concentrations in groundwater were in samples collected from waters in organic-rich silty loam and clay of the Salish Sediments and marine and glacial-marine deposits of the Capilano Sediments. They also found that in these two units the concentration of arsenic tended to increase at greater depths. The bedrock is not known to be rich in arsenic. This, coupled with the

correlations observed between arsenic concentrations and surficial geology, implies that local bedrock geology is not an important contributor to the observed arsenic concentrations in groundwater (Wilson *et al.* 2008a).

#### **DISCUSSION**

Historical well water geochemistry datasets, available through the British Columbia Ministry of the Environment and Environment Canada, are used to evaluate which samples, wells and geographical areas of Langley have groundwater conditions that suggest arsenic mobility. The datasets contain data collected throughout the study region over several years. Some of the sample entries in the datasets are extensive in geochemical information as they contain pH, and concentrations of major, minor and trace elements, including arsenic. Most of the data entries however are limited, lacking arsenic and other minor and trace species. Most samples were not analysed for redox potential or for the speciated concentrations of arsenite and arsenate. Sample collection methods varied making the quality of the analytical data suspect because important indicators of arsenic mobility, such as pH and the concentrations of redox sensitive elements, can be altered when samples are not properly collected or stored (Ficklin & Mosier 1999). Geochemistry data from an excess of 300 wells is available. Some of this data is however not used in the study due to unreliability and incompleteness of its geochemical entries.

For the first stage of the study, available geological and hydrogeological information is used to develop a conceptual model and the hydrogeological framework of the study area. By doing so, potential geochemical processes leading to arsenic mobility in groundwater can be inferred. The potential geochemical processes are evaluated using published studies on arsenic mobility in order to determine which of the processes are more likely to be exerting a greater control on arsenic mobility and which primary and

secondary hydrogeochemical criteria best serve as indicators of arsenic mobility in the region. These indicators are then queried within the local historical dataset to develop distribution maps. The results obtained are plotted on an arsenic mobility risk assessment map. The produced arsenic risk assessment map is tested against available arsenic data in the region as a means of evaluating the effectiveness of the indicators chosen. It should be noted that tagging samples and wells as having high risk of arsenic mobility does not necessarily imply that the water contains high arsenic concentrations. Other factors that often control arsenic concentrations that are not widely evaluated in the study include hydrogeological processes and local variations of sources of arsenic in bedrock geology and sediments.

This study will test the applicability of the discussed indicators to historical geochemical datasets with little or no arsenic data available. These indicators should help determine which areas are more likely to have higher arsenic concentrations in water and where more sampling is needed. Extensive well water sampling will ultimately be conducted in order to test the arsenic mobility risk assessment presented. Sample analyses will include field measured Eh, arsenite and arsenate concentrations and a number of redox sensitive and pH sensitive species so that appropriate suggestions on redox and pH controls to arsenic mobility can be made. The observations made with this study will help determine which other areas of British Columbia with similar groundwater environments may have arsenic mobility conditions that triggers the need for further water sampling.

### CONCLUSIONS

At the time of the submission of this extended abstract the background research on arsenic mobility is complete and the acquisition of the hydrogeological and geochemical datasets as well as the development of the preliminary conceptual model and hydrogeological framework is

underway, thus comprehensive results and conclusions will be presented at the conference. Preliminary data analyses show a positive correlation between arsenic and pH, with the highest arsenic concentrations occurring at a pH above 8. Weak correlations were found between arsenic and anionic species, such as  $\text{HCO}_3^-$ , Mo, B and F. Fe concentrations range from 0.001 mg/l to values as high as 100 mg/l, which, coupled with the correlation observed by Wilson *et al.* (2008a) of arsenic and water depth within the Salish and Capilano units, may be an indicator of reduction. Arsenic mobility may therefore be occurring as a result of both high pH and reduction. Due to the variability of data quality and completeness within the historical datasets, a variety of indicators are used in the production of the mobility risk map. These include pH, and the concentrations of  $\text{HCO}_3^-$ , Mo, B, F, Fe, Mn,  $\text{SO}_4$  and  $\text{NH}_4$ . Further study is needed in order to better evaluate processes leading to observed arsenic concentrations. This will be addressed with the historical data analysis presented at the conference, and appropriately tested with subsequent field work and laboratory analyses.

### ACKNOWLEDGEMENTS

We thank the British Columbia Ministry of Environment, Environment Canada, Hans Schreier and Martin Suchy for providing historical groundwater geochemistry datasets and Michael Simpson for logistical help.

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## Spatial assessment of trace elements in Taylor Valley Antarctic Glaciers: Dominance of eolian deposition

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**ABSTRACT:** We have examined the major ion and trace element chemistry in four 60 to 110 cm deep snowpits from three Taylor Valley (TV) glaciers (Commonwealth, Canada, and Howard) all located within 20 kilometers of the Ross Sea. Taylor Valley (77° 30' S, 163° 15' E) in South Victoria Land and is part of the McMurdo Dry Valleys (MCM), the largest ice-free area in Antarctica. On the north side of TV, Commonwealth and Canada glaciers originate in the Asgard Range, whereas Howard Glacier flows from the Kukri Hills in the south side of the valley. Snow chemistry of these glaciers is strongly influenced by cross-valley winds that deposit eolian materials, including mineral dust and soluble salts. Trace elements (As, Cd, Cu, Eu, Mo, Nd, Pr, Rb, Sm, Sn, Sr, and U) in recent TV glacier snow are almost exclusively derived from eolian dust. Variability in spatial trace element concentrations and concentrations at depth reflect the episodic nature of TV wind events.

**KEYWORDS:** eolian deposition, Antarctica, snow, trace elements

### INTRODUCTION

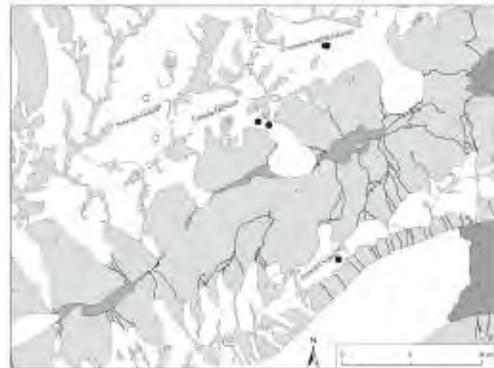
Lithogenic eolian deposition is a primary chemical contributor to TV snow (Lyons *et al.*, 2003; Williamson *et al.*, 2007; Witherow *et al.*, 2006). Eolian transport of local soils and lake sediments is a documented dispersal mechanism for valley floor life as well as life immured in glacier ice and cryoconite holes (Christener *et al.*, 2003; Nkem *et al.*, 2006). The solubilization of eolian soil on MCM glacier surfaces may be an important, but previously undocumented, source of trace elements to the streams and lakes (Green *et al.*, 1986; Green *et al.*, 2005). Understanding chemical variation associated eolian deposition is especially important as the availability of trace elements may be essential to the ecosystems reliant on glaciers and glacier melt waters (Bargagli, 2000).

### SITE DESCRIPTION

#### Taylor Valley, Antarctica

TV spans 34 km northeast to southwest from the Ross Sea to the Taylor Glacier and has an area of 400 km<sup>2</sup>. To the north, TV is bounded by the Asgard Range and

to the south, the Kukri Hills (Figure 1). Taylor Valley contains numerous valley glaciers (35% of the total area) whose melt produces perennial streams and three closed-basin lakes (Fountain *et al.*, 1999). The valley floor is covered with lacustrine sediment and poorly developed soil of various ages (Marchant *et al.*, 1996). These soils and sediments are readily mobilized and transported through-



**Fig. 1.** Taylor Valley, Antarctica: glaciers in white, soil in light grey, streams and lakes in dark grey. Snow pit sampling locations are identified with black circles.

out the valley (Lancaster, 2002) with the primary pathway being along the valley floor corridor from the SE to NW or from the NW to SE (Nylen *et al.*, 2004).

### Canada, Commonwealth and Howard Glacier

The Commonwealth Glacier, originating in the Asgard Range, is the second easternmost glacier in the Taylor Valley. Canada Glacier is further inland. Directly across the valley from Canada Glacier is Howard Glacier, which flows from the Kukri Hills. The south-facing glaciers in the Asgard Range cover a greater area than those in the Kukri Hills. Eight years of stake measurements suggest that Commonwealth Glacier may be gaining mass, whereas Howard Glacier is in equilibrium (Fountain *et al.*, 2006). Overall mass balance is not known for Canada Glacier. However, the Canada Glacier ablation zone generally losses mass (up to 12 cm weq/yr) year-round (Fountain *et al.*, 2006). Although mass balance varies between glaciers, all TV glaciers are at their maximum extent since the Last Glacial Maximum (Denton *et al.*, 1989; Fountain *et al.*, 2006).

### METHODS

Four snowpits ranging from 0.6 to 1.1 m were excavated from the upper accumulation zones of Commonwealth, Canada and Howard glaciers were sampled for trace elements and major ions. Canada Glacier was sampled in both January and December 2006 less than 0.5 km apart. Commonwealth (60 cm) and Howard glaciers (110 cm) were sampled only during December 2006. Using the methods of Witherow *et al.*, 2006 snowpits are estimated to represent between 5 and 15 years of accumulation, with some sites potentially wind-redistributed.

LDPE bottles for trace element analyses were soaked in a 10% (v/v) Fisher<sup>TM</sup> trace metal grade HCl/DI. Bottles were then triple rinsed with DI and filled with 10% (v/v) Fisher<sup>TM</sup> trace metal grade HNO<sub>3</sub>/DI. After rinsing with DI, bottles were filled with 1% ultraclean Optima<sup>TM</sup> grade HNO<sub>3</sub>/DI and stored in plastic bags in a

class 100 clean hood. To minimize contamination, samples were collected using “clean hands, dirty hands” techniques (Fitzgerald, 1999).

Trace element samples were acidified to 2% (v/v) using Optima<sup>TM</sup> HNO<sub>3</sub> prior to melting for analyses. Snow samples were not filtered, so the results represent dissolved and colloidal species as well as acid soluble concentrations dissolved from particulates. Trace elements added through acidification were negligible.

A Thermo Finnigan Element 2 Inductively Coupled Plasma Sector-Field Mass Spectrometer (ICP-SF-MS) with guard electrode was employed for trace element analyses. RSD values derived from internal check standard never exceeded 10%. Accuracy was better than 15% for all elements as determined by analyzing the certified reference standard NWRI TM-RAIN 95 trace metal fortified rainwater, every 5 to 8 samples.

### RESULTS/DISCUSSION

#### Sources of trace elements to Taylor Valley Glaciers

To determine the non-seasalt (nSS) contributions of trace elements we have normalized mean concentrations of ions to Cl<sup>-</sup> and subtracted the contributions from seasalt (Nozaki, 1997). We assume that all of the Cl<sup>-</sup> in the sample was from marine aerosol or marine-derived salt and nSS major ions and trace elements can be calculated. For example the percentage of nSS-SO<sub>4</sub><sup>2-</sup> is calculated as:

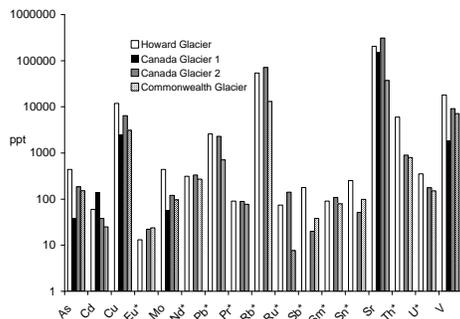
$$\%nSS-SO_4^{2-} = \left[ \frac{[X]_{snow} - [X]_{ocean}}{[Cl^-]_{snow} - [Cl^-]_{ocean}} \right] \times 100$$

Trace element concentrations in Canada, Commonwealth, and Howard glaciers were 100% nSS. In fact, all trace elements measured had median element:Cl<sup>-</sup> ratios 3 or more orders of magnitude greater than seawater averages (Nozaki, 1997).

We compared snowpit element:S ratios to average annual emission rates measured in December 1986, December 1988, December 1989, and January 1991

from Mount Erebus, the closest active volcano (<80 km) (Zreda-Gostynska and Kyle, 1997). By normalizing trace element concentrations to sulfate we found that the volcanic contributions of As, Cd, Cu, Mo, Pb, Rb, Sn, and V snowpit concentrations were less than 1%.

Our results suggest that crustally derived-material represents the major source of trace element contributions to TV snow. Crustal contributions to the TV glaciers are particularly high due to their proximity to local soil sources and their low annual snow accumulation rates (Welch *et al.*, 1993; Witherow *et al.*, 2006). Furthermore, exposure to strong winds appears to influence the amount of eolian material received. Only the Howard Glacier snowpit lacked shielding from surrounding peaks. Therefore, Howard Glacier snow had significantly greater maximum concentrations of all trace elements with the exception of Rb and Sr than the other three snowpits (Fig. 2).

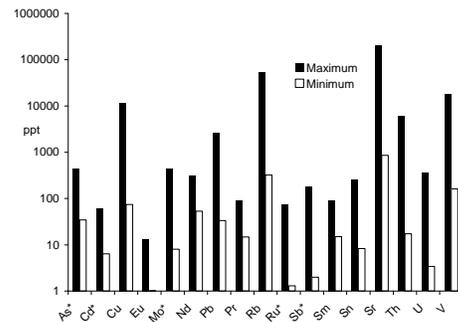


**Fig. 2.** Maximum concentrations observed in Taylor Valley glacier snowpits in parts-per-trillion (\* not measured in Canada Glacier 1).

Furthermore, elemental concentrations at depth, and hence through time, ranged several orders of magnitude in all snowpits because wind events are episodic and variable in speed and duration (Nylen *et al.*, 2004). Howard Glacier is plotted for example (Fig. 3).

**CONCLUSIONS**

TV glaciers are the primary source of water to life-supporting streams and lakes. Understanding the spatial and temporal variation in glacier snow geochemistry



**Fig. 3.** Maximum and minimum concentrations observed in Howard Glacier snow in parts-per-trillion (\* minimum value is below the detection limit).

may begin to elucidate the chemical and hence, ecological, variation observed in streams and lakes. This study suggests that:

- (1) Eolian deposition dominates the deposition of trace elements on TV snow.
- (2) Wind exposure is, therefore, important controls of eolian deposition. Howard Glacier snow was the most wind exposed and had the greatest trace element concentrations
- (3) Episodic wind events explain the wide range in trace element and Ca concentrations observed TV snow.

**ACKNOWLEDGEMENTS**

We thank Anthony Lutton for his assistance with the ICP-MS and Joel Barker and Cecelia Mortenson for their help in the field. Thank you also to Dave Lape for constructing a snow sampler.

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## Heavy metal loads in sediments influenced by Mežica Pb-Zn abandoned mine, Slovenia

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**ABSTRACT:** The main objective of this study was to identify heavy-metal concentrations and associated mineral phases using an ICP and SEM-EDS in the heavily metal polluted sediments of the Meža River Valley, characterize them according to their source and genesis, and assess the degree of negative impact arising from Pb-Zn mining and smelting activities in the Mežica mining district and the ironworks in the Ravne area (Meža River Valley, NNE part of Slovenia). The highest Pb and Zn concentrations were measured in stream sediments of the Meža River and its tributaries in the areas of former mining and smelting activities in Mežica and Žerjav and the highest contents of Co, Cr, Cu and Ni were identified in the area of the Ravne ironworks.

**KEYWORDS:** heavy-metal bearing phases, mining, ironworks, SEM-EDS

### INTRODUCTION

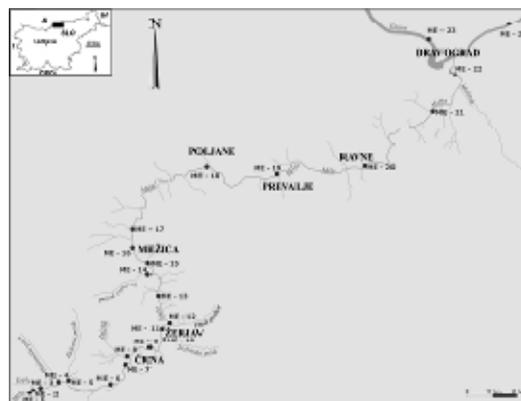
In the Meža Valley around 19 million tons of lead-zinc ore were produced and processed for more than 300 years. Previous investigations of Meža River sediments have shown elevated concentrations of lead and some other metals (Fux & Gosar 2007). At the end of the 20<sup>th</sup> century, the Meža River had the highest concentrations of heavy metals in any Slovenian stream (Lapajne *et al.* 1999). After the mine and processing plants ceased operation, the direct transfer of heavy metals into the environment decreased sharply. However, deposits of poor ore and ore processing wastes have persisted as a source of heavy metal pollution. From those places heavy metals have washed out into the nearby streams, including the Meža River and more downstream locations such as the Drava River.

Previous investigations of soil and river sediments, carried out by Vreča *et al.* (2001), Šajn & Gosar (2004), and Šajn (2006) have shown that the upper Meža Valley is still highly polluted from past mining activities that ceased more than 10 years ago.

### SAMPLING AND ANALYTICAL METHODS

In the upper stream of the Meža River, including significant tributaries (e.g. Topla, Helenski potok, Mušenik, Jazbinski potok, Junčarjev potok), the stream sediment samples were collected approximately 1 km apart. From Mežica to the Drava River the sampling distance was increased to 10 km. Additionally, two samples of the Drava River sediments were taken before and after its confluence with the Meža River (Fig. 1).

Two fractions (< 0.125 mm and < 0.063 mm) of air-dried and sieved sediments



**Fig. 1.** Location of study area with sampling locations.

were analyzed at the ACME Analytical Laboratories Ltd. (Vancouver, Canada).

The content of heavy metals in sediments was determined by sample digestion with 10 ml of the mixture of HClO<sub>4</sub>, HCl, HNO<sub>3</sub> and HF at 200°C, followed by Inductively Coupled Plasma Emission Spectrometry (ICP) (ACME, 2003).

Identification of heavy metal-bearing particles in seven stream sediment samples (grain size fraction < 0.063 mm), coated with gold, was performed in the BSE mode on a JEOL JSM 6490LV SEM coupled with an Oxford INCA Energy EDS. Semi-quantitative chemical analysis was performed on polished, carbon-coated samples of river sediment embedded in araldite resin, using EDS point analysis and X-ray mapping. Heavy metal mineral phases were assessed from the atomic proportions of the constituent elements, obtained by semi-quantitative analysis. EDS data correction was performed using the standard ZAF-correction procedure included in the INCA Energy software© (Oxford Instruments, 2006).

## **HEAVY METALS IN STREAM SEDIMENTS**

### **Lead (Pb) and Zinc (Zn)**

Lead content varies between 80 mg/kg and 14,200 mg/kg in the < 0.063 mm fraction and between 76 mg/kg and 19,300 mg/kg in the < 0.125 mm fraction. Zinc content ranges from 260 mg/kg to 22,500 mg/kg in the < 0.063 mm fraction and from 264 mg/kg to 37,900 mg/kg in the < 0.125 mm fraction.

The highest contents of Pb and Zn were measured between Žerjav and Mežica (ME-11, ME-13, ME-15) and between Poljane and Prevalje (ME-18, ME-19). The increase in Pb content between Žerjav and Mežica was interpreted as a consequence of heavy metal pollution by air deposition of soil near the smelter in Žerjav, and of the contribution of heavy metal-polluted Helenski potok (ME-5) and mining waste dump in Mežica (ME-15). Elevated concentrations of Pb and Zn between Poljane and Prevalje (ME-18, ME-19) are most probably a consequence

of mine water discharge through a 6 km long tunnel from Mežica mine to the Meža River, since no other source of heavy metal pollution has been found in the area.

The highest contents of Pb and Zn in tributary sediments were measured in Helenski potok (ME-5) and Junčarjev potok (ME-14) and are interpreted as a consequence of discharge from mining waste dumps and tailings in the tributaries area.

### **Cadmium (Cd), Molybdenum (Mo) and Arsenic (As)**

Cd, As and Mo share similar trends with Pb and Zn in upper Meža Valley, because they all occur as trace elements in ore minerals from the Mežica ore deposit (Štrucl 1984; Fux & Gosar 2007).

The second source of these elements are the Ravne ironworks in the lower Meža Valley where the highest contents of Mo are reached in the < 0.063 mm fraction (ME-20) and are higher than the contents in the < 0.125 mm fraction.

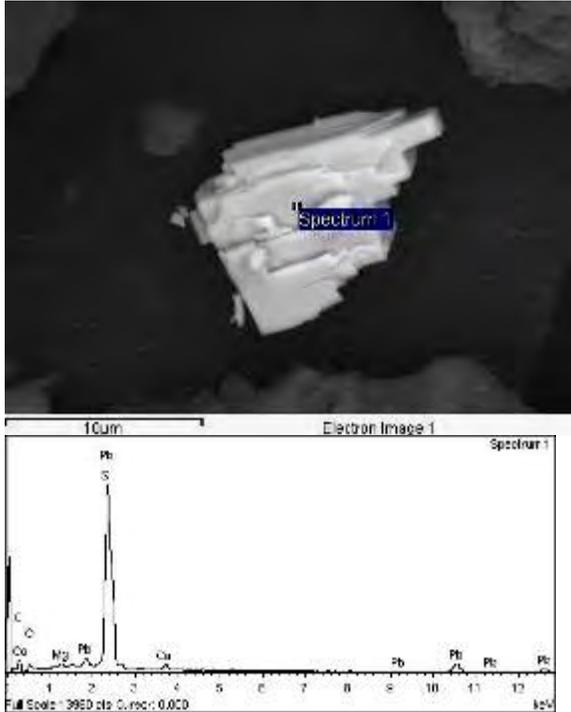
Relatively high contents of As in Drava River samples (ME-23 and ME-24) are a consequence of the Drava River catchment area characteristics.

### **Cobalt, Chrome, Copper and Nickel (Co, Cr, Cu and Ni)**

Near Ravne (ME-20) the contents of Co, Cr, Cu and Ni are increased in the < 0.063 mm fraction compared to contents in the < 0.125 mm fraction, which is due to different methods of processing at Ravne ironworks (Kaker & Glavar 2005; Alijagić & Šajn 2006).

### **Individual particle analysis**

Seven stream sediment samples of Meža River with its tributaries (Topla, Helenski potok, Mušenik, Jazbinski potok, Junčarjev potok) (ME-1, ME-5, ME-14, ME-17, ME-18, ME-20) and Drava River (ME-24), were analyzed using SEM/EDS. They contained Pb, Zn, Cr, Ni, Mn, Mo, Cd, Ti, V, W, Zr, Ce, Sb, Cu, Y, Sr, Ba, and Ag, found in different heavy metal-bearing phases.



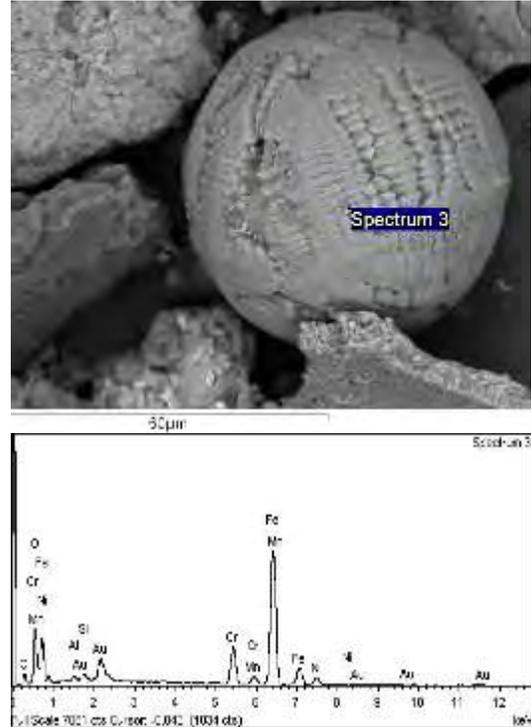
**Fig. 2.** SEM image and EDS spectrum of galena (sampling point ME-14).

The main outcomes of SEM/EDS analysis are as following:

In sediments of the Mežica mining and smelting area, mineral phases such as cerussite ( $PbCO_3$ ), galena ( $PbS$ ) (Fig. 2), pyromorphite ( $Pb_5(PO_4)_3Cl$ ), descloizite ( $PbZn(VO_4)(OH)$ ), bindheimite ( $Pb_2Sb_2O_6(O,OH)$ ), sphalerite ( $ZnS$ ), and smithsonite ( $ZnCO_3$ ) were identified. These minerals are derived from both geogenic and technogenic processes in the Mežica mining district.

Technogenic phases, such as various Fe-alloys ((Cr,Ni)-ferroalloy, (Cu,Ni)-alloy, and (Fe, Si)-alloy), Fe-oxides ((Cr,V,Fe)-oxide, (Mo,W,V,Cr,Fe)-oxide, (Mo,W)-oxide, (W,Cr,Fe)-oxide), and spherical particles ((Cr,Ni)-oxide or chrome-nickel-spinel (Fig. 3), (Cr,Fe)-oxide or chrome-spinel), were recognized in the area of the Ravne ironworks.

Mineral phases of geogenic origin, found in most of the investigated sediments, are barite ( $BaSO_4$ ), strontianite ( $SrCO_3$ ), rutile ( $TiO_2$ ), ilmenite ( $FeTiO_3$ ),



**Fig. 3.** SEM image and EDS spectrum of aerosol particle (sampling point ME-20).

titanite ( $CaTiSiO_5$ ), zircon ( $ZrSiO_4$ ), chalcocopyrite ( $CuFeS_2$ ), monazite ((Ce,La,Nd) $PO_4$ ), and xenotime ( $YPO_4$ ). Their source is most probably weathering of bedrock in the catchment area.

## CONCLUSIONS

Chemical analysis of the Meža River and its tributaries revealed significant heavy metal pollution of the upper Meža River sediments with lead, zinc, and some molybdenum, cadmium and arsenic enrichments. The trend of Cd and As is similar to trend of Pb and Zn, which is in agreement with the fact that Cd and As are associated with Pb and Zn in ore minerals (Štrucl, 1984; Fux & Gosar, 2007). In the lower Meža valley, these heavy metal concentrations decreased somewhat.

In the lower Meža River Valley concentrations of cobalt, chrome, copper and nickel are increased around Ravne as a result of the ironworks industry.

Geogenic and tectogenic heavy metal-bearing phases in sediments of the Meža River were identified by means of SEM/EDS. Knowledge of the mineralogy of heavy metal-bearing phases is important in understanding their stability, solubility, mobility, bioavailability, toxicity and developing remediation strategies.

#### ACKNOWLEDGEMENTS

The authors are grateful for financial support of this study to Slovenian Research Agency (ARRS) and RESTCA European seventh framework program for financial support for attendance to IAGS symposium.

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## Relationship of heavy metals between rice and soils in Zhejiang, China

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**ABSTRACT:** Rice and cultivation-layer soils were collected in the rice harvest season of 2006 in the key agricultural regions of Zhejiang province. Heavy metals and some soil physicochemical indicators were determined. It was demonstrated that heavy metal concentrations in rice were usually related to their concentrations in cultivation soils. In general, the Biologic Accumulation Coefficients (BAC) of heavy metals of rice to soil have a good relationship with physicochemical factors of soils including organic matter, pH, CEC and granularity. The results provide a pathway for making adjustments to soil physicochemical conditions such as organic matter and pH at the areas with higher background of heavy metals or contaminated sites so as to control heavy metal transportation from soil to edible parts of rice.

**KEYWORDS:** *heavy metal, physicochemical factors, soil, rice, bio-accumulation coefficient, Zhejiang*

### INTRODUCTION

Zhejiang province is located in eastern China and has a relatively developed economy. The main plain of the northeastern part of the province was formed by alluvium, and coastal, lake and marsh sediments. There are several small plains along the eastern coastline formed by alluvium and marine sediment. These plains have undergone thousand of years of agricultural cultivation.

A multi-purpose regional soil geochemical survey with a sampling density of one sample every square kilometer for top soils (0-20cm) and one sample every 4 square kilometers for bottom soils (150-200cm beneath surface) was conducted. Organic matter, pH and concentrations of fifty two elements were determined during a 2002-2005 study by the geological survey of Zhejiang province. This survey showed that a number of areas contain elevated concentrations of heavy metals in soils. Compared to the regional geochemical data obtained in the early of 1990's heavy metal (including As, Bi, Cd, Cu, Sb, Se, Tl, V, Zn) accumulation and acidification were apparent at several areas (Zhou *et al.*, 2004). It is likely that recent

industrialization and urbanization has caused degradation of the soil quality.

This study assesses the potential impact of the changes in the soil condition on agricultural product safety and examines the transportation of heavy metals from soils to rice.

### SAMPLING AND ANALYSIS

Sampling sites were selected based on the regional soil survey and a related study in seven sub-areas, each with coverage of several dozen to hundreds of square kilometers and with representative geological setting and geochemical characteristics. Rice and cultivation layer soil at 146 sites were sampled at a density of one site per square kilometer during rice harvest season, October 2006.

Heavy metals in rice and soils as well as several physicochemical indicators of soils including Organic matter (OM), pH, Cation- Exchange Capacity (CEC) and soil granularity were analyzed. As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Zn and OM of soils, and As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se and Zn of rice were determined at the central chemical lab of the Institute of Geophysical and Geochemical Exploration. The CEC of the soils was measured at the analytical institute of

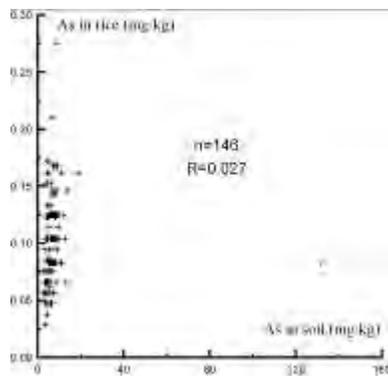
Jiangsu Geological Survey of China. Soil granularity was determined at the China University of Geological Sciences.

**RESULTS AND DISCUSSION**

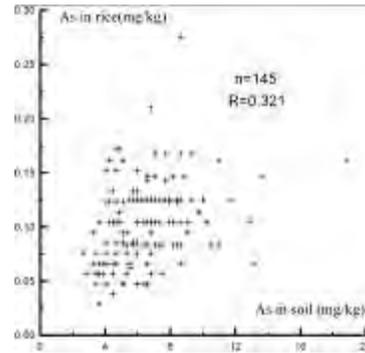
**Relationship of heavy metals between rice and soils**

The correlation coefficients of heavy metal concentrations between rice and soils for 146 samples are Cd 0.932, Cr 0.172, Cu 0.181, Hg 0.276, Ni 0.410, Se 0.178 and Zn 0.264 respectively, which indicates a fairly good relationship between these elements. As the accumulation of Cd, Cu, Se and Zn in soils increased, the concentrations of the rice also increased. Although the concentrations of these elements in rice are much lower than the safety threshold value in most samples and have no immediate impact on human health, the increase of soil concentration of heavy metals will eventually enhance risk through rice uptake in the food chain. Therefore diminishing the input of heavy metals to soil is urgent to maintaining long-term soil cultivation suitability.

There was no significant relation of the concentrations of As, Mn and Pb between rice and soils. Scatter plot showed that the correlation coefficient of As increases from 0.027 to 0.321 after deleting one set of data outliers (see fig.1 and 2). But the correlation coefficients of Mn and Pb couldn't be improved by deleting anomalous data sets. Several researchers (Lu *et al.*, 2005; Su *et al.*, 2008; Zhou *et al.*, 2007) obtained similar results between



**Fig. 1.** As concentration in rice vs. soils from of 146 sample sets.



**Fig. 2.** As concentration in rice vs. soils after excluding one anomalous sample set.

crops and soils, and they proposed that Pb in edible parts of crops was mainly from aero-precipitation.

**Physicochemical factors influencing rice's BAC of heavy metals**

Biologic Accumulation Coefficient (BAC) of heavy metals in rice is defined as:

$$BAC = \frac{C_b}{C_s} \times 100\% \quad (1)$$

$C_b$  --heavy metal concentration in rice;  $C_s$  --heavy metal concentration in soil.

BAC values and related statistics are presented in table 1.

It is apparent that rice's BAC values of Cd and Zn are greater than 10%; the BACs of Cu, Mn, Hg, As and Se are much lower; the BACs of Cr, Ni and Pb are the lowest. This can be attributed to elemental

**Table 1.** Statistical parameters of rice's BAC of heavy metals (n=146)

	mean	median	SD	VC
BAC <sub>As</sub>	1.72	1.60	0.71	0.41
BAC <sub>Cd</sub>	26.73	18.22	24.33	0.91
BAC <sub>Cr</sub>	0.26	0.26	0.14	0.54
BAC <sub>Cu</sub>	4.02	3.45	2.76	0.69
BAC <sub>Hg</sub>	3.01	2.59	2.02	0.67
BAC <sub>Mn</sub>	3.45	3.28	1.35	0.39
BAC <sub>Ni</sub>	0.69	0.57	0.45	0.65
BAC <sub>Pb</sub>	0.36	0.27	0.43	1.19
BAC <sub>Se</sub>	1.56	1.17	1.69	1.08
BAC <sub>Zn</sub>	14.59	14.13	5.56	0.38

SD--standard deviation;VC-- variation coefficient.

abundance and bio-geochemical characteristics including bio-available contents and the uptake ability of rice (Salomons *et al.*, 1995; Zhou *et al.*, 2005; Jiang and Zhang, 2002; Wu *et al.*, 1999; Mou *et al.*, 2004). It is also observed that the variation coefficients for most heavy metals are greater than 0.5. This may be because rice species, soil parent material, and soil type are varied greatly between the 146 sampling sites so that the uptake ability of rice to presence of heavy metals is of large difference from site to site.

The correlation coefficients between rice's BAC and soil physicochemical indicators were calculated (see table 2).

**Table 2** . Correlation coefficients of BAC and physicochemical indicators

	OM	pH	CEC	FC
BAC <sub>As</sub>	0.188	-0.230	-0.539	-0.213
BAC <sub>Cd</sub>	0.132	-0.212	-0.307	0.113
BAC <sub>Cr</sub>	0.189	-0.006	0.150	-0.278
BAC <sub>Cu</sub>	-0.041	-0.102	-0.252	-0.203
BAC <sub>Hg</sub>	-0.369	0.269	-0.287	-0.035
BAC <sub>Mn</sub>	0.013	-0.180	-0.215	-0.447
BAC <sub>Ni</sub>	0.160	-0.257	-0.242	0.183
BAC <sub>Pb</sub>	-0.344	0.302	-0.333	-0.121
BAC <sub>Se</sub>	-0.295	0.212	-0.497	-0.161
BAC <sub>Zn</sub>	-0.438	0.301	-0.561	-0.370

FC refers the percentage of fine silt and clay component with grain-size less than 5  $\mu\text{m}$ .

Table 2 illustrates that the BACs of As, Cd, Cr and Ni tend to increase as soil organic matter increases. Although the detailed mechanism needs to be studied, the phenomena may be due to the influence of the soil condition (including OM contents) on the species and bio-ability of these heavy metals. Contrarily the BACs of Hg, Pb, Se and Zn decrease greatly as soil organic matter is increased which provides a possible pathway to control Hg, Pb and Zn transfer into food by adding organic fertilizer.

The effect of pH on BACs of heavy metals is complicated. The BACs of rice of As, Cd, Mn and Ni tend to decrease as pH

increased. It can be supposed that the bio-available contents of heavy metals decreased as pH increased. But the BAC's trend of Hg, Pb, Se and Zn is somewhat anomalous. One possible reason is that sample sites are scattered in large region and soil properties and rice genotype are varied greatly so that pH influence is less than other factors. However Pb concentration in rice may be mainly from atmosphere so that there is no relation in soil-plant system.

CEC and fine silt and clay component (FC) have similar effects on rice's BAC. The competitive uptake of the alkaline-earth cations may result in a reduced heavy metal BAC for rice. Soils with higher percentage of fine silt and clay provided more CEC so that it has similar effect on the BAC.

## CONCLUSIONS

This paper presents some trends for heavy metal patterns in rice-soil systems on a regional scale in Zhejiang province. The major findings are summarized below: (1) Heavy metal concentrations in rice are related to concentrations in soils. Thus soil heavy metal contamination should be strictly controlled.

(2) Biologic Accumulation Coefficients (BAC) of rice are influenced by soil properties such as organic matter, pH, CEC, and granularity component.

(3) Although further study needs to be conducted to determine the effect of other soil properties, the influences of organic matter and pH on rice's BAC provide an important pathway to predict heavy metal risk on the safety of rice and other agricultural products. This may mean that as soil contamination continues soil properties such as pH may need to be adjusted using products such as lime and organic fertilizer.

## ACKNOWLEDGEMENTS

We would like to give our thanks to the analytical technicians for their hard work on the sample analysis and to the geochemical technicians at the Geological Survey of Zhejiang province for their assistance in the field work.

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## Anthropogenic Gadolinium as a Micropollutant in Drinking Water

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**ABSTRACT:** Rare earth elements (REE) are often used as geochemical tracers due to their coherent behaviour in natural systems. While studies of REE in geochemistry rely on the assumption that these systems are free from anthropogenic input, they are, however, increasingly affected by anthropogenic micropollutants. Excessive amounts of gadolinium (Gd), a rare earth element, have been reported in rivers and groundwaters from numerous regions with high population density and advanced health care systems. The source of the excess Gd is its usage as a contrast agent in magnetic resonance imaging (MRI). The Gd is stabilized as a water-soluble and highly stable organic complex which is transported unimpeded through sewage systems and waste water treatment plants (WWTP) into rivers and aquifers. We provide data that documents that anthropogenic Gd is also present in municipal drinking water in several cities in Germany. The presence of anthropogenic Gd in drinking water strongly suggests that pharmaceuticals which behave similar to anthropogenic Gd may also be present.

**KEYWORDS:** *anthropogenic gadolinium, rare earth elements, tapwater, contrast agent, nephrogenic systemic fibrosis*

### INTRODUCTION

The rare earth elements (REE) form a group of elements that have coherent geochemical behaviour due to their trivalent charge and similar ionic radii. They can, however, be fractionated from one another as a result of geochemical processes operating under specific physico-chemical conditions. In order to outline general trends within and differences between the individual REE, concentrations are usually normalized to a reference system (e.g. to shale). Deviations of individual elements from the generally smooth trend are referred to as anomalies.

While studies of natural REE and their variation are abundant and their behaviour in natural systems is reasonably well understood, their increased usage in high-tech products and applications that have become essential for our modern life styles is making it harder to conduct research on natural processes.

The increasing demand for REE in applications ranging from petroleum cracking catalysts to fertilizers, or from essential computing hardware to nuclear power plants means that research and

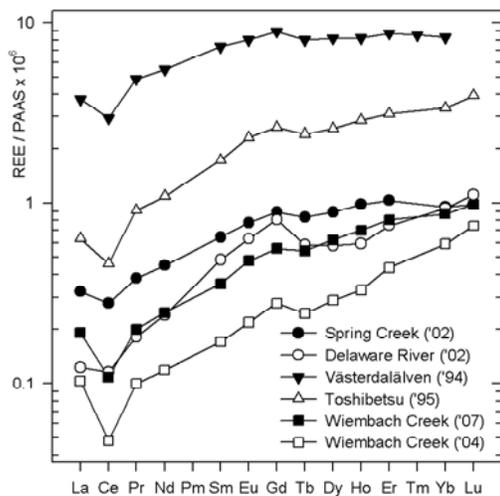
monitoring studies need to be intensified to understand their increasing input into the environment. REE are found in natural waters at ultratrace concentrations, and natural concentrations can be easily masked by small amounts of anthropogenic influence (Bau & Dulski, 1996). Another disadvantage of their low abundance is that even in known cases of contamination there are no emission limits. Presently, there is relatively little work to assess the long-term effects of REE on ecosystem health.

Tapwater, surface water and WWTP effluents were sampled, filtered (0.2µm) and acidified to pH 2.0. REE were separated and preconcentrated following the method described in detail by Bau and Dulski (1996). REE concentrations were determined by inductively coupled plasma mass spectrometry.

### ANTHROPOGENIC GADOLINIUM

Figure 1 shows dissolved REE concentrations normalized to shale (McLennan, 1989) for rivers that are uncontaminated. The general trend is an enrichment of heavier REE as compared to lighter REE, with few minor deviations.

Cerium is insoluble when present in a tetravalent state, and is depleted compared to its neighbouring elements, causing negative Cerium anomalies in oxic systems. Lanthanum, Gd, and Lu have higher complexation stability constants when compared to the other trivalent REE, due to their specific electron configurations. They may therefore be found in slightly higher concentrations, and display small positive natural anomalies. The conclusion from these rivers is that major anomalies are not expected in systems uncontaminated by human impact.

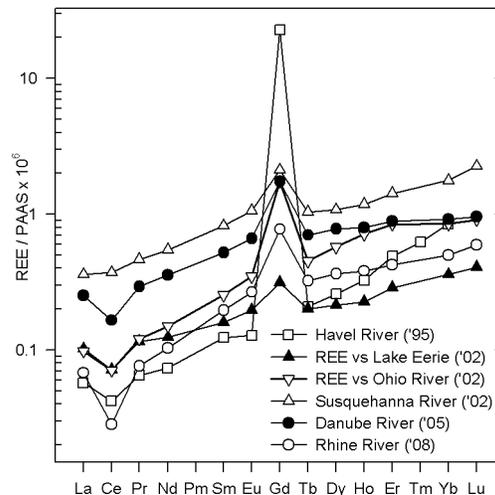


**Fig. 1.** Rare earth element plots of uncontaminated rivers. Samples marked with circles are from Bau *et al.* (2006) and those with triangles from Bau & Dulski (1996). Samples marked with squares are from this study.

Figure 2 shows REE patterns for a selection of rivers showing positive anthropogenic Gd anomalies. These anomalies are found across the world in Japan, Australia, Europe and the U.S., in areas of high population density. The anthropogenic Gd in river waters can be related to the use of Gd compounds as contrast agents in MRI (Bau & Dulski, 1996). Availability of modern medical facilities, therefore, is a prerequisite for producing such Gd anomalies. This is shown by the lack of a positive Gd

anomaly in the Chao Phraya River (Thailand) which passes through the densely populated Bangkok City (Nozaki *et al.* 2000), but lacks readily available MRI facilities.

The effluent waters of a waste water treatment plant (Ruhleben) in Berlin (Fig. 3) show the highest positive Gd anomaly observed to date. Strong positive Gd anomalies are common in effluents of other treatment plants across the world (e.g. Australia, USA, Austria, Germany, and Czech Republic) due to the inability of the treatment processes to remove the highly stable and water soluble Gd complexes. This is also the cause for their presence in river and lake waters and in groundwater which receive these effluent waters either directly (input into rivers) or indirectly (infiltration).

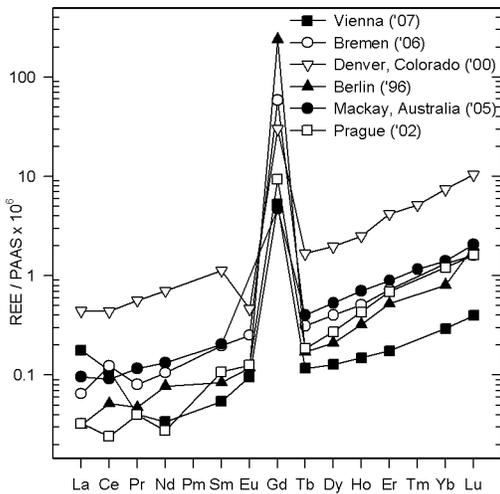


**Fig. 2.** Rare earth element plots of contaminated rivers. Samples marked with triangles are from Bau *et al.* (2006). The sample marked with open squares is from Bau & Dulski (1996). Samples marked with circles are from this study.

**Gadolinium in Tapwater**

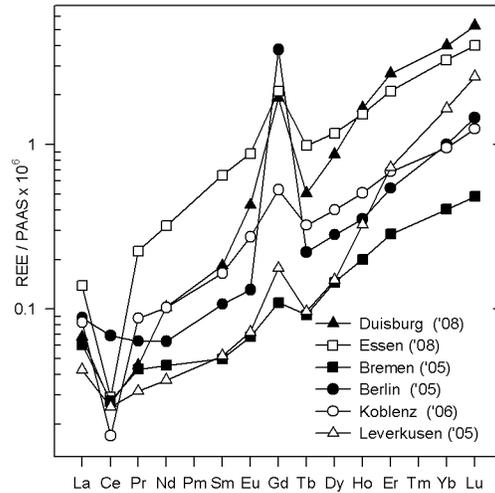
While there is little reason to worry about anthropogenic Gd in river or ground water, elevated Gd in tapwater is alarming. Grobner (2006) has described the link between exposure to Gd-based contrast agents and nephrogenic systemic fibrosis (NSF) in patients with kidney failure,

making the issue of anthropogenic Gd in tapwater even more relevant. More cases of NSF have been reported elsewhere, causing the U.S. Food and Drugs Administration to force drug manufacturers in 2006 to include a boxed warning on the product description of Gd-based contrast agents. Figure 4 shows dissolved REE in drinking water from different German cities. The highest positive anthropogenic Gd anomaly is found in Berlin. This is due to a combination of the large contribution of treatment plant effluent to the urban water system compared to the discharge from rivers, and the water recycling policy using bank infiltration to replenish groundwater (Knappe *et al.* 2005).



**Fig. 3.** Dissolved REE data for waste water treatment plants in different countries. Notice the orders of magnitude difference in Gd values. Data for Denver from Bau *et al.* (2006), Berlin from Bau & Dulski (1996), Mackay from Lawrence *et al.* (2006) and Prague from Möller *et al.* (2002). Samples from Vienna and Bremen are from this study.

The other cities show varying but nevertheless significant amounts of anthropogenic Gd in their tapwater. With the exception of Bremen (20% anthropogenic Gd), all samples show more than half of total dissolved Gd to be of anthropogenic origin, with up to 95% for the Berlin sample. The anthropogenic



**Fig. 4.** Dissolved REE in tapwater from various German cities investigated in this study.

component is estimated by subtracting the extrapolated natural (background) Gd concentrations from total dissolved Gd as shown in equation 1, where  $N$  denotes a normalized value (to shale) and  $*$  denotes a natural (background) value.

$$\log Gd_N^* = 0.67 \log Tb_N + 0.33 \log Sm_N \quad (1)$$

While this equation can only serve as an approximation of the true anthropogenic content of a sample due to its simplistic binary approach, it is an easy yet useful way of determining the relative contributions of the natural and anthropogenic Gd in a sample. One powerful application of this approach is its use as a tracer for the presence of WWTP effluent in surface water, groundwater and drinking water. Quantifying anthropogenic Gd content in these waters would be a fast and cost-efficient way of screening for other truly dissolved compounds such as antibiotics, steroids and antihistamines. Quantifying the mixing ratios of contaminated to uncontaminated sources in groundwater, for example, has been demonstrated by Knappe *et al.* (2005). Morteani *et al.* (2006) have shown a

correlation between anthropogenic Gd and estrogens in the sewage plants and surface water of Prague, Czech Republic, utilizing this relation as a method for pinpointing sewage leaks.

### CONCLUSIONS

The presence of anthropogenic Gd in water systems in densely populated areas with readily accessible magnetic resonance imaging facilities is by now a widely observed phenomenon, whereas anthropogenic Gd in tapwater is less frequently reported. We have shown that this results not from the lack of anthropogenic Gd in these systems, but rather the lack of research focusing on this issue. The presence of anthropogenic Gd in drinking water should not be overlooked, given preliminary results that link it to diseases, such as nephrogenic systemic fibrosis, and the lack of knowledge about potential other long term effects of exposure. Moreover, quantifying anthropogenic Gd in drinking water can be used as a means of characterizing drinking water quality in urban areas in terms of how well the WWTPs can remove truly dissolved compounds such as Gd complexes or common pharmaceuticals that are used in large quantities.

### ACKNOWLEDGEMENTS

We thank the staff of the Geochemistry Laboratory at Jacobs University Bremen, and Peter Dulski of GFZ Potsdam. This research is funded by the German Science Foundation.

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## Correlation of Atmospheric Soil and Atmospheric Lead in Three North American Cities: Can Re-suspension of Urban Lead Contaminated Soil be a Major Source of Urban Atmospheric Lead and Cause Seasonal Variations in Children's Blood Lead Levels?

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**ABSTRACT:** Soils in older cities are highly contaminated by lead from past use of lead in leaded gasoline and due to the use of lead in exterior paints. In this study the temporal variations in atmospheric soil and atmospheric lead in three North American cities are examined. This study tested the hypotheses that atmospheric lead and atmospheric soil concentrations obtained from the Interagency Monitoring of Protected Visual Environments (IMPROVE) exhibit statistically significant correlations in three North American cities and that atmospheric soil and atmospheric lead follow seasonal patterns with highest concentrations during the summer and/or autumn. Results indicate that atmospheric soil and atmospheric lead were correlated in Detroit between November 2003 to July 2005 ( $r = 0.47$ ,  $p < 0.001$ ); In Pittsburgh between April 2004 to July 2005 ( $r = 0.40$ ,  $p < 0.001$ ); and in Birmingham between May 2004 to December 2006 ( $r = 0.35$ ,  $p < 0.001$ ). The hypothesis that atmospheric soil and atmospheric lead follow seasonal patterns with highest concentrations during the summer and/or autumn could not be rejected. It is suggested that atmospheric lead and atmospheric soil concentrations are correlated due to re-suspension of urban lead contaminated soils. It is further suggested that in order to decrease urban atmospheric lead concentrations, lead deposition, and children's seasonal exposure via hand to mouth activity, urban lead contaminated soils should be remediated or isolated.

**KEYWORDS:** *lead, soil, re-suspension, blood, poisoning, children*

### INTRODUCTION

In the USA, motor vehicles used gasoline containing tetramethyl and tetraethyl Pb additives from the 1920s to 1986. By the 1950s, Pb additives were contained in virtually all grades of gasoline. By 1986, when leaded gasoline was banned, 5–6 million metric tons of Pb had been used as a gasoline additive, and about 75% of this Pb was released into the atmosphere (Chaney & Mielke 1986; Mielke & Reagan 1998). Thus, an estimated 4–5 million tons of Pb has been deposited into the US environment by way of gasoline-fueled motor vehicles (Mielke 1994). Accumulation of soil Pb created by leaded gasoline is proportional to highway traffic flow (Mielke *et al.* 1997).

In the 1970s, the presumed dominant source of soil Pb contamination was Pb-based house paint (Ter Haar and Aronow, 1974). A subsequent study of garden soils conducted in metropolitan Baltimore,

Maryland, began to raise questions about that assumption. Soil around Baltimore's inner city buildings, predominantly unpainted brick, exhibited the highest amounts of Pb, and soils outside of the inner city, where buildings were commonly constructed with Pb-based paint on wood siding, contained comparatively low amounts of Pb, suggesting that Pb based house paint could not account for the observed pattern of soil Pb (Mielke *et al.* 1983). The same pattern was also found in Ottawa, Canada (Ericson & Mishra 1990).

The quantity and distribution of soil Pb have been studied in numerous places in North America (see Laidlaw & Filippelli, 2008). All these North American cities exhibited the same distance decay characteristic of high soil Pb contamination in the inner city and decreasing contamination toward the outer parts of the city as initially identified

in garden soils of Baltimore (Mielke *et al.* 1983). Further, similarities in this distance decay pattern of soil Pb supports the idea that Pb-based house paint was not the sole source contributing to these observed differences.

Soil lead concentrations have been observed to be associated with children's blood lead concentrations using multiple study designs – cross-sectional, ecological spatial, ecological temporal, prospective soil removal and isotopic (Laidlaw & Filippelli, 2008).

Average monthly blood Pb (BPb) values of children from urban areas tends to increase significantly in summer months (Haley & Talbot 2004; Laidlaw *et al.* 2005; Yiin *et al.* 2000). Early work by Mielke *et al.* (1992), Johnson & Bretsch (2002), and Johnson *et al.* (1996) suggested that blood Pb seasonality may be related to the interaction between climate and Pb contaminated soils. Yiin *et al.* (2000) actually measured seasonal changes in dust Pb levels and correlated blood Pb levels with seasonal dust Pb concentrations. Yiin *et al.* (2000) conducted a study to examine seasonal changes in residential dust Pb content and its relationship to blood Pb in preschool children. The study found that windowsill wipe samples were most correlated with blood Pb concentration and the variation of dust Pb levels for floor Pb loading, windowsill Pb loading, and carpet Pb concentration were consistent with the variation of blood Pb levels, showing the highest levels in the hottest months of the year (June, July, and August).

Laidlaw & Filippelli (2008), Laidlaw *et al.* (2005), and Filippelli *et al.* (2005) have demonstrated that seasonal variations in children's blood lead levels in Syracuse, Indianapolis and New Orleans could be predicted using soil moisture and atmospheric variables suggesting that re-suspension of urban soils contaminated by past use of leaded gasoline and paint were causally related to seasonal variations in blood lead. These papers concluded that urban lead contaminated soil was being re-suspended when soils were dry in the summer and autumn when

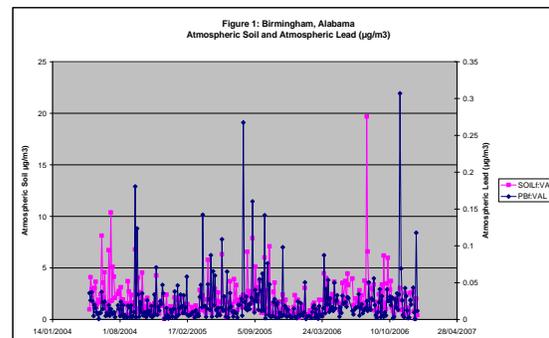
evapotranspiration is maximised. Their assumption that soil lead is being re-suspended and is responsible for a large portion of the lead in the atmosphere is supported by lead isotopic analysis of atmospheric lead in Yerevan Armenia (Kurkjian *et al.* 2001) which indicated that following elimination of the use of lead in gasoline, 75% of atmospheric lead in the Yerevan atmosphere was derived from re-suspended soil.

Soil resuspension has the capability of entraining significant volumes of Pb into the air of urban areas. Harris & Davidson (2005) calculated that resuspension of soil is responsible for generating 54,000 kg of airborne Pb each year in the South Coast Air Basin of California (SOCAB) and will remain a major source well into the future. Similarly, Lankey *et al.* (1998) concluded that 43% of Pb emissions in the South Coast Air Basin in California resulted from the resuspension of soil and road dust.

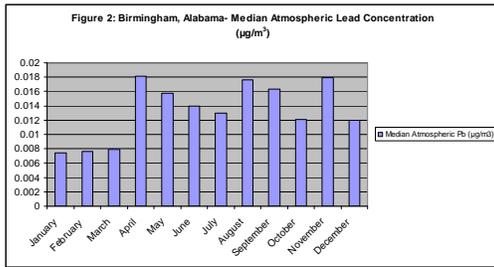
In this study, data from Birmingham, Alabama; Pittsburgh, Pennsylvania; and Detroit, Michigan were selected to assess seasonal patterns and assess seasonal relationships between atmospheric soil and atmospheric lead.

The following hypotheses were tested:

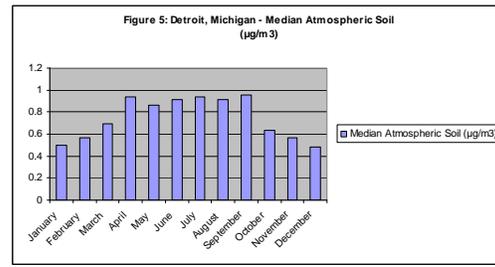
- 1) Atmospheric air lead and atmospheric soil concentrations exhibit statistically significant correlations in three major North American Cities; and



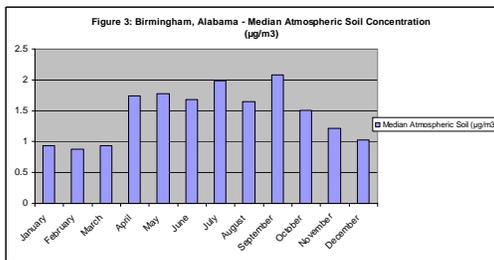
**Fig. 1.** Plot of atmospheric soil and atmospheric lead in Birmingham, Alabama ( $r = 0.35$ ,  $p < 0.001$ ).



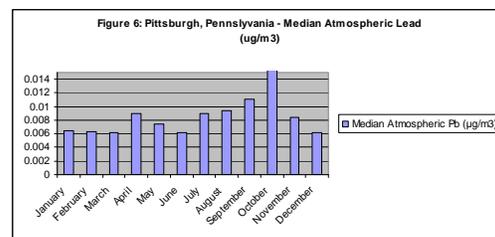
**Fig. 2.** Median atmospheric lead concentrations at IMPROVE air monitoring station in Birmingham, Alabama (May 2004 to December 2006).



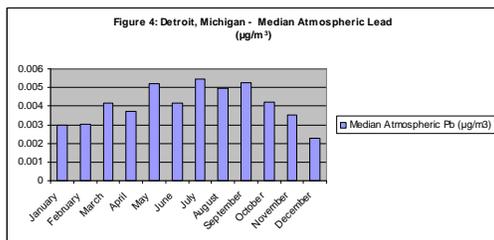
**Fig. 5.** Median Atmospheric soil concentrations at IMPROVE air monitoring station in Detroit, Michigan (November 2003 to July 2005).



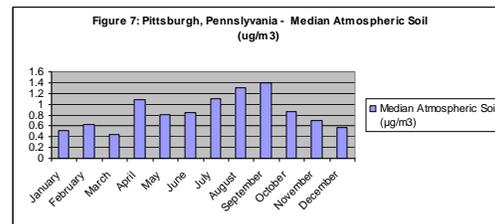
**Fig. 3.** Median Atmospheric soil concentrations at IMPROVE air monitoring station in Birmingham, Alabama (May 2004 to December 2006).



**Fig. 6.** Median atmospheric lead concentrations at IMPROVE air monitoring station in Pittsburgh, Pennsylvania (April 2004 to July 2005).



**Fig. 4.** Median atmospheric lead concentrations at IMPROVE air monitoring station in Detroit, Michigan (November 2003 to July 2005).



**Fig. 7.** Median Atmospheric soil concentrations at IMPROVE air monitoring station in Pittsburgh, Pennsylvania (April 2004 to July 2005).

- 2) Atmospheric soil and atmospheric lead follow seasonal patterns with highest concentrations during the summer and/or autumn.

## CONCLUSIONS

1) In order to decrease urban atmospheric lead concentrations, lead deposition, and subsequent children's exposure via hand to mouth activity, urban lead contaminated soils should be remediated or isolated.

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## Impact of Evolving Hypoxia on the Remobilization of As and Se in the Lower St. Lawrence Estuary (Québec)

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**ABSTRACT:** Dissolved oxygen concentrations in the bottom water of the Lower St. Lawrence Estuary have decreased by more than 50% since the 1930s, and are now < 60µmol/L. This might affect the diagenesis of redox-sensitive elements such as Mn, Fe, As and Se. These metals, which are normally concentrated in the oxic layer of the sediment, could escape to the overlying waters if the sediment oxygen penetration depth were to decrease as oxygen in the bottom water becomes depleted. Fe, Mn, As and Se fluxes across the sediment-water interface were measured as a function of the overlying water oxygen concentration in short-term controlled-laboratory incubations of sediment cores. No significant changes of Fe, Mn and As fluxes (Se analyses are on-going) were observed. Cores sampled between 1982 and 2007 reveal changes in sediment chemistry over the last 25 years. Dissolved and reactive Fe and As concentrations have increased significantly, although their total solid-phase concentrations have remained invariant. This is interpreted as a progressive response of the sediment to the decreasing levels of bottom water oxygen.

**KEYWORDS:** *hypoxia, oxidation, reduction, diagenesis, authigenic*

### INTRODUCTION

Upon burial in the sediments, organic matter is microbially oxidized in a sequence dictated by the Gibbs Free Energy yield of each reaction (Froelich *et al.*, 1979). The oxidants are used in this sequence: respiration of oxygen, denitrification, manganese oxide reduction, iron oxide reduction, sulphate reduction and fermentation (Van Cappellen & Wang, 1996). This leads to a vertical redox zonation of the sediment column.

In coastal environment, detrital and authigenic Fe and Mn oxides, which accumulate in oxic surface sediments, play a pivotal role in determining the geochemical behaviour of arsenic (Mucci *et al.*, 2000) and selenium (Belzile *et al.*, 2000). Arsenic and selenium differ in their affinities for metal oxide surfaces. Although both adsorb onto iron oxides, arsenate (As(V)) adsorbs more strongly than arsenite (As(III)), and selenite (Se(IV)) adsorbs more strongly than selenate (Se(VI)) (Belzile *et al.*, 2000).

Furthermore, Se(IV) is scavenged preferentially by manganese oxides (Belzile *et al.*, 2000), and it is thought that manganese oxides catalyse the oxidation of As(III) to As(V) (Mucci *et al.*, 2000).

Following the reductive dissolution of reactive Fe and Mn oxides during suboxic and anoxic diagenesis, As and Se are released to the sediment porewaters (Aggett & Kriegman, 1998). Dissolved species can thus migrate upwards and be reprecipitated in the oxic layer or escape to the water column. They can also migrate downwards where As may co-precipitate with sulphides under reducing conditions (Mucci *et al.*, 2000; Belzile, 1988) and Se will react spontaneously with dissolved Fe to form FeSe or FeSe<sub>2</sub> (Takayanagi & Belzile, 1988). Hence, As and Se retention in the sediments depends on the availability of Fe and Mn oxides which, in turn, depends on the thickness of the oxic layer. The redox conditions at or near the sediment-water interface will therefore determine whether the sediments serve as a source or a sink

for these elements (Saulnier & Mucci, 2000). In this study we investigate the impact of hypoxia on: 1) the response of Fe, Mn, As and Se fluxes to a decreasing oxygen concentration in the overlying waters and, 2) the long-term evolution of As and Se concentrations in the solids and porewaters of the Lower St. Lawrence Estuary sediments.

### STUDY AREA

The Lower St. Lawrence Estuary (LSLE) occupies the 300 km landward end of the Laurentian Channel with depths of 300-350 m. The water below 150m depth originates in the offshore slope region of the north-western Atlantic and is a mixture of North Atlantic and Labrador Sea waters (Bugden, 1991). This water is isolated from the atmosphere by a permanent pycnocline, and the dissolved oxygen concentration decreases progressively as the water flows landward to the head of the estuary. The oxygen concentration in the LSLE bottom water has decreased from 130  $\mu\text{mol/L}$  in 1930 to about 60  $\mu\text{mol/L}$  today (Gilbert *et al.*, 2005) and is thus hypoxic. Hypoxia is defined by  $[\text{O}_2] < 62.5 \mu\text{mol/L}$ , which is the level necessary to sustain most animal life (Diaz & Rosenberg, 1995).

### METHODS

Sediment cores were recovered on board the R/V Coriolis II in July 2007 at four stations in the LSLE using a Bowers & Connelly Multicorer and an Ocean Instrument Mark II box corer. Upon recovery, box cores were transferred to a specially-designed glove box and sub-sampled under a constant flow of  $\text{N}_2$  to limit oxidation. Porewaters were extracted from the sediment using Reeburgh-type squeezers, filtered through a 0.45  $\mu\text{m}$  filter, acidified with a 2% equivalent volume of ultrapure, concentrated  $\text{HNO}_3$  and kept refrigerated until analysis. Solid sediment samples were kept frozen until freeze-dried and ground for analysis.

Cores recovered with the multicorer were immersed in a water bath kept at 4°C and transferred to an on-land laboratory. Each core remained 7 days in

a controlled oxygen concentration bath followed by 48 hours incubation in the dark. At regular intervals, filtered overlying waters were collected for oxygen and trace metal analyses. The water removed during sampling was replaced by an equivalent volume of bottom water of known composition and oxygen concentration. The incubations were carried out at three different overlying water dissolved oxygen concentrations: 90, 50 and 20  $\mu\text{mol/L}$ .

Total dissolved Fe and Mn were analyzed directly by flame atomic absorption spectrometry (AAS). As was measured by AAS with hydride generation (HG-FIAS). Total dissolved Se concentrations were determined by hydride-generation atomic fluorescence spectrometry (Chen *et al.*, 2005).

The freeze-dried sediments were subjected to both a total dissolution and a selective extraction. The latter, as described in Chester & Hughes (1967), is carried out in a hydroxylamine hydrochloride and acetic acid (HA) solution and designed to isolate reactive phases. With the exception of total Se, extracted metals were determined by the method described for porewaters. Total solid Se concentrations were measured by AAS with HG-FIAS (analysis ongoing).

### RESULTS AND DISCUSSION

Both Mn and As were released to the overlying water during the incubations but no detectable release of Fe was observed in any of the incubations. At the highest oxygen level, the fluxes varied by as much as one order of magnitude between and within the different study sites (Table 1), and no significant trends could be discerned as oxygen concentration evolve towards anoxia. These results imply that the sediments require more than 9 days to respond to chemical changes occurring in the overlying waters. Accordingly, Katsev *et al.* (2007) estimated that it may take on the order of 100 years to reach a new steady state.

Station	[O <sub>2</sub> ] ~ 90µmol/L		[O <sub>2</sub> ] ~ 50µmol/L		[O <sub>2</sub> ] ~ 20µmol/L	
	[Mn]	[As]	[Mn]	[As]	[Mn]	[As]
24 A	-0.13	-0.12	-	-	-	-
24 B	-0.11	-0.08	-	-	-	-
24 C	ND	-0.04	-	-	-	-
23S A	-0.93	-0.45	-	-	-	-
23S B	-0.31	-0.69	ND	ND	-0.24	-0.34
23 B	<dl	-0.08	-	-	-	-
23 C	-0.17	-0.36	ND	ND	-0.55	-0.60
23 D	-0.14	-0.44	ND	ND	-0.14	-0.47
20 B	<dl	-0.26	-0.09	-0.36	<dl	-0.03
20 C	<dl	1.27	-0.18	ND	-0.01	-0.55
20 D	-0.14	-0.32	ND	-0.13	-0.03	ND

**Table 1.** Fluxes of Mn (mmol/m<sup>2</sup>/d) and As (x10<sup>-3</sup> mmol/m<sup>2</sup>/d) in short-term, duplicate and triplicate incubations of cores at three overlying water oxygen concentrations. *ND*: no data, - : core not incubated, <dl: below the detection limit. Negative fluxes are from sediment to water.

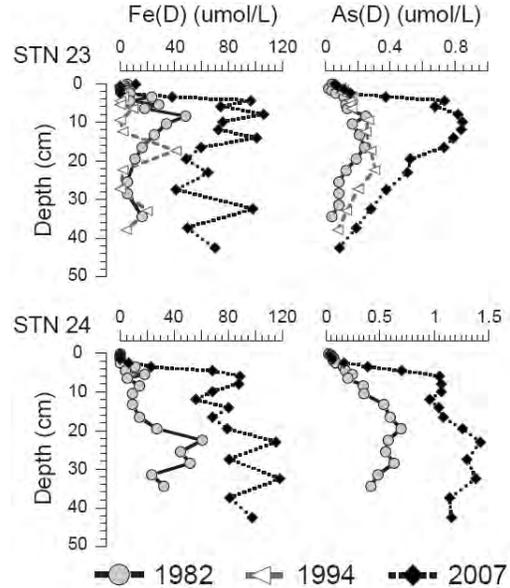
Whereas total concentrations of solid Fe and As remained relatively constant over time (not shown), dissolved Fe and As in the porewaters have increased substantially since 1982 (Fig. 1). The concentrations in the suboxic zone have doubled or tripled. Similarly, HA-extractable Fe and As concentrations increased significantly at stations 23 and 24 since 1982 (Fig. 2). This increase is concomitant with an accumulation of AVS in the sediment over the last 10 years (G. Chaillou, unpublished).

Stations 23 and 24, located in the LSLE, have been subjected to hypoxic conditions since the 1980s. With depletion of oxygen in the bottom waters, the sediment oxygen penetration depth decreased, and Fe oxides, concentrated in the oxic sediment layer, were reductively dissolved and released adsorbed arsenic. Hence, the low oxygen levels during the last 25 years in the bottom waters is reflected in more reducing conditions in the sediment and increases in both dissolved and HA-extractable Fe and As.

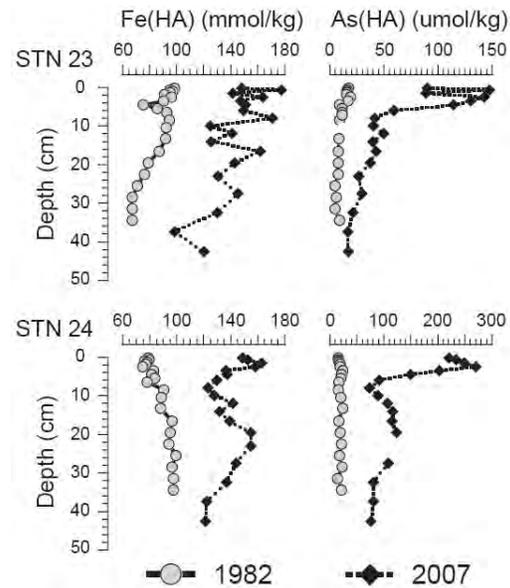
Preliminary results reveal similar trends for Se at station 23. Ongoing analyses will allow us to estimate the flux of Se at the sediment-water interface.

**CONCLUSION**

The concentrations of dissolved and HA-extractable Fe and As have increased



**Fig. 1.** Porewater iron and arsenic concentrations at stations 23 and 24.



**Fig. 2.** HA-extractable, solid iron and arsenic concentrations at stations 23 and 24.

significantly since 1982 in the suboxic sediment of the LSLE. These changes coincide with the decreasing oxygen concentration in the bottom waters. We attribute the changes in the sediment to both an increase of the AVS content and a thinning of the Fe oxide-rich surface layer. If the bottom water oxygen concentration continues to decrease, the iron oxide layer

will shallow further and the capacity of the sediment to adsorb As and retard the flux of As to the bottom water will diminish. When the sorption capacity of the sediment is exhausted, the sediment will no longer modulate the release of dissolved As from the sediment.

#### ACKNOWLEDGEMENTS

This research was funded by a NSERC Strategic grant to B.S. and A.M. Additional financial support to S.L. was provided by the Department of Earth and Planetary Sciences/McGill and the GEOTOP-UQAM-McGill research centre.

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## Geochemistry of catchment outlet sediments: evaluation of Mobile Metal Ion™ analyses from the Thomson region, New South Wales, Australia

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**ABSTRACT:** Outlet sediment (or overbank) samples from 99 catchments in the Thomson region have been examined by conventional geochemical analytical methods and by partial digestion using Mobile Metal Ion™ (MMI) extraction. Elements such as Pb have good correlation with known mineral deposits using conventional (near-total digestion) methods, whilst elements such as Cu, Au and Ag show a better correlation with known mineral deposits when MMI concentrations are used. This study shows that very low density sampling of catchment outlet sediments (here 1 site/1540 km<sup>2</sup>) provides useful and possibly predictive geochemical information for mineral exploration in areas dominated by transported regolith.

**KEYWORDS:** *Overbank sediment, geochemistry, mineral exploration, MMI, Thomson Orogen*

### INTRODUCTION

Overbank sediment samples collected near the outlets of large drainage basins are commonly used to obtain regional geochemical information (e.g. McConnell *et al.* 1993; Demetriades 2008). Having been deposited on floodplains in low energy environments adjacent to major drainage channels; they are fine-grained and have the potential to represent large areas of, or the average composition of, entire catchments. Representative sampling of large areas has critical implications for geochemical surveys applying low sampling density strategies. Such a survey is currently being carried out for the whole of Australia (Caritat *et al.* 2008). This paper presents and discusses some of the results from a pilot study conducted in the Thomson region, in northwestern New South Wales, as a forerunner to the national survey.

### GEOLOGICAL SETTING

#### Location

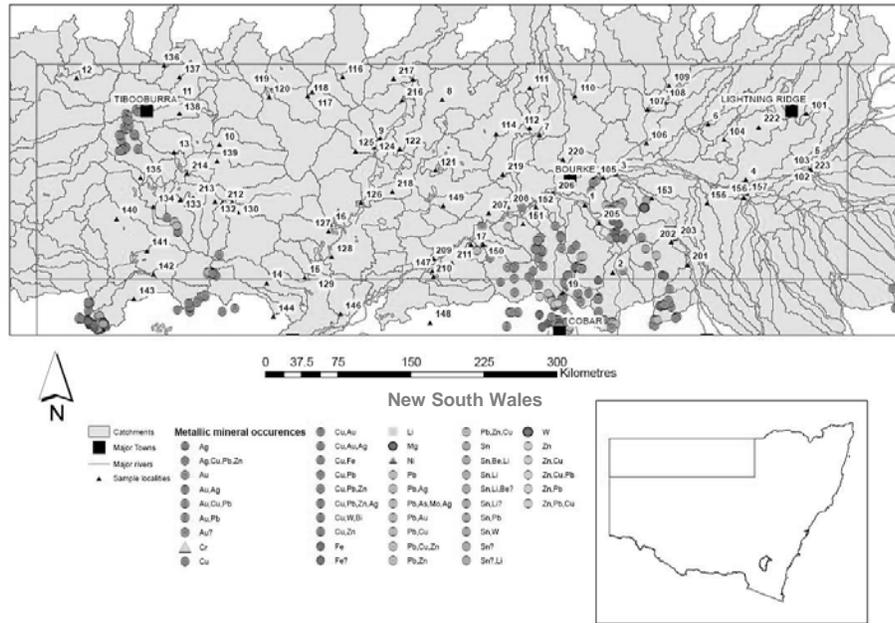
The Thomson project area covers an area of 154,521 km<sup>2</sup> and is located in north-western New South Wales (Figure 1). It contains the Thomson Orogen, one of the most poorly understood orogenic belts in

Australia due to its remoteness and the degree of surficial cover. Named after the Thomson River in central Queensland, it is part of the greater Tasmanides of Eastern Australia.

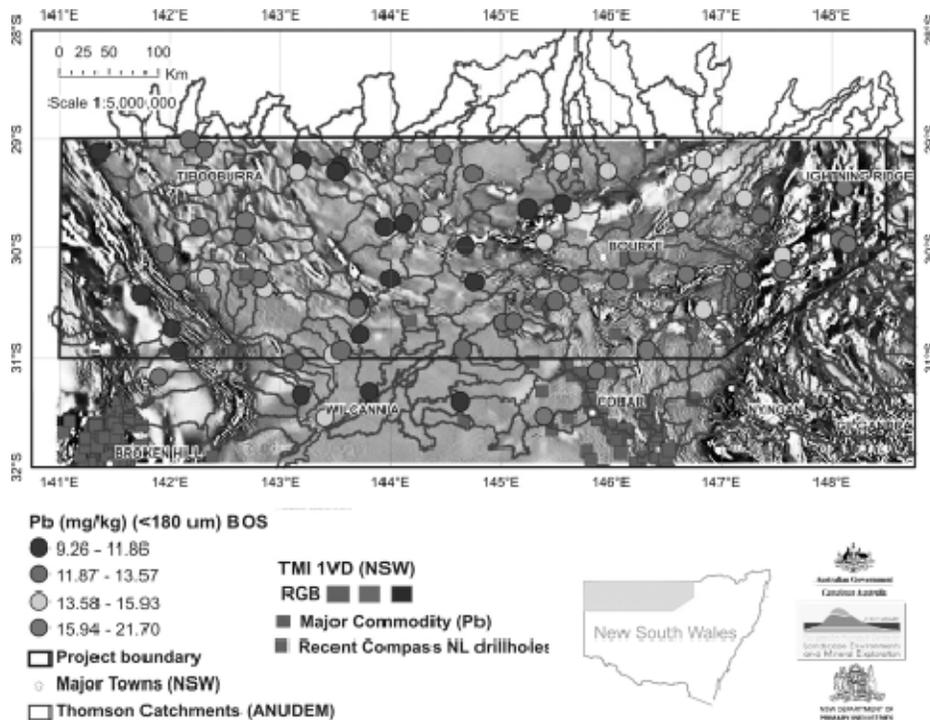
#### Geology

Various mineral prospects and minor metal occurrences are found in the study area, including Pb, Zn and Sn deposits north-east of Broken Hill, Au deposits near Tibooburra and Au, Cu and Pb deposits north of Cobar (Figure 1).

The area is dominated by transported regolith with minor outcrop of crystalline basement rocks. In the east, black cracking clays, clay pans and gilgai are associated with the expansive Quaternary alluvial plains of the Darling, Barwon, Bogan and Warrego River systems. There is also an area in the north-west around Tibooburra in which cracking clays are common. The alluvium of ephemeral streams in the west and south-east is principally composed of reworked eolian material. Erosional rises and plains in the centre of the study area north of White Cliffs relate to silicified palaeodrainages. Calcareous soils comprise a large part of the landscape in the south-west.



**Fig. 1.** Catchment outlet sediment sampling sites and known mineral occurrences, Thomson Orogen, New South Wales, Australia.



**Fig 2.** Geochemical map of Pb concentration in <180 μm fraction of the bottom outlet sediments (BOS), with known Pb occurrences, over the 1<sup>st</sup> Vertical Derivative of Total Magnetic Intensity image.

### Climate

The western portion of the Thomson project area is classified as desert, with rainfall <250 mm/yr. The eastern portion is classified as grassland, with rainfall 250-500 mm/yr (Caritat & Lech 2007). Summers are hot and dry, winters cool. Highly variable rainfall results in ephemeral streams, particularly in the west, and many of the creeks and rivers flow only during flood events, which can be significant events. The low-gradient, sinuous and anastomosing streams, creeks and rivers broaden to include flood plains often several kilometres wide. It is during these events that fine silts and clays from the upstream catchment are deposited on the floodplains.

### SAMPLING AND ANALYTICAL METHODS

Locations for the outlet sediment (overbank) samples are shown in Figure 1. In all, 99 catchments were sampled giving an average sample density of 1 site/1540 km<sup>2</sup>. At most sites three samples were taken: (a) a top outlet sediment (TOS) from 0-10 cm depth; (b) a bottom outlet sediment (BOS) from ~60-90 cm depth; and (c) a shallow outlet sediment (SOS) from 10-25 cm depth specifically for MMI determinations. Two size fractions (<180 µm and <75 µm) were prepared from the TOS and BOS samples. The SOS sample for multi-element MMI (MMI-M) analysis by method ME-MS17 was provided to ALS Chemex in its bulk form.

Field pH, Munsell soil colour (dry & moist), EC 1:5 (soil:water), pH 1:5, XRD, laser particle size analysis, XRF (multiple elements), ICP-MS (after HNO<sub>3</sub>/HClO<sub>4</sub>/HF/HCl digestion for multiple elements), ICP-MS (after HF/HCl/HNO<sub>3</sub> digestion for Se), ISE (for F), GF-AAS (for Au), and ICP-MS after MMI extraction were performed. Full details of the sampling and analytical methods are given in Caritat & Lech (2007).

### RESULTS AND DISCUSSION

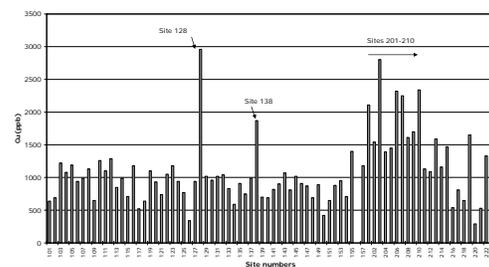
#### XRF and Near-Total Analyses

Areas with high metal concentrations mostly occur close to outcrops of

crystalline basement. There are high Cu values north of the Barrier Ranges (in the south-west of the study area), east of Tibooburra and north of Cobar. Cu concentration is generally higher in the BOS sample for both size fractions. Pb was determined by ICP-MS after four acid digestion and shows elevated concentrations in the <180 µm fraction of the BOS around Cobar, and near the Barrier Ranges in the south-west of the survey area (see Figure 2). Sb, also determined by ICP-MS after four acid digestion, is also high around Cobar and on the Yancannia map sheet in the central-west. Au, determined by GF-AAS, on the other hand does not show the same geochemical patterns in the two size fractions, and there is no consistent pattern across the Thomson region for this element by this method. This also applies to Ag by ICPMS after four acid digest.

#### Mobile Metal Ion Extraction

Systematic trends are shown after MMI extraction and analysis for a number of elements, including Cu, Au and Ag. Figure 3 shows the range of MMI values obtained for Cu in overbank (SOS) samples.

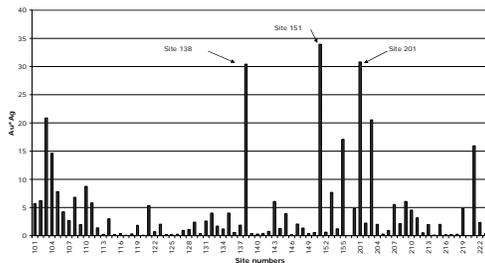


**Fig. 3.** Cu concentration in catchment outlet sediment samples after MMI extraction.

Large variations in catchment outlet MMI Cu values are evident. Sites 201-210, located in catchments with known mineral occurrences north of Cobar (Figure 1), have values above 1500 ppb Cu, over three times the “background” values of the lowest sites. Site 128, which has nearly six times the values of lowest sites, is in the middle west, and Site 138 is within the Tibooburra catchment, which includes the Albert Goldfield, a gold camp

with elevated values measured independently in lag and calcrete.

A multiplicative index is a powerful discriminator where two (or more) elements associated with mineralization are sought as geochemical indicators, since the index will only be strong where all selected elements are well represented. Figure 4 shows the multiplicative Au\*Ag index for overbank outlet sites after MMI extraction.



**Fig 4.** Multiplicative Au\*Ag index for catchment outlet sediment samples after MMI extraction.

Again there is considerable variation in values. Site 138, east of Tibooburra, again appears anomalous; this site is some 20 km east of the Albert Goldfield (elevated Au, Ag and Cu) where soils with MMI Au in excess of 100 ppb have been recorded within the same catchment. Sites 151 and 201 also have high Au\*Ag (Figure 4) and are located north of Cobar in the vicinity of known Au, Ag, Cu occurrences.

## CONCLUSIONS

- (1) A number of sites with anomalous catchment outlet sediment geochemistry are associated with catchments containing known outcropping mineral occurrences, confirming the value of the approach.
- (2) Not all catchments with known mineral occurrences have anomalous catchment outlet sediment geochemistry.
- (3) Partial extraction such as MMI analysis provides additional and distinct

geochemical information to that provided by strong acid and XRF analysis. This may be due to an improved signal-to-noise ratio (MMI analysis) for what is effectively 2D (surface) analysis versus three dimensional (bulk) methods.

(4) Active alluvial sites are normally avoided in prospect scale MMI analysis; in this case active alluvium has been used on purpose to obtain information representative of large catchments.

(5) Very low density sampling can provide reliable, representative geochemical information on a regional basis, with total and partial extraction data yielding complementary information.

## ACKNOWLEDGEMENTS

This work is published with the permissions of the Chief Executive Officer, Geoscience Australia, and the Executive Director, Mineral Resources, NSW DPI.

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## Five-Year History of a Biologically Based Treatment System that Treats High Concentrations of Effluent from an Industrial (Smelter Operation) Landfill

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**ABSTRACT:** For the past ten years, a biologically based engineered wetlands treatment system has operated in Trail BC, site of the worlds largest integrated lead zinc smelter. Effluent from an historic capped landfill is collected and delivered to a multi-cell engineered wetlands treatment system designed and operated by a private company. The system is unique in treating effluent at high concentrations (mean Zn concentration over 5 years is 268 ppm; mean As concentration is 168 ppm) year-round. A single source of carbon is used. The system is free of plugging (typically with metal sulphides) or short circuiting (effluent by-passing the matrix and therefore not treated). This paper examines metal removal and total loading, considers seasonal differences, analyzes a spike event ([Zn] > 3800, [As] > 3600), and suggests some of the potential biotic and abiotic removal mechanisms operating.

**KEYWORDS:** *treatment, effluent, Industrial smelter, landfill*

### INTRODUCTION

The use of passive systems to treat acid mine drainage was first suggested and studied in bench scale applications as early as 1978, (Government of Pennsylvania website, Science of Acid Mine Drainage), and more than 300 artificial wetlands to treat acid mine drainage were constructed in the U.S. between 1984 and 1990 (Wieder 1989). In 1990, it was suggested that the metabolism of sulfate-reducing bacteria (SRB) was the most useful biological process in wetlands designed to treat metal contaminated water (McIntire 1990). Anaerobic bioreactor systems were designed that maximized sulphate reducing bacterial populations and activity with an organic substrate to promote bacterial growth (McIntyre *et al.* 1990).

Although considerable effort has been applied to the development of these systems, there are many details of their operations that are not understood and longevity remains an issue (Neculita *et al.* 2007). Important characteristics required for a successful ABR design include the following:

1. Near neutral pH
2. Available carbon from an additional organic source
3. A solid matrix, (sand and/or gravel) around which SRB can establish micro-environments
4. An anoxic environment
5. A supply of sulfate sufficient that the sulphate reducing bacteria can out-compete other bacteria for the available carbon.
6. A means to physically retain the metal sulphides that are produced (Neculita *et al.* 2007):

Ideal designs have a depth between 0.6 and 1.5 M (Neculita *et al.* 2007) to reduce short circuiting. Vertical upflow is better than downflow (Tsukamoto *et al.* 2004). A hydraulic retention time of at least 3 – 5 days is optimal (Kuyucak *et al.* 2006). There are no reports on systems operating for extended periods (more than 3-4 years). Failures due to plugging, short circuits, and exhaustion of organic carbon are widely reported (Neculita *et al.* 2007).

This report is a five-year history that describes a system in Trail, British

**Table 2.** Mean concentrations removed over five-year period of operations showing break-down between ABR cells and plant based cells.

<b>Mean Concentrations at Input and Percentage Removed (2003 through 2007)</b>						
	<b>As (ppm)</b>	<b>% Removed</b>	<b>Cd (ppm)</b>	<b>% Removed</b>	<b>Zn (ppm)</b>	<b>% Removed</b>
<b>Input</b>	165.5		5.1		264.4	
<b>1st ABR</b>	18.5	88.8	0.8	84.4	65.3	75.3
<b>2nd ABR</b>	6.9	62.6	0.11	86.3	32.3	50.5
<b>Combined</b>		<b>95.8</b>		<b>97.9</b>		<b>87.8</b>
<b>1st Plant</b>	3.6	47.4	0.02	80.9	65.6	-102.9
<b>2nd Plant</b>	2.2	40.4	0.02	24.1	26.2	60
<b>Typha</b>	2.7	-24.3	0.03	-110.7	12.8	51.2
<b>Pond</b>	0.5	82.9	0.02	52.6	3	76.8
<b>Total %</b>		<b>99.7</b>		<b>99.7</b>		<b>98.9</b>

Columbia designed and operated by Nature Works for Teck Metals Limited. The system was constructed in 1997 and rebuilt in 2002 to operate year-round. It treats effluent from historic capped landfills. It is capable of treating effluent with high concentrations of metals Zn (up to 3800 ppm) and As (up to 3600 ppm). However, mean concentrations over a five-year period are lower (Zn 267.6; As 167.6). The system was designed to treat Zn, Cd, Pb and other metals based on bacterial reduction of sulfate. Bacterial processes for removal of Zn and some other cations were known to occur when the system was designed, but unexpectedly high concentrations of As were also removed. The mechanism for As removal is not yet clearly understood.

### Sampling and Analysis

Flow rate is monitored by in line flow meters. The leachate contains  $Zn_3(AsO_4)_2$  – a highly abrasive, relatively insoluble salt – leading to periodic pump burn-out. This results in a reduction in performance efficiency.

Regular sampling has taken place since 2002. Sampling frequency has not been consistent. It initially took place weekly during summer months; then weekly during spring and summer and bi-weekly during winter (when accessible); finally bi-weekly during summer and monthly during winter operations. Samples are tested in the field for pH, DO, ORP and  $[Fe^{2+}]$ ,

$[FeT]$ , &  $[SO_4^{2-}]$ . Samples are submitted to Teck analytical services where ICP-MS for total and dissolved metals is completed.

The system design is based on two upflow anaerobic bioreactors (ABRs) followed by three horizontal sub-surface flow (HSSF) wetlands cells. The water flows by gravity through the cells. Once treated, the water is stored in a holding pond and subsequently used for irrigation of a tree farm.

### Results

A spike event was used to determine the retention time of the cells. Data from the spike event, flow rate, and changes in metal concentrations in cells were considered, allowing calculation of retention time. Percentages were used as a normalizing function for data analysis.

Removal rates have been consistent over the five-year period showing that removal is not concentration dependent (Tables 1 & 2). The overall percentages of metals removed remain high at close to 99% for all years. The system design allows sampling of two distinct compartments: (ABRs) and the plant based treatment cells. Examining metal removal, it is apparent that much of the As, Cd and Zn are removed in the ABR cells (Table 2). Arsenic and Cd are removed at better than 95% in the two ARB cells, but Zn removal achieves only 88.7%. This table also shows occasional release of Zn and Cd from plant cells.

### Metal Removal and Metal Loading

The system has treated nearly 20,000 m<sup>3</sup> of metal contaminated water over 5 years. The concentrations of metals delivered to the system vary widely, with a drop in metal concentrations after the landfill was capped and after the arsenic was confined to a specially designed storage facility (Table 1).

The system was rebuilt in 2002, resulting in a reduction in the treatment efficiency. Metal removal was lower in 2003 following re-starting. Removal in the

**Table 1.** Mean input concentrations of contaminants showing levels of total and dissolved metals (in brackets).

Year	As	Cd	Zn
2003	108 (53)	4 (2.7)	266 (219)
2004	95 (13)	23 (1.3)	193 (101)
2005	534 (58)	17 (4.4)	709 (158)
2006	83 (27)	2 (0.5)	108 (46)
2007	23 (4)	1 (0.5)	62 (40)
Mean	168 (31)	5 (1.9)	268 (113)

ABR cells in 2003 was reduced by > 5% for As and by >10% for Zn.

Analyzing total metals sequestered in the system gives a measure of effectiveness. The system treats large volumes with high metal concentrations resulting in high total loading with high concentrations of metal retained. The total volume of material sequestered in the treatment system over 5-years is calculated by multiplying the flow rate for each year by the molar concentration of each contaminant. When this is done and the yearly totals are summed, the total weight of metals is 2990 kg of As, 85 kg of Cd and 7698 kg of Zn (more than 10,000 Kg).

### Seasonal Differences

The metabolism of SRB bacteria is not dependent on temperature (Tsukamoto et al, 2004), but there are definite seasonal variations observed in the system. Differences are small but statistically significant. The rates of removal for summer operations for As, Cd and Zn removal are 99.3, 99.4 and 99.2 %

respectively and 99.5, 99.2 and 98% for winter removal.

The One Way ANOVA test was used to determine statistical significance. Input concentrations between summer and the fall winter season were not significant; however, for dissolved As and Zn, total As and Zn differences were significant at  $p < 0.01$ .

### Spike Event

In Nov and Dec of 2005, high concentrations of Zn and As were released to the treatment system. In Nov., the concentration of Zn was 3800 ppm and As 3600. December. concentrations were Zn, 3000 ppm and As, 3000. By January, the concentrations were 260 ppm for Zn and 250 ppm for As.

The effect of the spike was to lower ABR removal efficiency from 99.5 to 81.4% for As, 99.5% to 97.2% for Cd and 94.5% to 83.5% for Zn. Overall removal efficiency decreased from 99.9% to 99.6% for As, 99.9% to 99.2% for Cd and 99.7% to 96.8% for Zn. Throughout this period SO<sub>4</sub><sup>2-</sup> continued to be removed and total loading for SO<sub>4</sub><sup>2-</sup> was reduced by 740 ppm. Differences between removal percentages were not statistically significant. Data shows that much of the Zn and As was initially retained in ABRs, but over time these elements were dissolved and released.

### Removal Mechanisms

It is possible that metal removal is the result of a mechanical process, with solid (Zn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>) removed by filtration. To examine this, we modeled mineral stability using a custom designed computer program.

At input concentrations, the results show that Zn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> is stable over a wide pH range (-4 – 9) and is the dominant mineral present. At lower concentrations in subsequent cells it is less dominant. In the pond it is not an important species. Over time in the ABR's and plant cells, Zn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> appears to dissolve. This can be shown by an increase in the concentration of dissolved As species above the levels entering each cell.

### Formation of Sulfides

It is necessary to use statistical procedures to assess chemical dynamics. The amount of Zn, As and  $\text{SO}_4^{2-}$  that are removed were compared using linear correlation analyses. Examining the output from each cell for removal of these metals shows a marked correlation between Zn and  $\text{SO}_4^{2-}$  in the 2<sup>nd</sup> plant cell and *Typha* cell ( $r^2 = 0.8$ ), before decreasing to  $\sim 0.6$  in the pond. This high positive correlation supports that the formation of ZnS (sphalerite) is an important aspect. Values for As are not as high.

### Orpiment Formation

One As removal mechanism is the formation of orpiment ( $\text{As}_2\text{S}_3$ ). To test for it specially constructed flow-through bags containing the same mixture as the cell matrix ("tea bags") were inserted into large vertical piezometers in each ABR cell and left there for a summer. On removal, they were frozen and shipped to the Argonne National Laboratory for analysis using high energy X-rays (XANES). Results confirm the presence of  $\text{As}_2\text{S}_3$  (orpiment) produced only when both As and  $\text{SO}_4^{2-}$  are reduced.

### DISCUSSION

Reports suggest ABRs should have a depth of at least 0.6m and not be more than 1.5m (Neculita *et al.* 2007). In Trail cells are more than 5 m deep operating continuously for six years without plugging or short circuiting. Trail has high [Zn] (268 ppm) without signs of bacterial die off. Neculita (2007) suggests multiple sources of carbon are essential for longevity whereas in Trail a single source of carbon – pulp and paper biosolids - is used. The biosolids are composed of short wood fibres and biota biomass from their biological-based treatment system.

Flow rates to the Trail wetlands are relatively consistent, although there is an overall decline in metal concentrations (Table1). Over a 5-year period the system has treated 20,000m<sup>3</sup> of effluent and sequestered more than 10,000 kg of metals. The high flow rate and concentration of metals sequestered,

combined with reaction of the system to the spike event are evidence of robustness.

Evidence from the spike event indicates that the residency time in our bioreactor is higher than observed in other systems – two weeks during peak summer capacity, longer than for other systems which report 3 – 5 days (Kuyucak *et al.* 2006). Analysis of the spike event showed that despite the potential effects of a short term increase in As concentrations,  $\text{SO}_4^{2-}$  and metals continued to be removed, albeit more slowly.

Data from 2003 shows that there is a period when the system first starts during which metal removal in the ABRs is reduced. But for the full system in 2003, removal rates are consistent with the full 5-year period. This illustrates the advantage of a multi-cell approach.

This ongoing removal of  $\text{SO}_4^{2-}$  shows that SRB metabolism continues despite reports of toxic concentrations of heavy metals (Poulson *et al.* 1997).

A substantial removal of metals during the spike event followed by a release over time from the ABRs is seen, it may be inferred that filtration, adsorption and subsequent mineral formation contribute to metal removal. Although adsorption plays a part in the removal of metals, sites on the organic substrate are likely to be quickly saturated.

Bacterial activity plays an important role in removal. This is shown from analysis of linear correlation statistics for removal of  $\text{SO}_4^{2-}$  and Zn, and  $\text{SO}_4^{2-}$  and As, as well as the formation of orpiment. Dissolution of  $\text{Zn}_3(\text{AsO}_4)_2$  also shows bacterial activity.

The Trail system has shown that it is possible to design and operate a system year-round that treats high concentrations of metals. In Trail, the contaminated water is treated to the degree that from the final holding pond it is used for irrigation of trees to be planted in areas near the smelter.

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## Urban geochemistry and health in New Orleans: Soil Pb, blood Pb and student achievement by 4<sup>th</sup> graders

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**ABSTRACT:** Rigorous attention to geochemistry and metal toxicology are critical to healthy and sustainable urban environments. Lead (Pb) is a well known neurotoxin, especially to very young children. During the 20<sup>th</sup> century enormous quantities of Pb were used in consumer products including paint and vehicle fuel additives. As a result, Pb was dispersed into cities worldwide and accumulated in especially large quantities within inner city environments. Using empirical data from New Orleans, this study illustrates the negative correlation between urban Pb geochemistry, children's blood Pb, and scholastic aptitude in elementary schools. In order to become an environment suitably healthy for children, New Orleans requires an extensive remedial effort to control Pb dust.

**KEYWORDS:** *built environments, children, human impact, neurotoxicity, soil survey.*

### INTRODUCTION

Urban environments are increasingly the major location for housing the human population. As a result, it is essential to pay rigorous attention to the geochemical characteristics of urban environments and to assess the contribution that the accumulations of consumer products play on human health. This study evaluates the urban geochemistry and health as it relates to the neurotoxic effects, as indicated by student achievement of 4<sup>th</sup> grade students, and lead (Pb) that has accumulated in New Orleans.

### METHODS

This study examines the relationships of a database consisting of soil Pb, blood Pb (BPb) of children 6 years and younger, and scholastic achievement rates of 4<sup>th</sup> grade students from the Louisiana education assessment program (LEAP 21) in New Orleans. The data was from years 2000-2005 and reflects the pre-Hurricane Katrina conditions of New Orleans. Prior to the flood, schools were organized by attendance districts or neighborhood schools. This arrangement provided the opportunity to conduct a series of statistical tests to evaluate the associations between soil Pb, BPb and

overall 4<sup>th</sup> grade GPA scores matched for 105 schools of pre-Katrina New Orleans (Zahran et al., 2009).

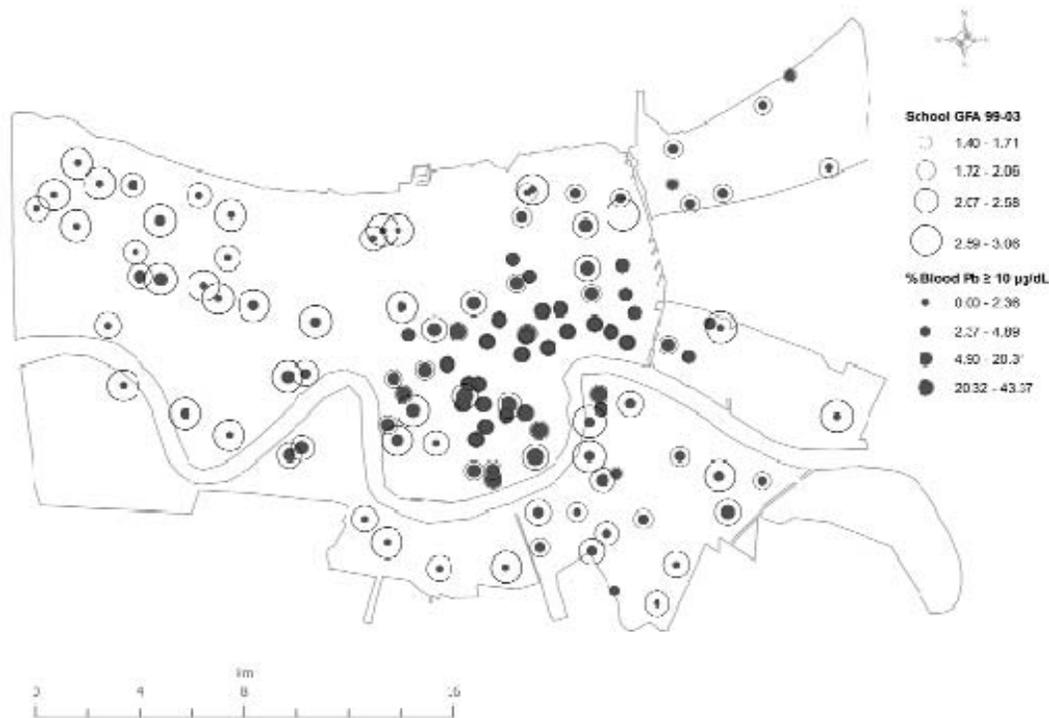
### RESULTS

A significant positive relation exists between soil Pb and blood Pb ( $r^2 = 0.85$ ,  $P < 0.0001$ ) (Zahran et al. 2009).

Figure 1 illustrates that blood Pb is inversely and significantly ( $P$ -values  $< 0.0001$ ) associated to school grade point average (GPA), that is, the average of English language arts ( $r^2 = 0.58$ ), Math ( $r^2 = 0.50$ ), Science ( $r^2 = 0.63$ ), and Social Studies ( $r^2 = 0.61$ ).

### DISCUSSION

Soil Pb is an important pathway of human Pb exposure (Mielke & Reagan 1998). Empirical evaluation between soil Pb and BPb indicated a strong positive and non-linear association between soil Pb and BPb (Mielke et al., 2007a). The soil Pb footprint of New Orleans indicates that in the case of public and private properties an enormous disparity exists between the inner-city and outlying areas of New Orleans that cannot be attributed to older Pb-based paint alone; dust Pb from the previous use of lead additives to gasoline provide a better explanation between



**Fig. 1.** Map of the quartiles of 4<sup>th</sup> grade school GPA and associated census tract % blood lead  $\geq$  10  $\mu\text{g}/\text{dL}$  (Zahran et al. accepted).

various areas of the city (Mielke et al., 2008). Poor African-American populations primarily live in the most Pb contaminated neighborhoods of New Orleans (Campanella & Mielke, 2008). Body burdens of Pb are especially large in the inner city where the childhood prevalence of blood Pb equal to or greater than the CDC 10  $\mu\text{g}/\text{dL}$  guideline is exceeded in many communities (see Fig 1). Within the communities with the highest blood Pb exposures, school failure rates exceed 50% in all subjects of the LEAP 21 scholastic achievement test.

Soil Pb is an enormous reservoir of Pb dust in the city and the quantity of Pb dust on the surface of the soil exceeds the quantity of Pb dust regulated in the interior by orders of magnitude (Mielke et al., 2007b). Soil Pb is mobile and during periods of low soil moisture such as late summer, significant increases occur in children's BPb compared with periods of high soil moisture (Laidlaw et al., 2005). Covering contaminated soil with clean soil is effective in reducing the amount of Pb on the soil surface and the cover appears stable, even after a major flood event (Mielke 2007; Mielke et al 2006a;b). An estimated \$US 76 million per year represents the costs of Pb poisoning in New Orleans (Mielke et al 2006a;b). These costs

underestimate costs related to the inequities of Pb poisoning because they exclude the cost of education and stresses from excessive violence (Zahran et al. 2009). Norway set precedence for a national program to systematically survey and remediate soil Pb and other contaminants which pose a threat to young children (Ottesen et al., 2008). A similar program should yield positive benefits to the children of New Orleans.

**CONCLUSIONS**

- (1) The built environment of New Orleans became severely contaminated by the enormous quantities of Pb released in the 20<sup>th</sup> Century.
- (2) Lead is a potent neurotoxin, and because children are exceptionally sensitive to lead dust during their early developmental years they must be protected from exposure.
- (3) The urban geochemistry of Pb is strongly associated with the blood Pb of children which in turn is associated with their learning outcomes.
- (4) During New Orleans post-Katrina recovery, the opportunity exists to improve the environment for the benefit of children's health, and promote education and the sustainability of the city. Norway's clean soil program provides precedence for this action.

(5) Urban environments, as the dominant location for most of the human population must be guarded against excessive accumulation of toxic substances, and the skills of geoscientists can assist with this endeavor.

#### ACKNOWLEDGEMENTS

Funding from Association of Minority Health Professional Schools / Agency for Toxic Substances and Disease Registry Cooperative Agreement 5 U50 TS 473408 to Xavier University of Louisiana; Blood Pb data contributed by Kathleen Aubin & Dianne Dugas, Section Environmental Epidemiology & Toxicology, LA Office Public Health, & Ngoc Huynh, LA CLPPP; LEAP from the Louisiana Department of Education.

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## Mercury concentrations in fungal tissues, as influenced by forest soil substrates and moss carpets

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**ABSTRACT:** This paper summarizes trends in mercury (Hg) concentrations in soils, mosses and fungal fruiting bodies of mixed forest locations in southwestern New Brunswick. The highest soil Hg concentrations occurred within the decomposing and humifying forest litter, but these concentrations decreased rapidly from the forest floor and A layers to the C layers in the mineral soil below. Hg concentrations in mosses and fungal fruiting bodies varied strongly by species, with further variations for the latter due to development stage (emerging, mature, over-mature), tissue type (stalk, cap) and sulphur (S) content, and the total Hg, S and carbon (C) concentrations within the mycelia-preferred soil substrates. All these variations make it difficult to use Hg concentrations in soils, mosses and fungi as broad-based indicators of environmental Hg pollution.

**KEYWORDS:** *Mercury concentration, forest soil, fungi, fruiting bodies, moss*

### INTRODUCTION

Hg is intricately distributed from the forest floor to the underlying mineral soil and subsoil (Grigal 2003). Vegetative uptake of Hg from the soil is generally low, except for some of the soil-based fungi that exploit organic soil substrates for readily metalized carbon (C) and nutrients such as nitrogen (N), phosphorus (P), Potassium (K), etc (Bending *et al.* 1995). The objective of this paper is to statistically relate the highly variable Hg concentrations within the upper soil layers (L, F, H, A) and in the fruiting bodies (mushrooms) of select fungal species to a number of factors. Factors include: (1) location according to a small but increasing atmospheric Hg deposition gradient (increasing from an inland location towards the coast and to an island), (2) soil layer types, namely the litter (L), fermentation (F), humifying (H) layers, and the A layer of the mineral soil, (3) the dominant moss type when present, (4) fungal species commonly found across southwestern New Brunswick.

### GEOLOGICAL AND REGIONAL SETTINGS

The areas selected for the study were forest locations in Fredericton, along the coast along the Bay of Fundy (Lepreau

and New River Beach) and on the island of Grand Manan. Bedrock formations underneath these locations vary but mostly refer to siliceous sedimentary rocks, covered by combinations of ablation till on basal till. Soils vary from thin podsoils on the uplands to gleysols on wetter locations. Forest vegetation is mixed, with red spruce, black spruce, white pine, balsam fir, aspen, white birch, yellow birch, red maple and sugar maple dominating the forest canopies. Moss cover varies from sphagnum on wet locations, feather mosses on moist locations, to plume and cap mosses and no mosses on drier locations. Atmospheric Hg inputs within the study region generally increase from north to south (NADP; Ritchie *et al.* 2006).

### METHODOLOGY

Soil (L, F, H, and A layers), mosses and fungal fruiting bodies were each collected from the same spots at the three locations. The L, F, H samples were ground to pass a 1 cm sieve; the mineral soil was sieved to retain its fine-earth 2mm fraction; mosses were separated into green versus dead tissues; the fruiting bodies were separated by stalk and cap. Subsamples were freeze-dried prior to

DMA-80 total Hg analysis, following the EPA 7473 method. The samples were also analysed for elemental organic C, N and S contents (LECO CNS analyzer). The resulting Hg concentration data were log-transformed, and were subject to multiple regression analyses that were originally developed for this study. The analysis includes using a host of independent variables as potential predictor variables, such as species type (mosses, fungi), tissue type (cap, stalk); development stage (emergent, mature, over mature), soil layer type (L, F, H, A), location (island, coast, inland), and C, N, and S contents.

## RESULTS AND DISCUSSION

Average elemental Hg, C, N, S concentrations and corresponding ratios are listed in Table 1 by tissue type and soil layer. The trends show highest in-soil Hg concentrations in the H layer, presumably on account of combined litter decomposition and strong Hg retention by the humifying substances. Across the soil layers, Hg concentrations and Hg/S ratios decrease strongly from the LFH layers to the C layers, while the Hg/C and Hg/N ratios increase with increasing soil depth. These trends suggest that Hg is concentrating at the soil-vegetation interface, and that Hg transfer into the deeper soil layers through biomixing and soil leaching is quite limited.

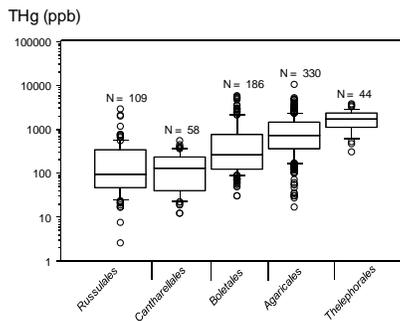
The generally high Hg concentrations in green moss tissues suggest an atmospheric source of accumulated Hg (Gjengedal *et al.* 1990). The higher Hg concentrations in Pleurozium under typically moist and dense forest covers would be due to an extra Hg capture by the forest canopy, and subsequent release to the moss carpet by way of throughfall and litterfall (St Louis *et al.* 2001). In this study, the lower Hg concentrations in Sphagnum would be related to more open forest and wetter ground conditions, while the lower Hg concentrations in Ptilium and Polytrichum would be related to the drier ground conditions in the forest interior of the sampling locations.

Across the fungal genera, average Hg concentrations range from 74 to 2161 ppb (Table 1), with large variations within family and species as well (details not shown). The overall trend by species refers to mycelial growth preferences, corresponding to LFH substrates and low Hg concentrations in Cantharellus, Cortinarius, and Russula, and to mineral soil substrates with high Hg concentrations in Amanita, Bankera, Boletus.

The variations of the within-soil Hg concentrations (Table 2) are, mostly significantly related to: (1) layer type, as characterized by the presence of the F and H layer relative to the L and A layers, (2) the combined depth of the L, F, H layer, with Hg concentrations decreasing as this depth increases, (3) location, with increasing Hg concentration from the inland location to the island, likely due to increasing atmospheric Hg deposition, (4) the total C and S concentrations within the soil, with Hg concentrations increasing with increasing S concentrations but decreasing with increasing C concentrations, (5) the carpeted presence of Sphagnum and Pleurozium mosses on the forest floor in comparison to other moss carpets or moss-free locations.

The Hg concentration variations within fungal tissues (Fig. 1) also follow a rather complex pattern (Table 3). For example, Cortinarius, Bankera, Cantharellus and Lactarius accumulate more Hg than what can be accounted for by variables such as: (1) the systematic stalk versus cap differences, (2) the reductions of the Hg concentrations from the emerging to the over-mature mushroom stage, (3) the C, Hg and S contents in the L, F, H, A layers, (4) the reduction of Hg uptake from soils with high S levels, (5) the increased Hg uptake from soils with high Hg concentrations, tempered by increased C concentrations.

The rather complex pattern of Hg concentrations in soils, mosses and fungal fruiting bodies makes it difficult to use Hg concentrations in these substrates as a general and unambiguous indicator of Hg



**Fig. 1.** Box plot for Hg concentrations (ppb, dry weight) in fungal fruiting bodies, by order.

toxicity derived from external Hg pollution loads. Among substrates, mosses are likely the best indicators of external Hg stress (Ruhling *et al.* 2004), but only under open, non-forested and non-shrubby conditions. Hg concentrations in fungal tissues are particularly variable, not only by species but also by substrate conditions, within-substrate Hg availabilities, and developmental stage of the short-lived fruiting body. The hyper-accumulation of Hg in the fungal fruiting bodies of *Bankera* and *Boletus* is of general interest in terms of being a notable Hg entry point into terrestrial food chains. In this study we suggest that loss of Hg from decaying fruiting bodies suggests a pathway of soil-retained Hg re-emission back into the atmosphere. The extent of such transfer, however, is not significant in terms of overall Hg gains and losses at the ecosystem level (details not shown).

## CONCLUSIONS

Hg concentrations in forest soils, mosses and fungal fruiting bodies are variable, and are influenced by many factors, such as the extent of forest-based capture of atmospheric Hg deposition, transmission of Hg from the forest canopy to the litter layer whether covered with mosses or not, and type of moss and soil layer conditions and configurations. Within the fungal fruiting bodies, further alternation of the Hg cycle occurs on account of mycelia substrate preferences and Hg allocation to stalk and caps, according to developmental stage.

## ACKNOWLEDGEMENTS

We like to thank Dr. David W. Malloch and the Forest Soil Laboratory team at UNB for valuable support during this study. This work was funded by Collaborative Mercury Research Network (COMERN), sponsored by the National Science and Engineering Council of Canada (NSERC).

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**Table 1.** Average Hg, C, N, S elemental composition by soil layer (Nasr 2007).

Substrate	Hg	C	N	S	C/N	C/S	Hg/C	Hg/N	Hg/S
	ppb		%				ppb / %		
<i>Sphagnum</i> ; shrubby, wet	152	50	1.50	0.15	33.3	333	3.0	101	1,013
<i>Ptilium</i> ; forest interior, dry	79	50	1.80	0.14	27.8	357	1.6	44	564
<i>Polytrichum</i> ; forest interior, dry	185	51	1.60	0.17	31.9	300	3.6	116	1,088
<i>Pleurozium</i> ; dense canopy, moist	267	49	2.00	0.18	24.5	272	5.4	134	1,483
L	141	50	1.60	0.13	31.8	419	0.3	9	116
F	260	45	1.60	0.16	29.1	292	0.6	17	169
H	299	37	1.50	0.16	26.2	267	0.8	20	212
A	110	10	0.50	0.05	23.7	235	1.5	28	350
B1	30	1	0.10	0.05	16.0	59	4.0	55	88
B2	18	1	0.10	0.04	11.9	34	4.4	45	56
C	7	0.1		0.06		3	11.4		13
<i>Cantharellus</i>	74	49	3.20	0.12	15.3	407	1.5	23	617
<i>Cortinarius</i>	192	45	4.70	0.17	9.6	273	4.3	41	1,164
<i>Russula</i>	242	48	4.40	0.18	10.8	260	5.1	55	1,322
<i>Hydnum</i>	249	47	3.80	0.12	12.4	396	5.3	66	2,092
<i>Tylopilus</i>	297	49	2.60	0.17	18.7	283	6.1	114	1,727
<i>Fuscoboletinus</i>	326	47	4.30	0.32	11.0	150	6.9	76	1,035
<i>Leccinum</i>	399	41	3.60	0.28	11.4	148	9.7	111	1,430
<i>Suillus</i>	431	49	3.90	0.18	12.5	272	8.8	111	2,394
<i>Lactarius</i>	482	46	3.90	0.13	11.7	341	10.5	124	3,597
<i>Amanita</i>	712	47	5.40	0.22	8.7	218	15.1	132	3,296
Bankera	1761	47	3.50	0.17	13.5	275	37.4	503	10,298
<i>Boletus</i>	2161	41	5.60	0.84	7.4	49	52.2	386	2,560

**Table 2.** Summary of regression results for Hg concentrations (ppb) in L, F, H, A soil layers.

Regression variable	Regr. coef.	Std. error	Std. coef.	t-value	p-value	R <sup>2</sup>	Partial corr.
Intercept	160.8	12.3	160.8	13.1	<0.0001		
F-layer (0,1)	89.5	6.9	0.4	12.9	<0.0001	0.221	0.41
H-layer (0,1)	137.1	14.8	0.3	9.3	<0.0001	0.321	0.31
LFH depth (cm)	-10.9	1.2	-0.3	-9.1	<0.0001	0.391	0.3
Location *	33.8	4.2	0.2	8.1	<0.0001	0.431	0.27
Total S (%)	588.2	76.5	0.3	7.7	<0.0001	0.454	0.26
Pleurozium (0, 1)	58.3	10.6	0.2	5.5	<0.0001	0.468	0.19
Sphagnum (0, 1)	44	8.2	0.1	5.3	<0.0001	0.485	0.18
Total C (%)	-1.2	0.3	-0.2	-4.5	<0.0001	<b>0.498</b>	0.16

Location: -1 for mainland, 0 for coast, 1 for island.

**Table 3.** Summary of regression results for Hg concentrations (ppb) in fungal tissues.

Regression variable	Regr. coef.	Std. error	Std. coef.	t-value	p-value	R <sup>2</sup>	Partial corr.
Intercept	0.8	0.1	0.83	7.99	<0.0001		
Developmental stage	0.3	0.03	0.27	7.81	<0.0001	0.114	0.408
<i>Cantharellus</i>	-0.8	0.11	-0.29	-7.41	<0.0001	0.245	-0.388
<i>Cortinarius</i>	0.3	0.05	0.25	6.75	<0.0001	0.338	0.358
<i>Russula</i>	-0.4	0.06	-0.24	-6.69	<0.0001	0.429	-0.355
Bankera	0.6	0.11	0.21	5.94	<0.0001	0.52	0.32
Cap (0), stalk (1)	-0.2	0.04	-0.19	-5.74	<0.0001	0.556	0.31
Location	0.3	0.05	0.21	5.31	<0.0001	0.582	0.289
<i>Polytrichum</i>	0.3	0.06	0.18	4.92	<0.0001	0.617	0.269
<i>Boletus</i>	0.9	0.18	0.16	4.86	<0.0001	0.641	0.266
Total S (F-layer)	-1.7	0.46	-0.14	-3.7	0.0003	0.654	-0.205

Development stage: 0 for emerging, 1 for mature, 2 for over-mature

## Hydrogeochemical processes governing the origin, transport, and fate of major and trace elements from mine wastes and mineralized rock

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**ABSTRACT:** The formation of acid-mine or acid-rock drainage is a complex process that depends on petrology and mineralogy, structural geology, geomorphology, surface hydrology, hydrogeology, climatology, microbiology, chemistry, and mining and mineral processing history. The concentrations of metals, metalloids, acidity, alkalinity, chloride, fluoride, and sulphate found in receiving streams, rivers, and lakes are affected by all of these factors and their interactions. Certain generalizations can be made that help to simplify our understanding of the origin, transport, and fate of contaminants released from mineralized areas. Waters of low pH tend to maintain element ratios indicative of the main mineral or group of minerals from which they dissolved, except iron and silica. Estimates of relative proportions of minerals dissolved can be made with mass-balance calculations if minerals and water compositions are known. Releases of drainage waters and ground waters from mines, waste rock, and tailings piles into receiving streams can be identified through synoptic sampling and discharges quantified through tracer-injection studies. Once dissolved, metal and metalloid concentrations are strongly affected by redox conditions and pH. Iron is the most reactive because it is rapidly oxidized by bacteria and archaea and ferric iron hydrolyzes and precipitates at low pH (2.2).

**KEYWORDS:** *acid-mine drainage, trace elements, geochemical modeling*

### INTRODUCTION

The processes governing the production of acid-mine drainage and drainage from unmined but mineralized areas are usually numerous and complex. Although there have been many laboratory studies on the oxidation of sulphide minerals during the last 2 decades, fewer field studies have been done showing the behaviour of major and trace elements during downstream transport in fluvial systems. Of greater concern is the limited transfer of hydrogeochemical research knowledge to remediation teams attempting to alleviate trace element contamination from water supplies. This abstract outlines some of the generalizations that can be made regarding the geochemistry of trace elements mobilized from mineralized areas into surface and ground waters and attenuation processes during down-gradient transport.

### GEOLOGIC CONSIDERATIONS

Element mobility begins with the rock, mineral, and processed mineral materials. Source rocks and host rocks can have a

wide range of composition and mineralogy from silicic to ultramafic igneous rocks and from limestone to black shale sedimentary rocks. Known element associations are helpful (Clarke 1924; Rankama & Sahama 1950): e.g., concentrations of Co, Ni, Cr, Mg, and Fe are higher in mafic to ultramafic rocks whereas Mo, Be, Sn, and W are higher in granitoid (silicic) rocks. Hydrothermal alteration can further concentrate these elements in sulphide minerals to form ore deposits. Understanding these associations is an important foundation for predicting which metals might occur at a given site (Plumlee 1999).

The geology not only provides the chemical source for trace-element mobility but it also provides the physical framework for water-flow paths. The structural properties of the rocks, the porosity, permeable fractures, provide for water-mineral reaction and element mobility. The geomorphology contributes to water-table levels, aquifer permeability, surface-water travel times, and time periods for erosion and sediment transport. Examples of

these can be found in the Questa baseline results (Caine 2007; Vincent 2008).

**HYDROLOGIC CONSIDERATIONS**

Dissolved constituents are driven by chemical reaction and the water flow. Hydrologic processes are particularly difficult to quantify in mountainous, hard-rock terrains but they can be essential for identifying and quantifying natural sources of contaminants (Nordstrom 2008). Streams, lakes, and rivers are the receiving water bodies for acidic drainage, and their water compositions depend on the composition and flow of surface and ground waters into them as well as the in-stream reactions (Kimball *et al.* 1994). In settings where a long-term flow of acidic ground water continues into a river that experiences increasing droughts, the river water quality will decline because of decreasing amounts of clean meteoric recharge (Nordstrom 2009).

**REACTION DURING TRANSPORT**

Elements can be grouped according to whether they react substantially (non-conservative) or react little (conservative) during downstream transport. In acidic waters (pH<4), metal cations stay dissolved generally except ferric iron and the more insoluble metals such as Au, Ag, Pb, and Ba. An example of constant weight ratios for Mn/Zn, Cd/Zn, and Co/Ni relative to changing sulphate concentrations in a single small debris-fan aquifer with pH 3-4 near Red River, New Mexico is shown in fig. 1. Constant ratios indicate there is no attenuation of metals during down-gradient flow while the sulphate concentrations become diluted through mixing.

The composition of the inflow water to the debris fan, natural acid-rock drainage of pH 2.5-3, was computed by mass balances to be derived from the weathering of the following minerals:

Gypsum . . . . .	3.78 mmol/kg
Pyrite . . . . .	8.66 mmol/kg
Dolomite . . . . .	4.64 mmol/kg
Kaolinite . . . . .	1.40 mmol/kg
Oligoclase . . . . .	0.44 mmol/kg
Fluorite . . . . .	0.20 mmol/kg

Sphalerite . . . . .	0.11 mmol/kg
Illite/Sericite . . . . .	0.032 mmol/kg
Chalcopyrite . . . . .	0.029 mmol/kg
Goethite . . . . .	-7.40 mmol/kg
Silica . . . . .	-2.89 mmol/kg

The negative sign refers to mineral precipitation instead of dissolution. Such computations are done with PHREEQC (Parkhurst & Appelo 1999). An inescapable conclusion of mass balances is that during the weathering of pyritiferous hydrothermally altered rock, iron and silica are precipitated.

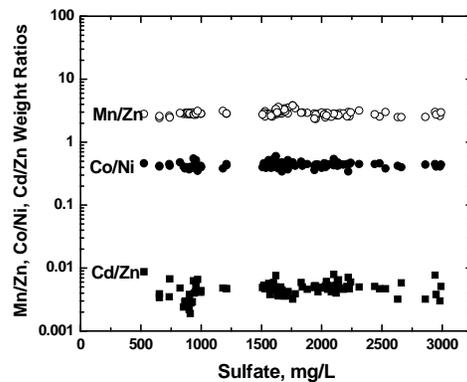
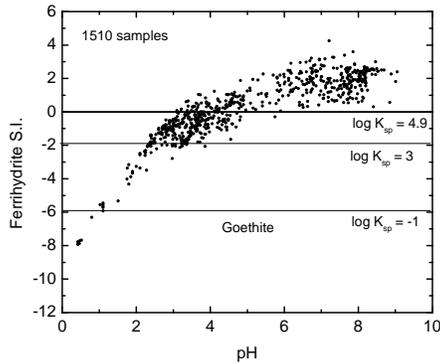


Fig. 1. Weight ratios for dissolved Mn/Zn, Co/Ni, and Cd/Zn in a single debris-fan aquifer of pH 3-4 and sulphate concentrations of 600-3000 mg/L (data from Naus *et al.* 2005).

**Fe(III) precipitation**

Oxidation of Fe(II) occurs rapidly at low pH but at measurable rates of about 1-5 mmol/L/h in surface waters by chemoautotrophic bacteria and archaea (Nordstrom 2003).

During the oxidation of dissolved iron and down-drainage neutralization of the acid water, hydrous ferric oxide (HFO) minerals precipitate, such as micro- to nano-crystalline goethite, schwertmannite, and ferrihydrite. The precipitate is usually a mixture of phases of uncertain composition and crystallinity. Using Fe(OH)<sub>3</sub>, or “ferrihydrite”, as a proxy for HFOs, more than 1500 samples of acid-rock drainage and receiving streams from locations in the western US were selected to calculate ferrihydrite saturation indices using WATEQ4F (Ball & Nordstrom, 1991). The results are shown in fig. 2.

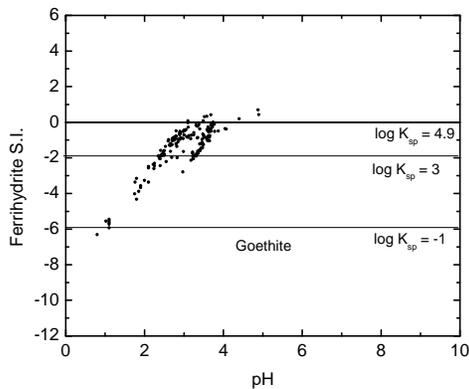


**Fig. 2.** Ferrihydrate saturation indices relative to pH for 1510 screened analyses from western US mine sites.

Supersaturation of up to nearly 4 orders of magnitude is indicated relative to a  $\log K = 4.9$  which reflects freshly precipitated HFO. When elimination of all data points which are below the detection limits for Fe(III) and for electrode measurements, values of Eh measured agree with Eh calculated from Fe(II/III) determinations and speciation calculations and the revised ferrihydrate saturation index diagram looks like fig. 3.

Saturation with respect to HFO is now seen to be maintained and the supersaturation seen previously is an artifact of HFO nanocolloids passing through the filter apparatus.

The 2 elements that are removed from solution most rapidly with iron oxidation and HFO precipitation are arsenic and



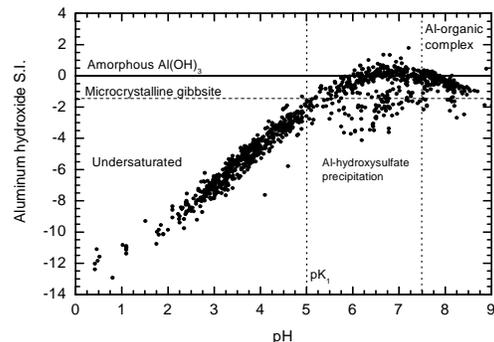
**Fig. 3.** Same as fig. 1 after removing all points below detection limits of Fe(III) and of redox electrode measurements.

thallium (Webster *et al.* 1994; unpublished data).

### Al precipitation

Aluminium also precipitates from acid surface waters when diluted or neutralized to a pH of  $\geq 4.5-5$  (Nordstrom & Ball 1986) because  $pK_1=5$  for  $Al^{3+}$  hydrolysis. For ground waters, there appears to be a buffering and precipitation of aluminium closer to a pH of 4 (Blowes *et al.* 2005; Naus *et al.* 2005). Using the same data set, saturation indices are plotted for  $Al(OH)_3$  in Figure 4. Three ranges of pH can be identified that describe aluminium geochemistry. For pH values  $<5$ , aluminium is conservative; for pH values of 5-7.5 a solubility limit is reached which corresponds to “amorphous”  $Al(OH)_3$  (or microcrystalline basaluminite, Bigham & Nordstrom 2000). For pH values  $> 7.5$  organic complexing likely dominates (Ball *et al.* 2005) and maintains concentrations higher than expected for microcrystalline gibbsite/kaolinite solubility.

Waters in fig. 4 that are substantially below the general trend are dilute surface waters that have not mixed with acid waters.



**Fig. 4.** Aluminium hydroxide saturation indices relative to pH for the same samples shown in fig. 1.

### Combining reaction with flow

Numerous codes are available that compute chemical reaction during flow provided that sufficient physical and chemical parameters are available (Nordstrom 2004). A practical approach has been developed by Kimball *et al.*

(1994) and Runkel *et al.* (1996) for surface waters affected by acid-mine drainage, transporting major and trace element contaminants in mountainous stream systems. First, synoptic sampling with tracer injection is used to obtain discharge values and mass loadings (Kimball 1997). Second, this data forms the basis for reactive-transport modelling (e.g., Caruso *et al.* 2008). Third, this approach can be used to evaluate remedial scenarios (Runkel & Kimball 2002; Walton-Day *et al.* 2007).

### CONCLUSIONS

This contribution summarizes state-of-the-science with respect to USGS research on the hydrogeochemistry of trace-element mobilization and attenuation from mineralized areas during transport in surface and ground waters. The primary aspects are:

- (1) geology forms the physical and chemical framework for solid sources of trace elements in mineralized settings
- (2) hydrology forms the physical and chemical framework for fluid mobility of trace elements
- (3) mass balances relates the partitioning of trace elements from mineral sources to the water
- (4) equilibrium solubilities provide an upper limit to dissolved concentrations of trace elements but formation of nanocolloids and organic complexing complicates interpretations.
- (5) combined reaction equilibria with fluid flow can offer practical approaches to understanding contaminant transport and to the evaluation of remediation scenarios.

### ACKNOWLEDGEMENTS

I thank Blaine McCleskey for assisting with preparation of the diagrams, Jim Ball for assistance with collection, analysis, and compilation of data, and the National Research Program and the USEPA for support of much of this research.

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## Geological controls concerning mercury accumulations in stream sediments across Canada

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**ABSTRACT:** This paper presents Geological Survey of Canada (GSC) data survey for mercury (Hg) concentrations in stream sediments ( $n \approx 144,000$ ) for select areas across Canada based on geological and topographic elevation differences between upland and lowland streams. Hg concentrations vary widely from 5 to 9,400 ppb per sample, with regional averages from 29 (central Nunavut) to 165 ppb (Vancouver Island, BC). An extensive cluster (100x400 km, oriented SE-NW) of Hg concentrations >4000 ppb is located in the east-central portion of the Yukon Territory. Regionally and locally, Hg concentrations tend to be consistently higher in upland streams than in lowland streams. The upland/lowland delineations were derived from coarse-gridded (national, 300 m) and fine-gridded (local, 30 m) digital elevation models (DEMs).

**KEYWORDS:** *Mercury concentrations, stream sediments, geological survey, upland/lowland delineation*

### INTRODUCTION

The upland/wetland transfer dynamics of mercury (Hg) across the landscape via streams and other flow channels pose health threats to aquatic ecosystems (Chasar *et al.* 2009). This paper presents select Geological Survey of Canada (GSC) data for Hg concentrations in stream sediments across Canada, with an overall intent to relate these data to local geographic, topographic, climatic and atmospheric Hg deposition conditions. Here, we explore how Hg concentrations in stream sediments relate to local bedrock type and its physical characteristics such as colour, texture and composition. Next, topographic elevation differences are examined through flow channel and upland/wetland delineations, using (i) the national 300m digital elevation model (DEM) and (ii) higher resolution DEMs including provincial DEMS and bare-ground LiDAR (Light Detection and Ranging) as primary delineation tools.

### GEOLOGICAL SETTING

The general framework for this study builds on national and provincial data layers of digitized, surface water features,

peatland inventory, digital elevation model, and bedrock geology, and raw data for atmospheric deposition (Hg), weather (mean annual precipitation, and mean monthly temperatures). The geological and lithological settings for each stream survey were assigned based on local bedrock type, by survey zone. Topographic flow accumulation, wet-area and cartographic depth-to-water (DTW) assessments were each obtained through DEM derivation (Murphy *et al.* 2009).

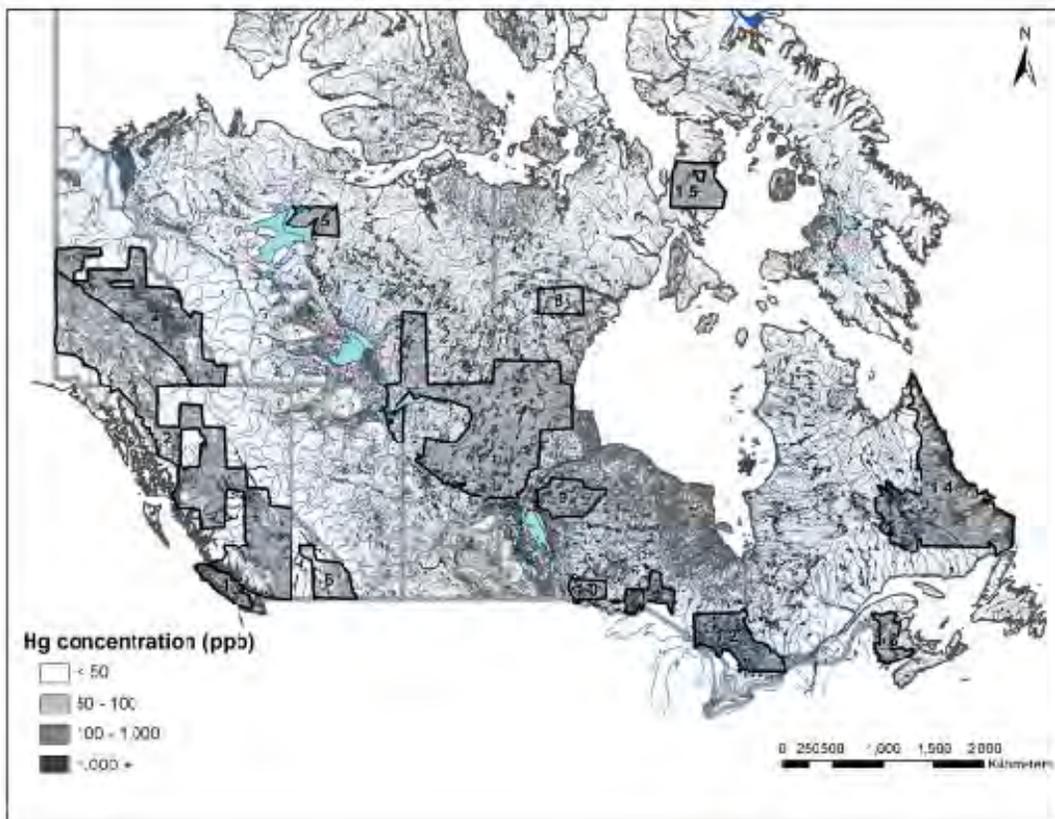
### MATERIAL & METHODOLOGY

Data were processed using ArcGIS to extract and interpret zonal statistics comparing Hg concentrations to stream sediment properties through geo-referenced map overlays. The following data-layers are examples: Canadian Landmass DEM (NRCAN 2007); Survey of Hg concentrations in stream sediments (NRCAN 2008); NASA SRTM DEM, CGIAR-CSI (2008); Surficial Materials of Canada (Fulton, 1995); Geological Map of Canada (Wheeler *et al.* 1997). These maps and associated data layers were compiled in ESRI shapefile (.shp) and layer (.lyr) formats within ArcMap GIS project files (.mxd).

**RESULTS**

The regional-based survey pattern of the GSC-determined Hg concentrations (ppb) in stream sediments across Canada is shown in Fig.1. Of particular interest are: (i) the high Hg concentration cluster near the central north-eastern border of the Yukon Territory (Survey Zone 3), (ii) the somewhat elevated background levels in the southern portions of the Canadian Shield along the Great Lakes, (iii) the scattered pattern of similar values throughout British Columbia, Labrador and

the Maritimes, and (iv) the generally low levels across the northern regions and lowland terrains. Average, lowest and highest values and associated standard deviations are listed in Table 1 according to survey region. This table also displays average upland-to-lowland Hg concentrations according to the nationwide upland-lowland, using the 300m DEM-grid delineation process. Fig.2 provides a local example for this process using the 30m DEM-grid delineation process.



**Fig. 1.** Outline of upland (white) / lowland (grey) delineation plus flow channels and lakes across Canada, based on the national DEM (300 m resolution), plus an overlay of the numbered regions (polyshapes with black outline) for the GSC stream-sediment Hg survey, showing Hg concentrations inside these regions, from white to dark grey.

**DISCUSSION**

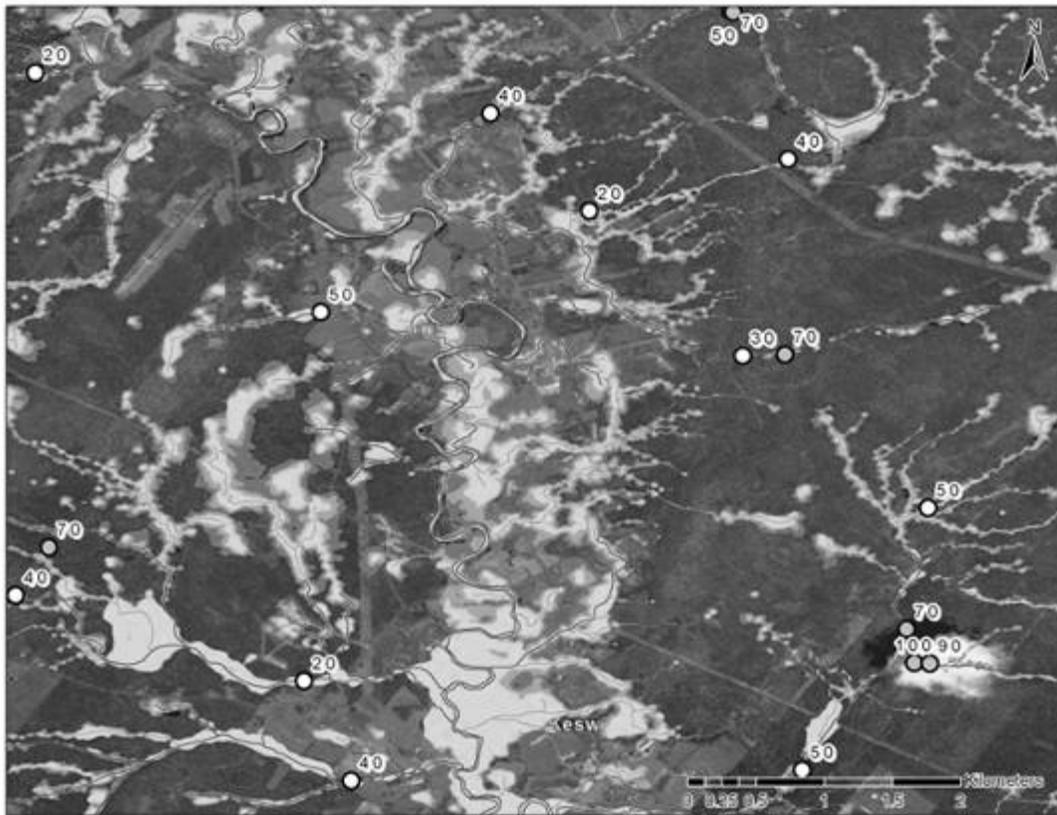
The results for the Hg concentrations in stream sediments presented in Fig.1 and Table 1 are preliminary, with more analyses to be done, and more GSC data to be added for Quebec, Newfoundland and Nova Scotia. On the whole, the

patterns are not directly related to the national Hg deposition pattern (details not shown), and are also not related to the global distillation pattern of volatiles, whereby Hg emitted from industrial and natural processes including forest fires from southern locations should incur an

increasing Hg presence within the arctic regions. The pattern of slightly lower Hg concentrations in lowland stream sediments would be due to lowland-specific Hg dilution and volatilization processes (Budd *et al.* 1993). This occurs in spite of the strong affinity between  $Hg^{2+}$  and dissolved organic matter (DOM, Bengtsson *et al.* 2008). However, DOM-transported Hg is subject to photochemically induced volatilization, which should increase with increasing sunlight exposure along widening stream channels and lake and river systems (Meng *et al.* 2005, Hall *et al.* 2008 & O'Driscoll *et al.* 2008). For the most part, in-stream Hg

concentrations are related to local mineralogies, with low concentrations associated with silicate and carbonate bedrock formations with no to few sulphide inclusions. In contrast, high Hg concentrations in stream sediments can be found in areas with elevated S mineralogies, such as Survey Zone 3 (Fig. 1), and areas with known ore deposits and mining activities (e.g., max. value for New Brunswick, Table 1).

The nationwide and regional pattern of Hg concentrations in stream sediments is of general interest because it establishes priority areas for further research



**Fig. 2.** An example of the upland/lowland delineation process, re-sampling the local 30m DEM grid to 10 m, with lowlands shaded from light to dark grey (corresponding to a cartographic depth-to-water index of 0 to 1 m, respectively) overlying the local air-photo mosaic. Also shown are the local GSC stream-sampling points (circles), with the stream-sediment Hg concentrations in ppb. Note the generally close correspondence between sampling points and the DEM-derived flow channels. Location: central New Brunswick, northwest of Fredericton (Keswick). The light area with a dark shadow towards the north-west in the lower right is a cloud.

**Table 1.** Hg concentration profile by survey zones and upland/lowland delineation (CV: coefficient of variation).

Survey zone (number)	n	Hg (ppb)				CV	Average Hg (ppb)		Upland/Lowland Ratio
		Average	Min.	Max.	StdDev		Uplands	Lowlands	
Nunavut, Central (8)	1,232	29	10	110	18	0.62	33	26	1.27
Nunavut, North-east (15)	2,118	44	10	150	20	0.45	45	43	1.04
British Columbia, East (6)	3,972	35	10	2,380	65	1.86	36	35	1.02
Manitoba, East (9)	5,111	45	10	801	21	0.47	49	44	1.1
Central Canada (7)	31,523	55	5	1,560	33	0.60	58	51	1.15
North West Territories, Central (5)	1,298	57	10	295	36	0.63	59	55	1.06
Yukon and BC, Rocky Mountains (2)	41,965	58	5	9,200	125	2.16	60	50	1.2
Ontario, ELA (10)	1,954	80	11	1,047	46	0.58	83	79	1.05
Labrador (14)	20,549	82	8	900	57	0.70	86	74	1.17
New Brunswick (13)	7,771	84	10	6,830	97	1.15	87	74	1.18
Yukon, east of Rocky Mountains (3)	11,372	110	8	5,950	149	1.35	113	96	1.18
Ontario, Central (12)	3,242	115	10	1,020	63	0.55	123	97	1.27
Ontario, Sudbury area (11)	9,157	126	10	5,000	101	0.80	131	117	1.12
British Columbia, Vancouver Island (1)	2,882	165	10	9,400	492	2.98	170	138	1.24
<b>Total</b>	<b>144,146</b>	<b>77.5</b>	<b>5</b>	<b>9,400</b>	<b>95</b>	<b>1.06</b>	<b>81</b>	<b>70</b>	<b>1.16</b>

regarding the transfer of Hg from uplands into rivers, lakes and local food chains, and the link between local geological structures and the health of fish-eating communities. The high-resolution delineation of local flow channels and adjacent wet areas also provides a new tool for (i) metal prospecting and related sampling strategies, (ii) interpreting local Hg deposition patterns, and (iii) hotspot visualization of Hg transfer and Hg methylation along upland-wetland transition zones (Mitchell *et al.* 2008).

### CONCLUSIONS

Mapping the GSC survey data for Hg concentrations in stream sediments in terms of local flow-channel and upland/lowland patterns provides a new means to evaluate these data in relation to local geologic and topographic conditions and configurations. Overlaying other geo-referenced data layers such as climate and atmospheric deposition maps including Hg deposition will reveal additional association-patterns between Hg in stream sediments and surrounding factors.

### ACKNOWLEDGEMENTS

This work is a collaboration between Environment Canada, NRCAN- GSC and UNB, and is financed through the CARA program of Environment Canada. Administrative and general support from T. Clair, CWS, Sackville, NB, is gratefully appreciated.

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## Quantifying hydrothermal, groundwater, and crater lake contributions to the hyperacid Banyu Pahit stream, East-Java, Indonesia

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**ABSTRACT:** Hyperacidic fluids from Kawah Ijen volcano (East-Java, Indonesia) contaminate the surrounding environment with high concentrations of potentially toxic elements. These fluids are released through the Banyu Pahit stream, which is used to irrigate farmland on the outer flanks of the Ijen caldera complex. This study has identified the sources of fluids contributing to stream flow in the uppermost 4 kilometers of the Banyu Pahit, including sources that are unaccounted for in previously reported studies of the Ijen magmatic-hydrothermal system. Detailed chemical analyses of these different source fluids (the crater lake and all neutral and acid springs) and of the stream itself at regular intervals indicate that volcanogenic input to the stream is not limited to seepage from the crater lake, but also includes significant input from the hydrothermal system via hot, hyperacidic springs located 1 and 3 kilometers from the crater. Springs may represent an important source of element flux to the surrounding environment. Their hydrothermal characteristics suggest that hyperacidic fluids may be used as a monitor of volcanic activity.

**KEYWORDS:** *hydrochemistry, volcanogenic pollution, acid brine, Kawah Ijen, Banyu Pahit*

### INTRODUCTION

Active volcanoes are sites of complex and dynamic hydrologic systems involving interactions between hydrothermal and magmatic fluids, groundwater, and surface water. Volcanic activity can produce high levels of natural pollution and often is accompanied by fluids having levels of toxicity similar to those of acid mine drainage, i.e., greatly exceeding WHO guidelines for human health (Edmunds & Smedley 1996; Sriwana *et al.* 1998; Delmelle & Bernard 2000). These fluids flow from crater lakes and hot springs into the surrounding environment and have strong negative impacts on human health and on the ecosystem (Parnell & Burke 1990; Pringle *et al.* 1993; Schaefer *et al.* 2008; Löhner *et al.* 2005). Understanding the hydrologic processes that control the sources, transformations, and distribution of these toxic fluids is necessary to assess their impact on local surface and groundwater resources (Rowe *et al.* 1995). Potentially, the temporal changes

in the chemistry of these fluids can also serve as monitors of volcanic activity.

This study examines the pollution of surface water by Kawah Ijen volcano, Indonesia. The headwaters of the hydrologic system from this volcano, a hyperacid brine lake, are conspicuously different in composition from the downstream waters. The objective of this study is to characterize and quantify the hydrologic processes that control the observed changes in the chemistry of the downstream waters. Results from hydrochemical analyses of the Kawah Ijen Crater Lake, Banyu Pahit stream and adjacent springs, including some previously unstudied springs explains the evolving chemistry of the Banyu Pahit in terms of a clearly identifiable set of sources and sinks.

### STUDY SITE

#### Banyu Pahit Stream System

Kawah Ijen is located on the eastern rim of the Ijen caldera in East Java, Indonesia (Figure 1). The crater of the volcano hosts

the world's largest naturally-occurring hot, hyperacid lake, with a volume of approximately  $32 \times 10^6 \text{ m}^3$  (Delmelle & Bernard 2000; Delmelle *et al.* 2000). Magmatic and hydrothermal fluids continuously condense into the lake, maintaining the very low pH ( $\approx -0.01$ ) and high temperature ( $\approx 38^\circ\text{C}$ ). Heavy metals in the lake water are present in elevated concentrations due to extensive rock dissolution in the acid brine (Delmelle &

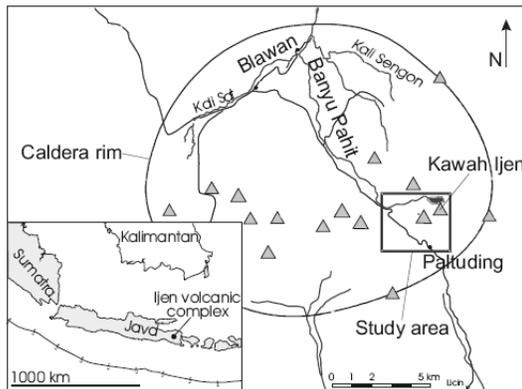
Bernard 1994; Delmelle *et al.* 2000). The lake water seeps through the flanks of the crater forming the headwaters of the Banyu Pahit stream (Figs. 1 & 2) which flows northward across the larger volcanic complex, and passes through the town of Blawan 17 km downstream before exiting the caldera and flowing across agricultural plains, where it is used for irrigation, and then to the ocean (Fig. 1). Although hydrochemical measurements show dilution of the toxic lake water by other sources along the Banyu Pahit stream, notably by two major tributaries near the town of Blawan, heavy metal concentrations and pH remain at toxic levels and pose major risks to health of the local population and ecosystems downstream (Delmelle & Bernard 2000; Löhr *et al.* 2005). Fluxes of toxic elements remain high further downstream, but despite this, the waters are still used to irrigate the agricultural plains (Delmelle & Bernard 2000)

Almost nothing is known about the uppermost 4 km of the Banyu Pahit stream due to difficult field access, although differences in stream composition across this interval have been reported. van Hinsberg (2001) suggested three potential explanations for the observed changes: 1) dilution by another fluid source, 2) fluid-rock interaction, and 3) mineral precipitation.

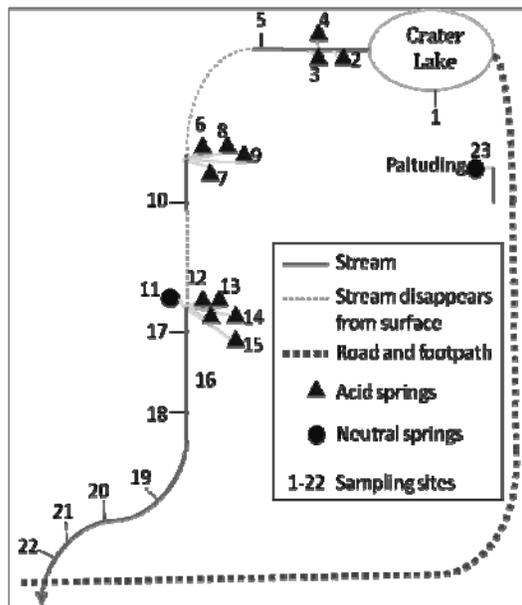
### SAMPLING AND ANALYTICAL METHODS

#### Field Work

Water samples were taken at 23 sites along the uppermost 4 km of the Banyu Pahit stream in July and August 2008 (dry season); from two clusters of acid springs adjacent to the stream (6-9 and 12-15), groundwater in the Banyu Pahit canyon (11) a neutral spring near Paltuding (23), the Kawah Ijen Lake (1), and at regular intervals of the Banyu Pahit stream (Figure 1, 2). Samples were filtered at  $25 \mu\text{m}$  into sample-rinsed 60 mL polypropylene bottles. Neutral samples were acidified with 2 drops of 18% nitric acid when fluid pH was less than 2. At each sampling site, pH, temperature, and electric conductivity were measured. At



**Fig. 1.** Overview map of the Ijen caldera, East Java, Indonesia.



**Fig. 2.** Schematic diagram showing the locations of sampling sites along the Banyu Pahit stream and those of nearby neutral and acid springs. The distance from the lake to Sample site 22 is approximately 4 km.

selected sites, aluminum, iron, and chloride concentrations were determined on-site by colorimetry. Stream discharge was also measured at regular intervals along this stretch of the stream.

**Chemical Analyses**

Concentrations of major cations in all samples were determined by acetylene flame Atomic Absorption Spectroscopy at the Trace Element Analytical Laboratories (TEAL) of McGill University. Analyses of trace element concentrations were carried out using Inductively Coupled Plasma Quadrupole Mass Spectrometry (also at TEAL). Concentrations of anions were determined by Ion Chromatography at the Hydrogeology Laboratory at McGill University.

**Observations and Discussion**

Table 1 illustrates concentrations and estimates of the total daily flux of selected elements out of the Kawah Ijen Lake into the Banyu Pahit stream, based on measurements from the 2008 field season. Also reported are concentrations and estimated daily fluxes for the downstream Banyu Pahit, near the town of Blawan.

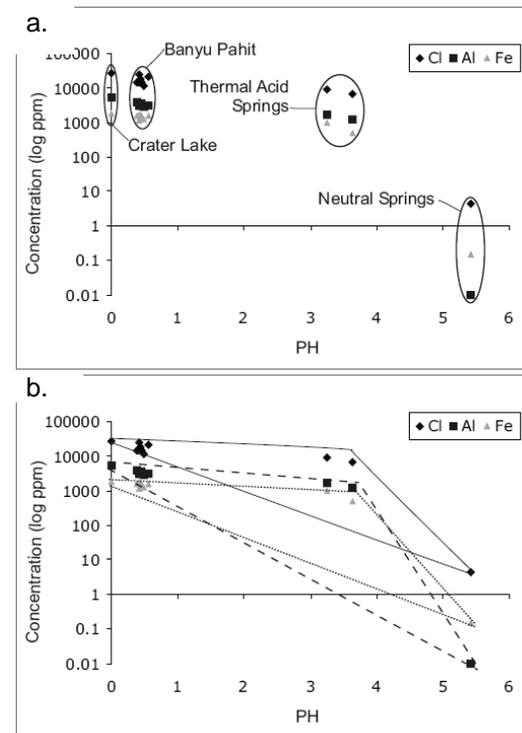
Exploration of this remote, previously understudied, section of the Banyu Pahit

**Table 1.** Concentrations and estimated daily fluxes of Al, Cd, and F through the Banyu Pahit stream system, based on approximate stream discharges of 60 L/s (from the Crater Lake) and 4000 L/s (near Blawan; from Delmelle & Bernard, 2000).

	Crater Lake		Banyu Pahit (near Blawan)	
	Concentration (ppm)	Estimated Daily Flux (kg d <sup>-1</sup> )	Concentration (ppm)	Estimated Daily Flux (kg d <sup>-1</sup> )
Al	5740	29,740	25.1	8,600
Cd	0.06	0.3	0.001	0.3
F	727	3,770	7.3	2,520

stream during July and August, 2008, provided two key observations which suggest a more complicated hydrologic system than previously realized. Firstly, the stream flows subterraneously for tens to hundreds of meters along two reaches. Secondly, a number of previously unobserved springs contribute to the flow of the Banyu Pahit stream. Based on preliminary colorimetric measurements, these springs show a distinct chemical grouping (Fig. 3a), which we interpret as neutral groundwater springs, acid springs with a hydrothermal component, and seepage from the crater lake. The Banyu Pahit, downstream of these springs, is demonstrably a mixture of crater lake, groundwater and thermal acid spring fluids (Fig. 3b).

It was also observed that acid fluids seem to be restricted to the Banyu Pahit



**Fig 3.** Chemical groupings of upstream Banyu Pahit source fluids, based on on-site colorimetry (crater lake, thermal acid springs, neutral spring and stream) (a). Mixing curves for the same groups (b).

stream valley and that springs of acidic composition only emerge along the southern side of the valley. Neutral springs were observed at the same elevation as some of the acid springs, but emerge only on the northern side of the valley. This could have important implications for constraining the boundaries of the hydrothermal system, understanding groundwater flow, and examining groundwater-hydrothermal system boundaries.

### CONCLUSIONS

The main conclusions from the current study are that:

(1) The Banyu Pahit stream is much more complex than previously thought, due to the input of neutral and acid spring water.

(2) Volcanogenic environmental contamination via the Banyu Pahit stream can be attributed to the hydrothermal system as well as Kawah Ijen Lake seepage, and models of the system must account for both.

(3) The hyper-acidic water seems to be contained within the Banyu Pahit stream valley, potentially constraining the extent of the Ijen hydrothermal system and placing important constraints on the hydrology of the Banyu Pahit valley.

Further chemical characterization of different sources of fluids to the upstream Banyu Pahit and quantification of their contributions will follow. These results will be used in conjunction with fluid-rock modeling of this section of the stream and discharge measurements in an end-member mixing analysis to quantify the respective contributions to the Banyu Pahit stream of crater lake seepage, hydrothermal fluids and groundwater. Detailed geological mapping of the stream valley by van Hinsberg during this same field season will help refine models of fluid-rock interaction.

### ACKNOWLEDGEMENTS

We would like to thank Glyn Williams-Jones, Nathalie Vigouroux, Guillaume Mauri, Eline Mignot, and Carole Gilbert for assistance, guidance and inspiration,

Jean-Francois Hélie, Bill Minarik, Glenna Keating, and Isabelle Richer for assistance with various chemical analyses, and Michel Baraer and Bernardo Brixel from the Hydrogeology lab group at McGill University. The research was supported by an NSERC Discovery grant to JMM and AEWJ.

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## Land use/land cover influences on the estimated time to recovery of inland lakes from mercury enrichment

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**ABSTRACT:** Sediment chronologies have been demonstrated to be reliable archives of the environmental record of mercury (Hg). We questioned if chronologies could be used to investigate the stressors related to time to recovery (TTR) from mercury enrichment to multiple future system states. Sediment cores from 30 inland lakes of Michigan were collected between 1999 and 2005, analyzed for total Hg, and dated using 210-lead. Linear models of recovery were calculated based on most recent decreasing trends of concentration or Hg flux to estimate the time required to reach geochemical background concentration and flux and current rates of Hg deposition. Predicted TTR were then compared to current watershed attributes. Results indicate that estimated TTR for background concentrations is positively influenced by agricultural and forested land use found along flow paths to the lakes. Whereas, urban land use along flow paths and watershed to lake area ratio may be more influential when compared to current wet deposition measurements. There were far weaker relationships between TTR and local Hg emission rates, suggesting that the watershed pathway may play a more significant role in the recovery of these systems.

**KEYWORDS:** mercury, 210-lead, land use, recovery, sediment chronologies

### INTRODUCTION

Anthropogenic activity has lead to Hg contamination of aquatic systems in the most remote places on the surface of Earth (Fitzgerald, *et al.*, 1998). This is due, primarily, to its unique physical properties that allow long range transport of Hg and deposition far from the original source. Due to its threat to ecological and human health in its methylated form it is important to understand the sources and pathways of Hg to aquatic systems. Sediment chronologies have been demonstrated to be reliable archives of the environmental history of lakes (Engstrom, *et al.*, 1994) and have been used to document the enrichment of Hg in aquatic systems due to human activities (Benoit, *et al.*, 1998; Swain, *et al.*, 1992). Sediment chronologies have been useful both for scientific inquiry and environmental management. For example, information from sediment chronologies demonstrates that removal of Pb from gasoline has resulted in the decreased loading to the environment since the enactment of environmental legislation in

the 1970s. Furthermore, it is suggested that abatement technologies for nitrogen and sulphur species has lead to the decreased emission of Hg from coal-fired power plants, this combined with decreased consumption explaining the decreased concentrations and loadings found in recent sediments of inland lakes (Engstrom & Swain, 1997). Therefore, since sediment chronologies have been used to demonstrate the environmental record of Hg accumulation we question whether they can be used to understand environmental recovery of the watershed.

Environmental recovery is commonly defined as a return of the system to a previously undisturbed state. Using sediment geochemical chronologies the previous undisturbed state can be determined graphically as the geochemical background concentration prior to anthropogenic disturbance. In the US, geochemical background concentration is usually defined as the concentration in sediment prior to European settlement ca. 1800. However, until environmental legislation is enacted

worldwide to eliminate Hg emission, geochemical background concentrations may not be an achievable system state. A better approach may be to consider different system states as more achievable scenarios. For this work we consider three separate definitions of system recovery 1) geochemical background concentrations, 2) geochemical background fluxes and 3) current rates of Hg wet deposition. Time to recovery from Hg contamination was then estimated using a linear model based on the most recent decreasing trajectory.

The primary pathway of Hg to aquatic systems is considered to be atmospheric transport and subsequent deposition, which has caused an accumulation of Hg in watershed soils (Mason, *et al.*, 1994). Recent work has shown that watershed disturbance such as clear cutting results in the increased export of Hg from the watershed to aquatic systems (Porvari, *et al.*, 2003) and others have found agricultural and urbanized land use to be important factors influencing Hg export (Fitzgibbon, *et al.*, 2008; Mason & Sullivan, 1998). Thus the recovery of aquatic systems from anthropogenic Hg may depend on watershed characteristics which will differ among watersheds. Therefore we compared time to recovery to watershed attributes (e.g., %urban, susceptibility to erosion, watershed to lake area ratio, etc...) to test the hypothesis that the rate of recovery from Hg enrichment is influenced by watershed controlled pathways and stressors.

### STUDY AREA AND METHODS

The State of Michigan spans a large geographic range and contains more than 10,000 lakes that vary in watershed land use from highly urban in the Southeast to agricultural watersheds midway through the state and highly forested watersheds in its Upper Peninsula. Between 1999 and 2005 30 sediment cores were collected aboard the Environmental Protection Agency R/V *Mudpuppy* or Michigan Department of Environmental Quality M/V *Nibi* using an Ocean Instruments MC-400 Lake/Shelf

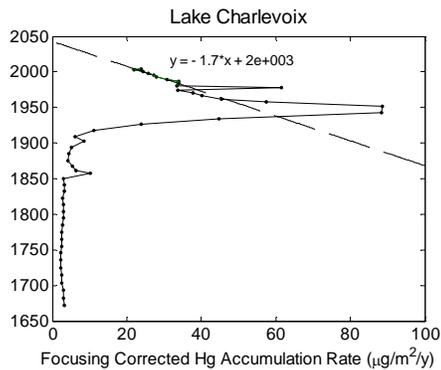
Multicorer. The MC-400 collects four simultaneous cores two of which were analyzed for total metals and 210-lead, respectively. Details of field methods, Hg analyses and 210-lead interpretation can be found elsewhere (Parsons, *et al.*, 2007).

Watershed attributes were determined using Arcview. Watersheds were delineated using the *watershed* command in ArcView on National Elevation Dataset digital elevation models (DEM) from the United States Geological Survey (USGS, 2008). Landuse/land cover data were obtained from the Michigan Geographic Data Library (MDNR, 2002). Soils data were taken from the United States Department of Agriculture's State Soil Geographic Database (USDA, 1994). Mercury emissions for the State of Michigan were obtained from the National Emissions Inventory for 2002 (Granke, 2006). Mercury deposition at the lake location was estimated by interpolation of regional wet deposition flux data for 2007 obtained from the Mercury Deposition Network (Illinois State Water Survey, 2008). Statistical analyses were performed in R<sup>®</sup>.

### RESULTS

Of the 30 lakes that were cored 9 reached geochemical background concentrations and had current concentrations and/or fluxes that are decreasing to present. Five additional lakes that did not reach geochemical background were included for comparison to current wet deposition. Linear models of recovery were estimated on the most recent decreasing trend of concentration and/or flux and by ignoring episodic or short term increases in fluxes or concentrations (Fig. 1).

Time to recovery (TTR) was calculated as the difference between the estimated time to system state (e.g., current wet deposition) and the year the lake was sampled. TTR varied from 0 to more than 134 y for recovery to wet deposition, from 8 to 168 y for background flux and from 9 to 70 y for background concentration. There was no consistent pattern among the estimates of TTR, that is, no single



**Fig. 1.** Focusing corrected Hg accumulation rate for Lake Charlevoix.

definition of recovery (e.g., wet deposition) always produced the greatest TTR. However, of the 6 lakes in which all three recovery states were able to be calculated background concentration was greatest in 4 of them.

Correlation coefficient p-values were calculated and are shown in Table 1 for a select group of watershed attributes. Background concentrations were significantly correlated to flow-inverted agricultural land use. Flow-inverted landuse (FLI) is the product of the inverse of the flowlength, determined using the *flowlength* command in ArcView, and individual land use. This calculation provides more weight to those land uses along flowpaths and/or close to the lakeshore. Similarly flow-inverted-squared landuse (FLI2) was calculated as the inverse of the product of the inverse of the squared flowlength and individual land use. Background concentration was also significantly correlated to Forest FLI2. Wet deposition TTR was most highly correlated to Urban FLI2, but only when a subset of the original data was used. There was also a significant correlation between watershed area and TTR to wet deposition. Background flux showed significant correlation to watershed to lake area ratio, but only when the highest TTR was removed from the dataset. Results of Hg emissions, from Michigan industry, within a 25 km radius of the lake centre are shown in Table 1. Although not shown, the 25 km data are consistent with emissions calculated at 10, 50, 75, and

**Table 1.** P-value correlation matrix of TTR for selected watershed attributes. Watershed attributes significant at  $p < 0.05$  are shown

Attribute	Wet	BG	BG
	Dep	Conc	Flux
Ag FLI	0.66	<b>4E-5</b>	0.83
Urban FLI	<b>3E-3</b>	0.10	0.80
Forest FLI2	0.29	<b>8E-3</b>	0.32
Hg.25	0.85	0.11	0.72
Watershed Area	<b>3E-3</b>	0.18	<b>0.015</b>

100 km radii in that no significant correlations at the  $p < 0.05$  level were found. Additionally, no single watershed attribute was consistent across all definitions of recovery at  $p < 0.05$ .

## DISCUSSION

Previous work has shown that urbanization and agricultural land uses increase the flux of Hg to river systems through the increase of impervious surface and erosion of soils, respectively (Mason & Sullivan, 1998). Thus, the correlation of TTR using background concentration to agricultural FLI might be expected, but the relationship was not manifested in the percentage of agricultural landuse within the watershed as it was in previous work (Fitzgibbon, *et al.*, 2008; Lyons, *et al.*, 2006). Rather this work indicates more specifically that it is those agricultural landscapes that lie along flowpaths to the lake that provided the better correlation. This suggests a significant pathway for Hg to inland lakes and may help in the management of watersheds. Although flowpath-based relationships have been found for sediment based work (Randhir & Hawes, 2009), to the authors knowledge these relationships have not been demonstrated for mercury's pathway to lakes. The poor correlation to emission of Hg within the State of Michigan provides further evidence for watershed attributes as important stressors for TTR, but may also indicate that the emission source variable needs to be broadened to regional scales or calculated using geometry other than circular geometry. The absence of a single consistent watershed attribute across all definitions of recovery suggests a change

of source from short (i.e., wet deposition) to long TTR (i.e., background concentration). This may be indicative of long term storage in agricultural and forest landscapes versus short term storage in more urban landscapes.

## CONCLUSIONS

The expected recovery time for lakes enriched by anthropogenic Hg additions varies based on the definition used for recovery. Watershed attributes (e.g., Ag FLI) were found to be important stressors and more highly correlated to TTR than Hg emissions within the State of Michigan. This suggests that a watershed approach should be considered when dealing with the recovery of environmental system and that reducing Hg emissions alone may not result in reduced fluxes of Hg to aquatic systems.

## ACKNOWLEDGEMENTS

We would like to thank: the Michigan Department of Environmental Quality for the funding of this work; the captain and crew of the R/V *Mudpuppy* and M/V *Nibi* for their assistance in core collection and Paul Wilkinson of the Freshwater Institute for help in the analysis and interpretation of 210-lead results.

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## Potential for contamination of deep aquifers in Bangladesh by pumping-induced migration of higher arsenic waters

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**ABSTRACT:** Recognition of arsenic (As) contamination in shallow, geochemically reducing aquifers in the Bengal Basin has resulted in increasing exploitation of groundwater from deeper aquifers that are generally more oxic and contain low concentrations of dissolved As. Pumping-induced infiltration of high-As groundwater could eventually cause As concentrations in the deeper aquifers to increase. Laboratory batch and column experiments on oxic sediments from a site near Dhaka, Bangladesh were used to identify and quantify geochemical reactions that could control transport of As and other constituents in contaminated groundwater through these sediments. Results from these experiments were used to simulate the potential rate of As transport through the oxic aquifer at the sampling site using the reactive-solute transport model PHAST, which couples hydrologic flow with geochemical reactions. Initial As concentrations in the simulations were 900  $\mu\text{g/L}$ . Interstitial velocity of contaminated groundwater through the oxic aquifer ranged from 3 m/yr to 30 m/yr. Modeling results showed that As reactions with sediments slowed the movement of As through the oxic aquifer to a rate of 0.01 m/yr for an interstitial velocity of 3 m/yr, and 0.22 m/yr for a velocity of 30 m/yr. Results from these experiments show that the oxic sediments have a significant but finite capacity to remove As from solution. Therefore, well screen depth below the anoxic/oxic boundary as well as rate of withdrawal need to be considered in locating new wells in low-As aquifers.

**KEYWORDS:** *arsenic, groundwater, Bangladesh, sediment reactions, transport modeling,*

### INTRODUCTION

Arsenic concentrations in shallow alluvial aquifers of the Bengal Delta Plain often exceed 10  $\mu\text{g/L}$  and are a major health concern for the millions of people who rely on these aquifers for drinking water. These aquifer sediments are typically reducing and gray in color. In solution arsenic occurs predominantly as As(III) along with some As(V). Drilling and coring in some parts of Bangladesh by the U.S. Geological Survey and others has revealed the presence of low-As (<10  $\mu\text{g/L}$ ) groundwater in oxidized sediments beneath the high-As aquifers. These oxidized sediments contain iron oxides and have the potential to attenuate As into deeper aquifers that have been proposed as a long-term and safe source of drinking and irrigation water.

### METHODS

Laboratory batch and column experiments were used to identify and quantify

processes affecting transport of arsenic through sediments collected from an oxidized aquifer at a site located about 10 km west of Dhaka, Bangladesh (Stollenwerk *et al.* 2007). Arsenic concentrations in groundwater associated with these oxic sediments were <5 $\mu\text{g/L}$ . The highest As concentrations in contaminated groundwater were 900  $\mu\text{g/L}$  at this site, 650  $\mu\text{g/L}$  as As(III) and 250  $\mu\text{g/L}$  as As(V).

Data from the laboratory experiments were used to calibrate a geochemical model capable of simulating the reactions between constituents in As-contaminated groundwater and oxic sediments. The reactive-solute transport model, PHAST (Parkhurst *et al.* 2004), which couples hydrologic flow with geochemical reactions, was then used to simulate the potential rate of As transport through the oxic aquifer at the sampling site. A range of As concentrations and groundwater velocities were simulated. Results

presented here are for an initial As concentration of 650 µg/L As(III) and 250 µg/L As(V). Simulated interstitial groundwater velocities were from 3 m/yr to 30 m/yr.

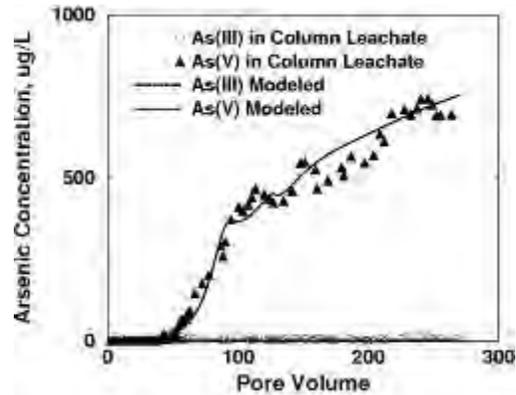
## RESULTS AND DISCUSSION

### Laboratory Experiments

Several reactions between constituents in As-contaminated groundwater and oxic sediments controlled As mobility in the laboratory experiments. Adsorption was the primary mechanism for removing As from solution. The adsorption capacity of the oxic sediments was a function of the concentration and oxidation state of As, and the concentration of other solutes that competed for adsorption sites. Although As(III) was the dominant oxidation state in contaminated groundwater, data from the laboratory experiments showed that As(III) was oxidized to As(V) by manganese oxide minerals that are present in the oxic sediment. Phosphate in contaminated groundwater caused a substantial decrease in As(V) adsorption. Silica, bicarbonate and pH caused only a small decrease in As adsorption.

Reactions between Fe(II) in contaminated groundwater (5.8 mg/L) and oxic sediment also affected As mobility. Ferrous iron was oxidized by manganese oxides to ferric iron which precipitated as hydrous ferric oxide, creating additional sorption sites. Evidence for this reaction included an increase in ferric oxide concentrations in reacted column sediments and manganese concentrations in leachate that were greater than in the initial eluent.

Measured concentrations of As(III) and As(V) in leachate from a column experiment are compared with simulated concentrations using the model PHAST in Figure 1. Arsenic concentrations in leachate were below detection for the first 50 pore volumes of contaminated groundwater eluted through the column. Although initial As(III) concentrations were 650 µg/L, oxidation of As(III) to As(V) by manganese oxides resulted in leachate concentrations of As(III) near detection limits for 270 pore volumes. All of the As



**Fig. 1.** Measured and modeled concentration of As(III) and As(V) in leachate from column experiment. Initial As(III) concentration = 650 µg/L; initial As(V) concentration = 250 µg/L. (Note: As(III) modeled concentrations were <1 µg/L and plot along bottom of x-axis.)

measured in leachate was present as As(V). The model simulated the As(III) and As(V) concentrations reasonably well.

### Field Scale Modeling

Extrapolation of laboratory results to the field scale is at best qualitative because of the complexity of the geochemical and hydrological systems in the Bengal Basin. Movement of As-contaminated groundwater towards a well screened in the uncontaminated aquifer is likely to contain both vertical and horizontal components of flow. For modeling purposes presented here, a relatively slow interstitial groundwater velocity of 3 m/yr (Stollenwerk et al. 2007) is compared with a more rapid interstitial velocity of 30 m/yr (McArthur et al. 2008).

For groundwater with 900 µg/L As moving into an oxic aquifer similar to our site at an interstitial velocity of 3 m/yr, the rate of transport of an As front defined as a concentration of 10 µg/L was simulated to be 0.01 m/yr. For an interstitial velocity of 30 m/yr, the rate of transport of a 10 µg/L front of As was simulated to be 0.22 m/yr.

## CONCLUSIONS

(1) Transport of As in contaminated groundwater through low-As oxic

sediments is inhibited by a complex set of reactions which include adsorption/desorption, precipitation/dissolution, and rate-controlled oxidation/reduction.

(2) Oxidic sediments have a significant but finite capacity to remove As from solution.

(3) The rate of As contamination of low-As aquifers as a result of pumping for drinking and irrigation water supply increases with As concentration and the rate of groundwater withdrawal.

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