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# MEDICAL GEOLOGY NEWSLETTER

Cogeoenvironment Working Group on Medical Geology  
Newsletter No. 6

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- **ARSENIC**
- **MERCURY AND METHYLMERCURY**
- **PLANTS IN BIOGEOCHEMISTRY**



## **MEDICAL GEOLOGY SHORT COURSE**

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## MESSAGE FROM THE CHAIRMAN, Olle Selinus

The development of medical geology is going faster and faster and I will just give you the highlights of last year and what we are planning to do in 2003. The newsletter is published twice a year but I believe that it is important to inform all members more often and therefore I have plans to start a regular e-mail letter to everyone, at least every second month just to inform of activities.

### What happened last year?

The primary activities during 2002 consisted of the organization and implementation of meetings and short courses on Medical Geology in Chile (February), Russia (At the 7<sup>th</sup> International Symposium on Metal Ions in Biology and Medicine in June), Netherlands (May), USA (June), China (November) and Japan (November), also covering neighbouring countries and regions. Another initiative has also been marketing Medical Geology in different media and also ongoing work with the book, Medical Geology, to be published through Academic Press. Continuing effort has also been sustained on all contacts, newsletters, website etc. The series of short courses on metals, health and the environment are now carried out all around the world. The leaders are Jose Centeno, Bob Finkelman and Olle Selinus. In addition to these, local scientists are also invited to demonstrate medical geology work going on in their respective regions. The most recent course was in Japan and about 50 scientists mostly from Japan but also from about 7 other countries participated.

More than 400 persons have been engaged in the work from almost 60 countries all over the world during 2002 (150 more than last year). About 600 contacts via e-mail have been made during 2002 with participants in the group. The webpage of the group <http://home.swipnet.se/medicalgeology> has been updated at least twice a month, often even more frequently. The website has now about 1000 visitors every month (a big increase since last year). Two newsletters have been published during the last year. The newsletter is now distributed to almost 500 people and institutes and can also be downloaded from

the website. A new poster has been produced and distributed in several countries in South America and other places. Cooperation with US Armed Forces of Pathology (AFIP) and USGS continues. One result of this cooperation is that many medics all around the world are regularly informed of the work going on in Medical Geology through AFIP. An exhibit at the National Museum of Health and Medicine focuses on medical geology and health problems associated with arsenic. The Public Health School of George Washington University will offer a one credit Topics class on Geosciences and Public Health. Jose Centeno, Joe Bunnell, and Bob Finkelman will be the instructors.

The ongoing work has also been presented by the chairman for different organisations. Examples are: In June a meeting was held in Washington DC Healthy Ecosystems - Healthy people, Linkages between biodiversity, ecosystem health and human health, June 2002, Washington DC USA. Joe Bunnell and Jim Zucchetto of the National Academy of Sciences chaired a Working Group on "Medical Geology: Earth Systems, Resource Use and Human Health." The Group reached consensus on a number of issues, including plans for additional promotion of Medical Geology as a sub-discipline, identification of research priorities, and key recommendations for this rapidly growing field.

In October a presentation was given in Helsinki, Finland. The people attending were all director generals of all geological surveys in Europe. In November the chairman presented the project at the XXIV International Congress of the International Academy of Pathology. A special symposium on environmental pathology and medical geology was arranged there. This was a very important meeting because this was the first time medical geology had been presented for this large audience of medics. In November we received a special invitation from the Royal Norwegian Academy of Sciences to present to it a lecture on medical geology.

## Publications

Several papers and notes have been published in different journals, drawing attention to and marketing the project. For the first time there was a paper on medical geology in Scientific American. This was published in February 2002, covering health effects of coal burning. Bob Finkelman was active in this paper. "Epidemiology News", a new newsletter on medical geology is published by USGS. In November 2002 there was a report on medical geology and an interview with the chairman in a Sunday issue of Neue Zürcher Zeitung, the largest newspaper in Switzerland. A publication, *Geology to Health*, edited by A.R. Berger and C. Skinner is in press at Oxford University Press, covering all the extended abstracts of the IGCP #454 meeting in Uppsala, Sweden in 2001. I am also glad to mention a new book "Medicinska Geologija" published in 2002 in Serbian language, 429 pages. The author, Miomir M. Komatina, is a member of the working group. This book will be described in detail in the next newsletter.

The Journal of Toxicologic Pathology has also announced that they will have a regular section on Medical Geology.

The book on Medical Geology, to be published by Academic Press, is proceeding. Most chapters are now being reviewed. The book has one Chief editor (O. Selinus), 6 associate editors (Ulf Lindh, Ron Fuge, Brian Alloway, Pauline Smedley, Bob Finkelman and Jose Centeno) and about 60 authors from all over the world; including both geoscientists and medics. The volume will be about 900 pages in length and will be published at the end of 2003. A brochure on medical geology and the IGCP project is in the planning stage. This will be undertaken in cooperation with the American Geological Institute (AGI), and will consist of about 50 pages in full colour. The target audience will be the general public, decision makers, etc.

## What is planned in 2003?

First I want to mention the short courses on Medical Geology:

**Lithuania**, Vilnius, May 2003, **China**, Guijiang, June 2003, **Brazil**, August 2003, **Great Britain**, Edinburgh, September 2003, **Australia and Fiji**, November 2003.

We also support international conferences such as:  
1st International Symposium on Geopollution and Medical Geology, Tokyo, Japan November 2002.  
7th ICOBTE, The International Society of Trace Element Biogeochemistry, Uppsala, Sweden, June 2003.  
10th International Symposium in Medical Geography, July 14 -18 2003, School of Geography, University of Manchester, UK.  
Sixth International Symposium on Environmental Geochemistry, September 2003, Edinburgh, Scotland  
Chilean Geological Congress - Medical geology Symposium. October 2003.  
Brazilian Society of Toxicology will also include Medical Geology in their conferences

I want to remind all members of the working group about the short courses. There are limited funds for participation in these, mainly from ICSU, the International Council for Scientific Unions and IGCP#454. During 2003 we will mainly concentrate on the courses in **Lithuania** in May (covering the former Eastern countries) and **Edinburgh** in September (covering the whole world). If you are interested in participating please contact the chairman, but I want to remind you that the resources are limited.

Finally I hope that all of you regularly look at the website (<http://home.swipnet.se/medicalgeology>), send material to the newsletter and also mail me if you have any questions. The more contacts the better!!

Olle Selinus, Chairman



## ARSENIC GROUNDWATER POLLUTION IN MEXICO

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Chronic arsenic poisoning resulting from polluted groundwater intake has been reported in many parts of the world such as Bangladesh, India, Taiwan, Argentina, and Chile.

Arsenic in groundwater often results from natural processes in mineralized areas. Mexico is one of the world leaders in arsenic production. It occupied the fourth place, following China, Chile, and Ghana with 2522 tons of arsenic in the year 2000. Arsenic is mainly used in the manufacture of wood preservatives, agricultural chemicals, and other products. Although arsenic is produced mainly in San Luis Potosí state (see Figure 1 for locations mentioned in this article), arsenic minerals have been reported in various metals mining areas. The occurrence of arsenic in Mexican subsoil has been reflected by high natural levels of As in groundwater at certain locations of México. Arsenic enrichment in some cases has been directly related to mineralization, and in others as a result of geochemical mobilization.

Comarca Lagunera (Durango and Coahuila states) located in the north part of the country was the first place where arsenic poisoning was studied in Mexico.<sup>1</sup> The arsenic enrichment of groundwater was related to hydrothermal processes.<sup>2</sup> About 400,000 dwellers of rural areas consumed drinking water containing more than 0.05 mg/L of As in this zone.<sup>3</sup> Symptoms of chronic arsenic poisoning such as Bowen's disease, hypopigmentation, hyperpigmentation, palmoplantar and papular keratosis, were found in part of the population consuming well-water with an arsenic concentration of 0.410 mg/L. Blackfoot disease was also observed in 0.7 % of exposed population.<sup>4,5</sup> In 1988, health threats to inhabitants decreased, since 70 % of the villages were provided with better-quality water from other sources.<sup>5</sup> Comarca Lagunera is also one of the most important dairy-cow raising zones in Mexico. Arsenic polluted groundwater was consumed by

dairy cattle. In 1992 a study including well-water, soil, forage, and cow's milk was developed in this area. Concentrations of As in milk ranged from <0.9 to 27.4 ng/g. Ten percent of the samples had concentrations higher than the 10 ng/g, suggested by the International Dairy Federation as a permitted arsenic level in milk. A milk biotransfer factor up to  $6 \times 10^{-4}$  was found in this research. Although As ranged from 0.24 to 3.16  $\mu$  g/g in alfalfa, which is the most important crop in the area, water was considered as the main source of arsenic for cattle.<sup>6</sup>

At Zimapán county, Hidalgo state in Central Mexico, inhabitants consumed polluted groundwater, containing up to 1.1 mg/L of As, for more than 15 years. Arsenic contents above 0.050 mg/L were found in almost half of the Zimapán Valley wells. Zimapán has been an important mining area since colonial times (XVI century). Although extraction and processing of Ag-Pb-Zn ores contaminated some shallow wells, the highest arsenic levels were related to the presence of arsenic-bearing minerals in the aquifer.<sup>7,8</sup> Geochemical processes (arsenopyrite oxidation and scorodite dissolution) also account for observed health-effects, since most of the drinking-water comes from naturally-polluted wells.

Analysis of human hair has been used as a relatively simple and inexpensive indicator of As intake. Statistically significant differences were observed between hair concentrations of people showing some degree of skin disease (hyper- and hypopigmentation, and hyperkeratosis), and Zimapán dwellers with no visible health effect. Some relationship between As concentrations in consumed water and hair was also observed.<sup>9</sup> Currently, most of the 12 000 inhabitants of Zimapán town are exposed to water containing up to 0.25 mg/L of arsenic, while some rural communities (Detzaní near Zimapán town) consume even more polluted water (0.5 mg/L of As).

In the Guadiana Valley northern Mexico, arsenic

concentrations up to 0.167 mg/L were related to the aquifer geology. In the year 2000, forty-eight percent of sampled wells in the rural area of the Guadiana Valley, contained arsenic over the Mexican drinking water standard of 0.05 mg/L. Fifty nine percent of the wells located in the southeast, northeast and northwest of Durango city (430 000 inhabitants) also exceeded that standard.<sup>10</sup>

Chronic arsenicism was reported in Acámbaro, Guanajuato state. In this case, arsenic pollution was ascribed to anthropogenic sources.<sup>11</sup>

Groundwater arsenic enrichment also occurs in several geothermal areas of Mexico. At Acozulco, at the east end of the Mexican Volcanic Belt, up to 0.206 mg/L of arsenic was measured in thermal springs.<sup>12</sup> At Los Azufres (Michoacán state), currently a geothermal energy area, brine spills from production wells containing arsenic (up to 24 mg/L) have polluted streams flowing out of that zone<sup>13</sup>.

High levels of As, Pb, and F, were also found in wells used for drinking water in Sonora state, northwestern Mexico. Fluoride and Arsenic concentrations showed a positive correlation. In Hermosillo, the largest city of Sonora, about 50% of the population receive drinking water from wells. The average As concentration was 0.021 mg/L, below drinking water standard, in Hermosillo city; nevertheless, one well had the highest As content (0.305 mg/L) of the studied area. In Obregón city, As levels of 0.250 ppm were measured in blood of inhabitants living in areas of high As concentration in water.<sup>15</sup> Groundwater arsenic pollution has also been found in other locations of México such as Zacatecas (an important mining zone), and Delicias.

Epidemiological studies have been carried out in some of the polluted areas. Studies included arsenic determination and speciation in urine samples of people exposed. Selenium intake in diet of arsenic-endemic areas has also been assessed.

In the year 2000, the drinking water standard of

arsenic in Mexico was 0.05 mg/L; since then, a decrease of 0.005 mg/L each year until 2005 has been programmed.<sup>16</sup> This reduction was adopted following the WHO guidelines aiming to a better population health. Alternatives must be developed to accomplish the new standard, since As concentration in groundwater will be above that level in various areas. The importance of this results also from the semi-arid characteristics of the country. Groundwater supplies about 70% of Mexican drinking water. The As pollution problem has been partially solved. Better-quality water from other locations is already supplied to part of the inhabitants of Comarca Lagunera. At Zimapán, different water treatment procedures have decreased As contents below the standard.<sup>17,18</sup> Nevertheless, water authorities decided to rather deliver non-polluted water from another aquifer.

Arsenic contaminated water is an endemic problem in some areas of México. Nevertheless, the intensity of health effects of affected people has not reached such a level of evidence to compel authorities to take immediate remedial actions. More studies are needed to evaluate arsenic pollution in all the country, and to reduce environmental risks from As polluted-water exposure in Mexico.

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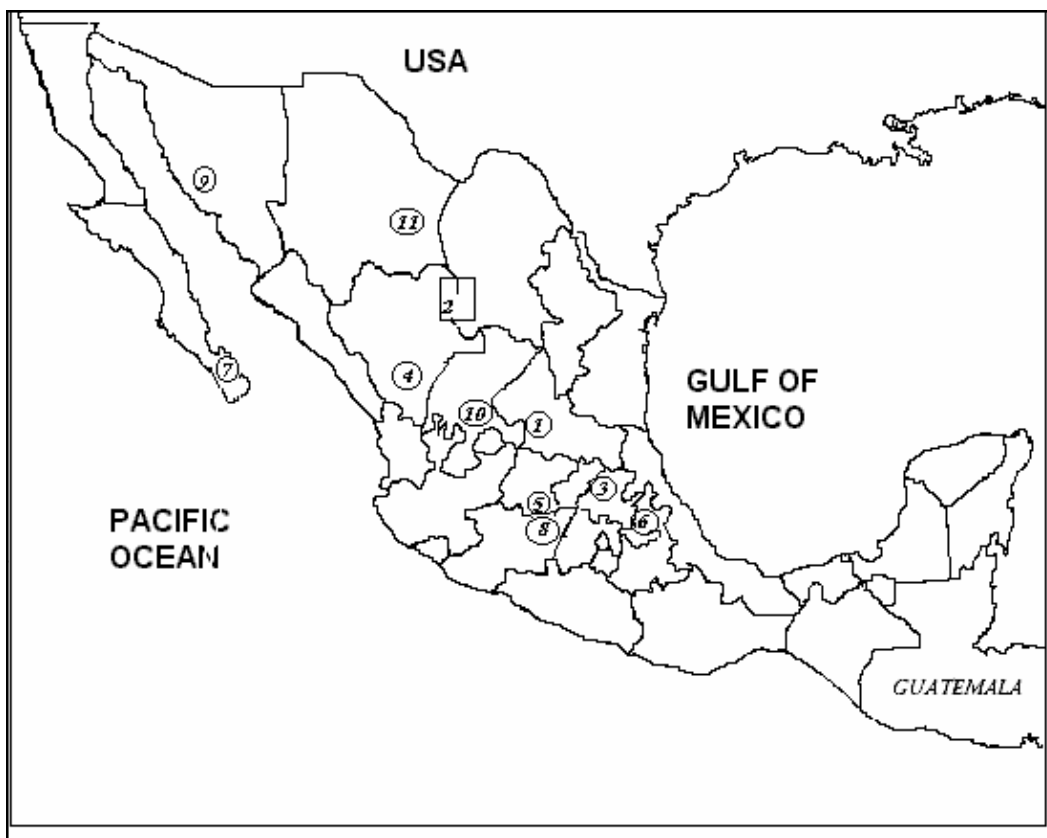


Figure 1. Groundwater arsenic polluted areas in Mexico. (1) San Luis Potosí, (2) Comarca Lagunera, (3) Zimapán, (4) Guadiana, (5) Acámbaro, (6) Acapulco, (7) San Antonio, (8) Los Azufres, (9) Hermosillo, (10) Zacatecas, (11) Delicias.

# ENVIRONMENTAL MERCURY AND METHYLMERCURY CONTAMINATION FROM THE PALAWAN QUICKSILVER MINE, PHILIPPINES

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## Introduction

The Palawan Quicksilver Mine (PQM), Philippines, is located on Palawan Island near several villages where approximately 2,000 residents live, and within about 3 km of important regional fisheries and recreational areas in Honda Bay (Fig. 1). From 1953 to 1976, the PQM produced about 2,900 t of Hg, a moderate sized Hg mine on an international scale. More than 2,000,000 t of mine-waste calcines (roasted ore) was generated during mining and about half of this waste was dumped into Honda Bay to construct a jetty, which was used as a mining port <sup>1</sup> (Fig. 2). Since 1995, high Hg levels have been observed in 21 people living near the mine, who also experienced symptoms of Hg poisoning and were subsequently detoxified with chelating drugs.

Mercury is a heavy metal of environmental concern because elevated concentrations are toxic to all living organisms. Mercury is one of the few pollutants where ingestion of contaminated food (primarily fish) has led to human deaths <sup>2</sup>. Mine-waste calcines can be especially hazardous because they contain highly elevated Hg concentrations and soluble Hg salts and Hg<sup>0</sup>, which under certain conditions, can oxidize to Hg(II) and subsequently transform into methyl-Hg (CH<sub>3</sub>Hg<sup>+</sup>) through microbial processes, primarily by the action of sulfate reducing bacteria <sup>3</sup>. Methyl-Hg is highly toxic, water soluble, and can biologically magnify with increasing trophic position in the food chain. Mercury contamination of fish and seafood is a common problem worldwide that can lead to Hg exposure to humans consuming such food sources <sup>4</sup>. Mercury contaminated sediment and water from the PQM are potentially hazardous to residents and wildlife when they enter local surface water and food

webs, especially in Honda Bay. To evaluate Hg contamination and Hg methylation in this area, total Hg and methyl-Hg concentrations were measured in (1) mine wastes and mine water from the PQM, (2) stream sediment and water from a pit lake and a local stream (Tagburos Creek), (3) mine-waste calcines and water in Honda Bay, and (4) water from local domestic wells.

## Results and Discussion

Mercury concentrations in PQM calcines and local sediments are highly elevated and variable (3.7—660 µg/g), which is typical of Hg mines throughout the world (Table 1; Fig. 3). Fine-grained and encapsulated cinnabar (HgS) was observed in some calcines, and the high variability of Hg within these calcines indicates that retorting was not totally or uniformly efficient, which is also typical of Hg mines worldwide. Nearly all of the Hg at the PQM was produced from ore containing cinnabar, but pyrite (FeS<sub>2</sub>) is also abundant. The presence of pyrite is potentially hazardous because it is a significant acid-water producing mineral, and Hg compounds are more soluble and reactive in acidic water. Thus, unfiltered water draining the PQM calcines is acidic, pH 3.1—4.3, and total Hg concentrations ranging from 18,000—31,000 ng/L in this water significantly exceed the 1,000 ng/L World Health Organization (WHO) drinking water standard for Hg <sup>5</sup> (Fig. 4). Total Hg concentrations are generally lower in water samples collected from surrounding domestic wells, the mine pit lake, Honda Bay, and the nearby stream, varying from 8—1,400 ng/L. However, nearly all unfiltered water samples collected in this study contain total Hg concentrations exceeding the 12 ng/L Hg standard recommended by the U.S. Environmental Protection Agency (USEPA)

to protect against *chronic* effects to aquatic wildlife<sup>6</sup> (Fig. 4).

The concentration of methyl-Hg in mine wastes, sediment, and water in the area is more important than total Hg contents because methyl-Hg is highly toxic. Methyl-Hg concentrations in the calcines and sediment samples varied from 0.13—21 ng/g, whereas methyl-Hg contents in water from the PQM site ranged from <0.02—3.1 ng/L. There is no regulatory methyl-Hg standard, but methyl-Hg contents in the Palawan samples are similar to those found at other cinnabar-dominant Hg mines, such as in southwestern Alaska, west-central Nevada, and Idrija, Slovenia (Table 1). At Idrija and in Alaska, mines are within aquatic ecosystems that have been contaminated with Hg. These ecosystems support marine and freshwater fish, and some of these fish contain Hg concentra-

tions exceeding the 0.3 µg/g (wet weight, fish muscle) standard commonly used in the USA<sup>4</sup>. Similar to these mines, the data for the PQM indicate translocation of methyl-Hg from mine-waste calcines and sediments to stream water, and then to Honda Bay. It is also likely that methyl-Hg in mine wastes and water in Honda Bay is transferred to biota, such as fish. Methyl-Hg has been shown to constitute greater than 95 % of the total Hg in consumable fish tissue<sup>7</sup>. Fish in Honda Bay have been known for several years to contain elevated total Hg concentrations (0.05—1.07 µg/g, wet weight, fish muscle)<sup>8-9</sup>. Residents in this area are exposed to Hg through food sources such as fish and seafood from Honda Bay. Palawan has a coastal population, where people typically consume fish and seafood daily. Daily consumption of fish from Honda Bay could exceed the USEPA suggested human intake of 0.1 µg methyl-Hg/kg bodyweight/day, and the WHO recommendation of 0.47 µg methyl-Hg/kg bodyweight/day<sup>4</sup>. Based on these recommendations, residents in this area should restrict consumption of seafood from Honda Bay.

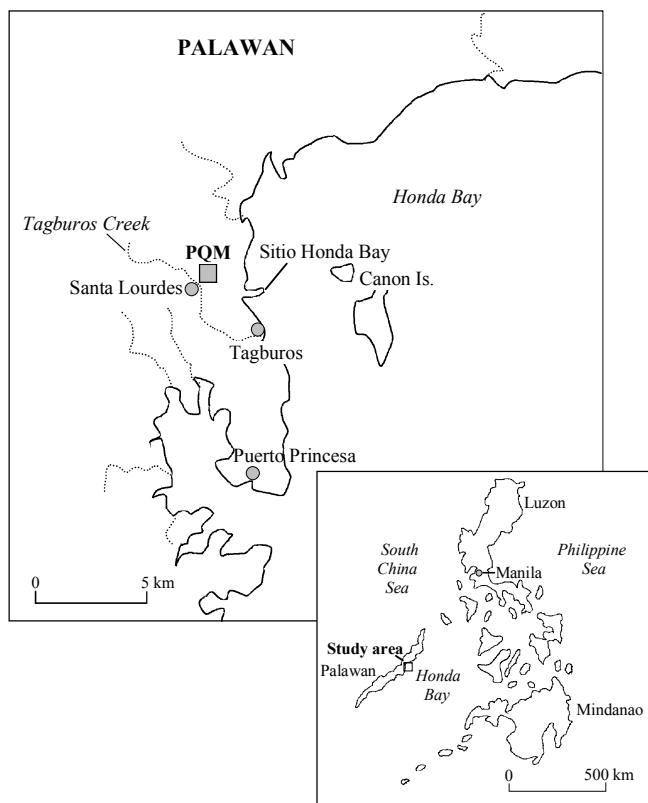


Figure 1. Location of the Palawan Quicksilver Mine (PQM), Palawan, Philippines.

## Conclusions

In and around the PQM, several adverse factors have contributed to local environmental Hg contamination, one of the most unfortunate was the placement of Hg-rich mine wastes into Honda Bay. Much of the methyl-Hg generated in the PQM calcines or in Honda Bay is transferred to water, and then to higher trophic levels such as marine fish and seafood that are human food sources. The PQM is a unique example of significant methyl-Hg formation near a Hg mine, Hg contamination of local marine seafood, and subsequent uptake of high levels of methyl-Hg by local residents consuming such seafood.

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## ENVIRONMENTAL MERCURY AND METHYLMERCURY CONTAMINATION (Cont.)



Figure 2. A view of mine-waste calcines that were used to construct the jetty in Honda Bay. This photo is at the waterline in Honda Bay and in the background are fish drying racks and motor vehicles.

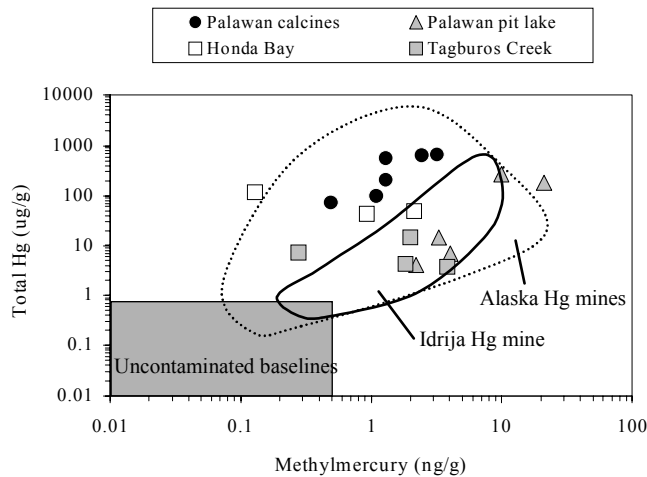


Figure 3. Total Hg concentration versus methylmercury in PQM calcines, Honda Bay calcines, pit lake sediments, and Tagbueros Creek sediments. For comparison, the range of data is shown for similar samples from Idrija, Slovenia<sup>10</sup> (solid line) and southwestern Alaska<sup>11</sup> (dashed line). Uncontaminated baseline data (shaded box) are from stream sediment samples collected distant from mines.

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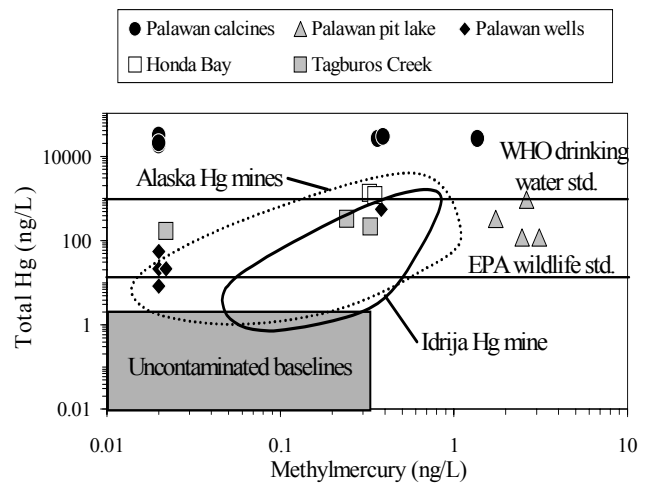


Figure 4. Total Hg concentration versus methylmercury in unfiltered water collected from in and around the PQM site. For comparison, the range of data is shown for similar samples from the Idrija Hg mine, Slovenia<sup>10</sup> (solid line), and Hg mines in southwestern Alaska<sup>11</sup> (dashed line). Also shown is the WHO 1,000 ng/L drinking water standard for total Hg, and the USEPA 12 ng/L standard for total Hg for the protection of adverse *chronic* effects to aquatic wildlife.

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<sup>13</sup>Gray, J.E., Crock, J.G., and Fey, D.L. (2002) Environmental geochemistry of abandoned mercury mines in west-central Nevada, USA. *Applied Geochem.* **17**, 1069-1079.

**Table 1.** Mercury and methyl-Hg concentrations from mines discussed in this report.

Location	Unfiltered water		Sediment or soil	
	Hg (ng/L)	Methyl-Hg (ng/L)	Hg (µ g/g)	Methyl-Hg (ng/g)
Mercury mine, Palawan, Philippines <sup>12</sup>				
Mine-waste calcines	18,000-31,000	<0.02-1.4	28-660	0.13-3.2
Pit lake	120-940	1.7-3.1	14-400	2.0-21
Stream below mine	170-330	<0.02-0.33	3.7-15	0.28-3.9
Water wells	8-550	<0.02-0.38	--	--
Mercury mines, southwestern Alaska <sup>11</sup>				
Streams below mines	1.0-2,500	0.01-1.2	0.90-5500	0.05-31
Untaminated baseline streams	0.10-1.4	0.04-0.2	0.02-0.78	0.10-0.30
Mercury mine, Idrija, Slovenia <sup>10</sup>				
Mine-waste calcines	--	--	4.8-727	1.3-14
Stream above mine	8	0.1	5.4	3.6
Streams below mine	5-200	0.08-0.50	0.31-291	0.12-10
Mercury mines, west-central Nevada <sup>13</sup>				
Mine-waste calcines	--	--	14-14,000	<0.05-96
Streams below mines	6.0-2000	0.039-0.92	0.80-170	0.12-0.95
Untaminated baseline streams	2.1-9.0	<0.02-0.27	0.008-0.44	<0.05-0.090

-- indicates no data or not applicable.

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## TOXIC MERCURY FROM THE INDUSTRIALISED WORLD IS FLOODING DEVELOPING COUNTRIES

Summarised by Lars Hylander

Representative for Centre for Metal Biology, Delegate at the First Meeting of Global Mercury Assessment Working Group, Geneva 9-13 September, 2002

United Nations Environment Programme (UNEP) has initiated an assessment on global scale of health risks and environmental impact of mercury (Hg). On September 9—13, the working group met in Geneva to finalize a 300-pages report. It was concluded that anthropogenic emissions of Hg has lead to about a three times increased deposition rate of Hg on a global scale and up to ten times increased deposition rate in the most industrialised regions of America, Asia, and Europe. Pike, shark, tuna, and other carnivorous fish often have concentrations of Hg above 0.5 mg/kg fresh weight, the threshold endorsed by WHO and many nations, above which fish should not be freely consumed. Mercury in fish is up to about 90 % present as methylmercury (MeHg), one of the most toxic compounds we know. It passes both the placenta and blood/brain barriers, delays mental development even at low exposure, and results in severe necroses of brain cells at higher exposure, resulting in blindness, deafness, paralysis, and other nervous problems. Increased knowledge about health hazards of Hg has resulted in a markedly decreased use in West Europe and North America. The dominant producer, a state company in Almadén, Spain, is, nowadays, selling Hg mainly to developing countries. It has sales offices in Peru, India, and the Philippines, where Hg is used in primitive gold mining and results in large emissions of Hg to air, water, and soil and subsequently to human exposure.

Another consequence of the decreased use of Hg in industrialised countries is that large amounts of surplus Hg are made available from stocks used in society. The chlor-alkali industry alone has about 15 000 tonnes of metallic Hg in stock, which they want to sell on the world market when they convert to Hg-free membrane technology. This corresponds to some 50 years of Hg production from the Hg mines in Spain. This Hg is at risk to enter industrial uses such as thermometer production, since ten years prohibited in Sweden and recently prohibited in the USA, too.

Also, Sweden has two chlor-alkali plants with 400 tonnes of metallic Hg. It is suggested that this Hg be disposed of in a deep bedrock repository in order to avoid it entering the world market and subsequent release to the environment.

Generally, awareness of the adverse effects of Hg is less abroad than in Sweden. Newborn kids get vaccines containing an organic Hg compound (thimerosal) in many countries. Factories employing Hg technologies, which have served their time, have in many cases been sold to developing countries. Therefore, in April 2001, UNEP invited all countries worldwide to a global risk assessment for Hg. All governments, intergovernmental and nongovernmental organisations, and private companies were invited to contribute. A draft was written by the UNEP staff and 109 delegates met in Geneva September 9—13, 2002 and wrote the final report. It was concluded that the widespread use of Hg has lead to pronounced environmental degradation and has caused illness or death to several thousands of persons. It was also concluded that we know enough to motivate actions against further dissemination of Hg and to initiate international actions to reduce health risks.

Except for Spain, Kyrgyzstan, and Ghana, all countries agreed to immediately stop the mining of Hg. Spain and Kyrgyzstan have the largest Hg mines still in operation. The Spanish mines have been run at a loss for more than a decade but continue operations thanks to subsidies from the owner, the Spanish government. The mining company also receives large subsidies from EU. Ghana wants to buy cheap Hg also in the future, Hg that its population uses in primitive gold mining. Mercury is used during gold mining to dissolve gold dust in sand, thereby forming amalgam. Pure gold is then produced by heating the amalgam so that mercury evaporates and is emitted to the air, leaving the pure gold behind. The government in Ghana chose cash revenues in exchange for the

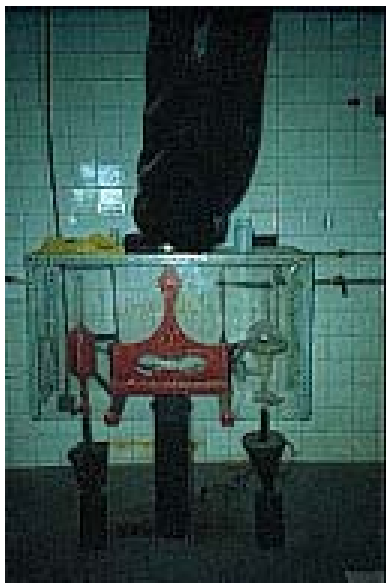
## TOXIC MERCURY cont.

health of its inhabitants.

Mercury vapour from gold mining, industries, and power plants operated with fossil fuels remain in the atmosphere up to one year and is transported by the winds around the globe. Consequently, Hg is largely deposited far away from the emission sources and a country cannot protect its population by preventing emissions of Hg within its borders. Greenland has hardly any emissions from industries or other human activities, but the Inuits are among the most severely affected by anthropogenic Hg emissions. This is because their natural food is fish and other animals accumulating Hg. Another reason is that Hg emitted in

industrial areas of America, Asia, and Europe to a large degree is deposited in the Arctic. The researchers have just discovered that large amounts of Hg is deposited over the polar regions when the first sunbeams interrupt the polar winter, called Hg deposition at arctic sunrise.

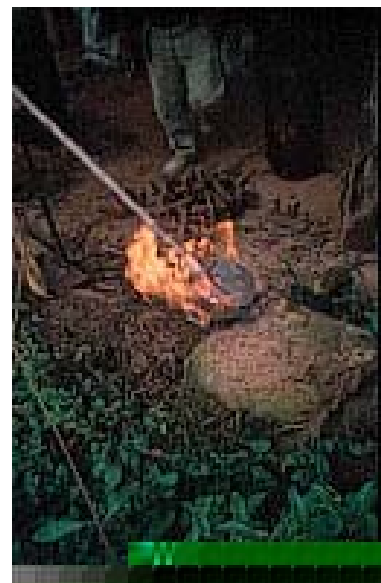
All this information is described in the final report, to be posted at [www.chem.unep.ch/mercury/](http://www.chem.unep.ch/mercury/). It will also be presented to all governments and the Governing Council of UNEP, which, in Kenya, next year will decide how to proceed to reduce adverse environmental and health effects of Hg.



The mercury tap at the tap station at the Hg mine and processing plant in Almaden, Spain. The photo shows two iron flasks of 2.5 litres (34.5 kg Hg), the international trading unit for Hg, ready to be filled with Hg. Will UNEP succeed in closing the tap at the mine in Almaden, the oldest and largest Hg mine in the world? It is still in operation thanks to government and EU subsidies.



A sheet with Hg applied to the surface, over which water with suspended ore particles is flowing. A miner is "massaging" the mercury surface with his bare hands, so that gold grains will more easily amalgamate with the Hg. In the background is his colleague feeding ore and water to the mill. Photo from Amazonas, Venezuela. Similar techniques are used in large parts of Africa, South America, south/east Asia, China and Siberia.



The simplicity is the technical advantage with using Hg in gold mining. The gold amalgam is easily purified by heating over a stock fire or a gas flame, here on an iron spade, making the Hg evaporate into the surrounding air.



# CHALLENGES OF USING PLANTS IN BIOGEOCHEMICAL STUDIES

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## Introduction

Biogeochemical studies are concerned with elemental composition and distribution in vegetation communities, especially in undisturbed natural terrain. Since vegetation is responsive to change in rock type, this technique may be used to derive geochemical information and to differentiate parent materials.

The objective of this article is to make a case for biochemistry by demonstrating that plant analytical techniques are suitable for detecting heavy metal concentration in the environment. Whether plants growing around an area of known mineralization can be used to delineate the mineralized outcrops, and whether the associated plants can take up excess amounts of the associated toxic metallic elements is critical to the use of plants for medical geological purpose.

## Challenges in Biogeochemical Studies

Visual survey of vegetation often includes observation of physiological modification in vegetation, in individual plants or whole plant communities. The subsurface geological condition and type of biogeochemical sample have been found to complicate this simplistic scenario.

### *Vegetation Zonation*

Vegetation reflects the interplay of several environmental factors. These include, for instance, the geochemistry of the soil at the rooting depth, the type of soil, aspect, rainfall, etc. The use of vegetation for general geological mapping and mineral exploration purposes should therefore be carefully applied, since it has been demonstrated that subsurface geology complicates these generalizations. For instance, distinct vegetation types could develop in areas with varied subsurface geological and geochemical composition. Therefore the application of geobotanical techniques should generally be complemented by

trace element analysis of the vegetation in order to detect subsurface mineralization, and the type of trace element mobilized in the biogeochemical environment.

### *Types of Biogeochemical samples*

Since plants absorb mineral elements, they should be cautiously used for biogeochemical and medical geological purposes. Four distinct types of biogeochemical samples are recognized. Non-barrier plants accumulate metallic elements continuously as the subsurface concentration increases. At the other extreme are barrier type plants, which generally do not respond to elemental concentration in the subsurface. In between are the somewhat informative plants, which do not take up elevated elemental concentrations in the same way as in the barrier-free plants. In some cases indicator plants could be barrier free with respect to a particular metallic element and a barrier with respect to other elements. This further complicates the simplistic model that plants faithfully reflect the subsurface geochemistry.

### *The Study Area*

A description of the study area is vital in biogeochemical studies. Specifically, climate has a strong impact on sampling season. In Kenya, the months of November to February are usually the hottest and driest, an ideal season for biogeochemical field surveys.

The geology of the area should be well understood, especially since geology delimits the distribution of biogeochemical samples.

### *Field Survey and Sampling Techniques*

A rapid field reconnaissance survey of the study area should first be conducted to determine the types and distribution of vegetation. This is followed by collection of biogeochemical samples for trace element analysis. Samples should be collected during the dry season, when vegetation is most stressed, and mineral concentration in the subsurface are highest. Repeat

sampling is recommended to assess whether the vegetation responds consistently over time to the concentrations of elements in the subsurface. The sampling period should take as short a time as possible to minimize climate variations that might influence elemental uptake by plants.

Following the reconnaissance survey, transects should be perpendicular to the general strike of the lithology, and sample points identified along transects. Since strong correlation exists between soil and plant element concentration, collection of soil samples is generally not necessary.

### *Sample Preparation*

Plant samples are separated into twigs and leaves for trace elements analysis. Separating twigs from leaves is essential since it is known that they concentrate different amounts of elements. Replicate samples should be prepared for repeat analysis.

Samples are prepared for quantitative trace element analysis by first flushing them with distilled water to remove adhering soil particles. They are then oven dried at 80°C and then ashed in a muffle furnace at 500°C. The ashing technique is vital since it reduces the sample size, and pre-concentrates the elements prior to elemental analysis. Dry ashing should usually be carried out in the presence of a small amount of air. Although too much air increases the danger of volatilization of some metallic elements, enough air supply is essential to avoid production of black charred material, which is apt to absorb metal and vitiate the assay.

### *Statistical Threshold Levels*

Statistical analyses of the element concentration data obtained from biogeochemical samples show the typical negative skewness of all geochemical data. It can therefore, be subjected to standard geochemical statistical analysis, to establish whether the concentration values are a reflection of true geochemical anomalies within the biogeochemical environment.

Statistical threshold levels should be calculated to

determine concentration values in the geobotanical samples. Biochemical data from plant samples are tabulated with the associated Universal Background Value (UBV), Local Threshold Value (LBV), and Local Threshold Value (LTV) for the selected heavy metallic elements. The LBV is determined as the mean element concentration plus one standard deviation, while the LTV is the mean concentration plus two standard deviations. Concentration values higher than the LTV should be considered anomalous. A smoothing algorithm on the element concentration data only smoothes the erratic nature of the data.

### *Element Concentration Plots*

The element concentration values obtained from the biogeochemical samples are presented in the form of element concentration plots. Drawing isograds, demarcating concentration ranges according to the established threshold levels generates element concentration plots.

## **Conclusion**

By assuming a constant geochemical background value, the biogeochemical techniques enable trace element analysis in areas where residual soils are varied or non-existent. Thus, the technique coupled with quantitative biogeochemical trace element analysis has been demonstrated to localize area of elevated heavy metal concentrations by establishing the anomalous occurrence of the pathfinder elements in the geochemical environment.

It seems that in cases where the biogeochemical indicator plants are known the technique of plant analysis is superior to other geological methods since no analytical work is required. Thus, maps of heavy metal can be drawn by observing the distribution of the indicator plants. Furthermore, preparation and analysis of plant material is much easier than soil and rock samples, are much quicker to collect, and are much lighter to carry in the field. Finally, analysis of herbarium samples would enable trace element concentration plots for large areas – especially in regional biogeochemical surveys.

# MEDICAL GEOLOGY SHORT COURSE SCIENTIFIC PROGRAM & REGISTRATION

## SCOPE AND PURPOSE:

The scope of this workshop is to share the most recent information on the relationship between toxic metal ions, trace elements, and their impact on the environmental and public health issues. The scientific topics of the Workshop will include environmental toxicology, environmental pathology, geochemistry, geoenvironmental epidemiology, extent, patterns and consequences of exposures to toxic metal ions in the general environment, biological risk assessment studies, modern trends in metal analysis and updates on the geology, toxicology and pathology of metal ion exposures.

## OBJECTIVES:

On completion of this Workshop, the attendees will be able to:

- Know and gain information on the type of evidence available about geological sources and processes, environmental health, toxicology, and pathological manifestations of exposures of toxic metal species.
- Know and gain information about geochemical processes, natural and anthropogenic sources, speciation, modes of occurrence; to assess the impact of trace elements and toxic metal ion species on human and environmental health.
- Have an elementary understanding of environmental toxicology, epidemiology, medical geology as applied to the study of toxic metal species and trace elements.

## SHORT COURSE LEADERS:

Dr. José A. Centeno, U.S. Armed Forces Institute of Pathology, Washington, DC

Dr. Robert B. Finkelman, U.S. Geological Survey, Reston, VA

Dr. Olle Selinus, Geological Survey of Sweden

## INVITED SPEAKERS:

Prof. Philip Weinstein, Dr Angus Cook, School of Population Health University of Western Australia, Crawley.

## ABOUT THE SPEAKERS:

**Dr. José A. Centeno** is a Senior Research Scientist and Chief of the Division of Biophysical Toxicology and the Education and Research Branch at the Department of Environmental and Toxicologic Pathology, U.S. Armed Forces Institute of Pathology (AFIP) in Washington, D.C. Dr. Centeno received his BS and MS in chemistry from the University of Puerto Rico at Mayagüez in 1979 and 1981, respectively; and a Ph.D. in Physical Chemistry from Michigan State University in 1987. He has presented over 100 invited seminars and lectures on various topics of environmental toxicology, biomedical research and human health

issues. He has served on the organizing and scientific committees of several international conferences, including General Chairman of the 6<sup>th</sup> *International Symposium in Metal Ions in Biology and Medicine* (May 7-10, 2000). He has served on several international environmental and human health committees including the International Agency for Research on Cancer, the U.S. TOSCA-Interagency Testing Committee and the International Working Group on Medical Geology. Over the last decade, he has focused attention on environmental and health impacts of trace elements, toxic trace metals and metalloids, and conducted research and teaching activities in Mexico, China, Taiwan, and New Zealand.

**Dr. Robert B. Finkelman** is currently the coordinator of coal quality activities at the U.S. Geological Survey (USGS) in Reston, VA. He received his Ph.D. in Chemistry from the University of Maryland in 1980, his MS in Geochemistry from George Washington University in 1970, and his BA in Geology from the City College of New York in 1965. For the past 25 years, Dr. Finkelman has been involved with coal quality issues both at Exxon Production Research Company and later, the USGS. Over the last decade he has focused attention on health impacts of geologic materials and conducted research in Yugoslavia, Romania, China, and New Zealand. Among his 370 publications are several papers dealing with human health impacts of coal and on mercury in coal.

**Dr. Olle Selinus** is a Ph.D. geologist working with the Geological Survey of Sweden (SGU). During the 1960s and 1970s he worked in mineral exploration with a mining company and at the GSS. Since the beginning of the 1980s, Dr. Selinus' research work has been focused on environmental geochemistry and geostatistical methods, including research on medical geology. He has served as the organizer of several international conferences in this field and has published over 40 manuscripts. Head of the Geochemical Division at SGU and in charge of research and development. He serves as officer of COGEOENVIRONMENT and as chairman of its International Working Group on Medical Geology, and co-chairman of the IGCP project #454 Medical Geology.

**Professor Philip Weinstein** is an environmental health physician and currently Professor of Population Health at the University of Western Australia, Perth. In addition to specialist medical qualifications in epidemiology and environmental health, he holds a PhD in Ecology, and was until recently Director of the Ecology and Health Research Centre, University of Otago, New Zealand. Phil has many research interests that touch on medical geology, including the health effects of drinking water quality, volcanic emissions, and contrasting land uses.

**Dr Angus Cook** is an environmental epidemiologist based at the School of Population Health, the University of Western Australia, Perth. Dr Cook graduated from the University of Auckland, New Zealand, in 1993, gained his medical registration in Canberra, Australia, in 1994 and has since been involved in public health research at the University of Melbourne, Monash University and the University of Otago. He has published on the health effects of environmental and occupational exposures to radiation, biosecurity and health, and the health effects of volcanic emissions. He is currently involved in a number of research projects, including: water quality and paediatric health, pesticide exposures and brain tumour incidence, historical exposures to heavy metals, and the use of epidemiological and geochemical measures to assess outcomes of land use

## REGISTRATION

**Cost GBP 40 includes two lunches, coffee breaks and documentation (syllabus and CD).**

**Scientists from developing countries: no cost. Scientists from developing countries should first contact Dr Olle Selinus, [olle.selinus@sgu.se](mailto:olle.selinus@sgu.se) or [olle.selinus@home.se](mailto:olle.selinus@home.se)**

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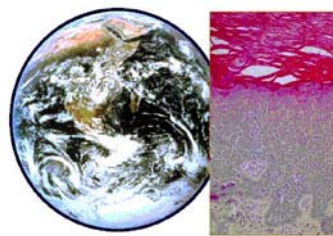
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# SHORT COURSE -MEDICAL GEOLOGY-

**METALS, HEALTH AND THE ENVIRONMENT**

**September 6-7, 2003  
Edinburgh, United Kingdom**

**At the 6<sup>th</sup> International Symposium on  
Environmental Geochemistry**



Environmental and health effects of  
toxic elements, metal ions, and minerals

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International Working Group on Medical Geology (IWGMG)

United Nations Educational, Scientific, and Cultural Organization (UNESCO)

International Council of Scientific Unions (ICSU)

## **WHO SHOULD ATTEND?**

The Workshop is intended for geologists, geochemists, ecologists, chemists, biologists, occupational and environmental scientists, medical professionals, toxicologists, epidemiologists, pathologists, bio-statisticians and any other health, environmental and geo-sciences professional with interest on Medical Geology issues, particular interest on the effect of toxic metal ion species on environmental and human health. An important aim of the Workshop is to provide the opportunity for forming contacts and networks between professionals working in different areas of environmental and human health

### *Day 1: Saturday September 6, 2003*

- 8:30-9:00 GENERAL REGISTRATION
- 9:00-9:15 WELCOME REMARKS  
*Dr. Olle Selinus, SGU*
- 9:15 – 9:30 Objectives and Short Description of the Workshop  
*Dr. Olle Selinus, SGU*
- 9.30-10.15 Medical Geology: An emerging discipline in environmental and human health.  
*Dr. Olle Selinus, SGU*
- 10.15-10.30 Coffee break
- A. Environmental Health : Sources of Exposure and Effects of Toxic Metal Ion**
- 10.30-11.15 The Diversity of Trace Elements and Toxic Metal Ions in Environmental Health and Human Diseases:  
*Dr. José A. Centeno, AFIP*
- 11:15-12:00 Natural and Anthropogenic Sources, Transport and Fate of Toxic Metal Ions in the Environment  
*Dr. Robert B. Finkelman, USGS*
- 12:00-12:15 Discussion and General Remarks
- 12:15-13:15 LUNCH
- B Environmental Pathology, Geochemical Studies and Health Effects.**
- 13.15 – 14.00 An Overview of Health Impacts of Coal and Coal Use: Arsenicosis and Fluorosis  
*Dr. Robert B. Finkelman, USGS*
- 14.00-14.45 An Introduction and Overview to Chronic Arsenic Poisoning: Natural History, Toxicology and Health Effects  
*Dr. Jose A. Centeno, AFIP*
- 14.45 – 15.00 Coffee break
- 15.00-15.45 Contribution from UK. To be identified
- 15.45-16.15 Discussion  
*Dr. Jose A. Centeno, AFIP*

### *Day 2: Sunday September 7, 2003*

- C. Special Topics on Environmental Toxicology and Human Health**
- Research on Metal Ions
- 9.15-10.00 Clinical and toxicological effects of mercury  
*Dr. Jose A. Centeno, AFIP, Washington, DC*
- 10.00-10.30 Medical Geology as applied to vector borne diseases, radionuclides, organics etc.  
*Dr. Robert B. Finkelman, USGS*
- 10.30-10.45 Coffee break
- 10.45-11.30 Health effects of volcanic emissions  
*Prof Philip Weinstein, Dr Angus Cook*
- 11.30-12.15 Medical Geology and health effects in Scandinavia  
*Dr Olle Selinus, SGU*
- 12.15-13.15 Lunch
- 13.15-14.0 Mining, health and the environment  
*Prof Philip Weinstein, Dr Angus Cook*
- 14.00-14.45 Contribution from UK
- 14.45-15.0 Break
- 15-15.45 Contribution from UK
- 15.45-16.15 Panel Discussion: Research Opportunities and Needs on Environmental Toxicology, Medical Geology and Human Health - All Speakers
- 16:15 – 16:30 Short Course Summary