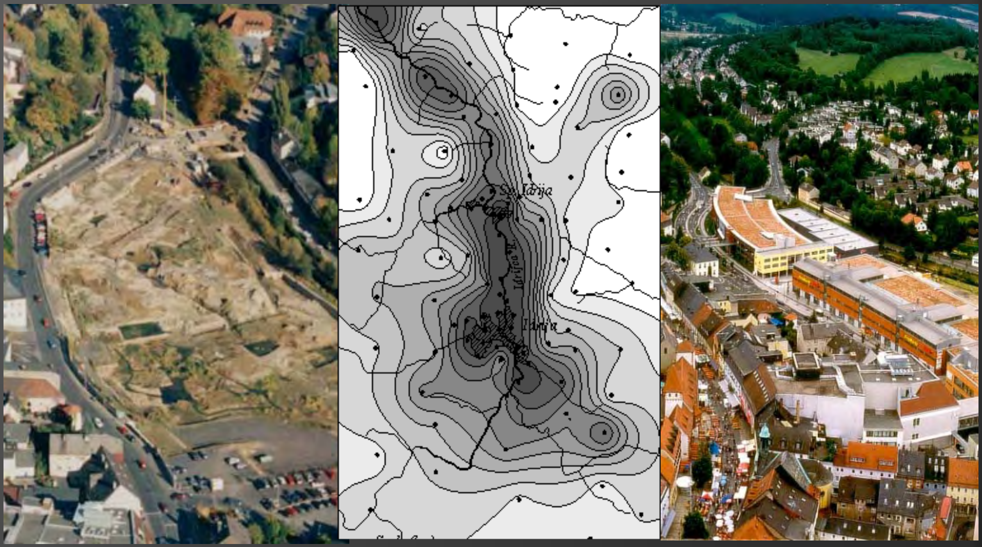
Final Report

Sino-German Workshop 2008

REMCOSITE



Remediation of Mercury Contaminated Sites

Guiyang, May 27 – 30, 2008

GRS

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REMEDIATION OF MERCURY CONTAMINATED SITES

GUIYANG, MAY 27 – 30, 2008

Bundesministerium
für Umwelt, Naturschutz
und Reaktorsicherheit

清華大學
Tsinghua University

GRS

Gesellschaft für Anlagen-
und Reaktorsicherheit
(GRS) mbH

FEDERAL MINISTRY FOR THE ENVIRONMENT, NATURE CONSERVATION AND NUCLEAR SAFETY

On 6 June 1986 the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety was established. Since then it has been responsible within the Federal Government for (lead-managing) national environmental policy.

Protecting against environmental pollution and radiation, managing resources and energy intelligently and efficiently and using the natural environment in a way that conserves the diversity of animals, plants, and habitats - these are the goals of the Federal Environment Ministry (BMU).

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Tsinghua University today subscribes to the education ideal of comprehensive mastery of Chinese and foreign, classic and modern knowledge in sciences and humanities.

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GRS is a scientific-technical expert and research organisation mainly supporting the BMU. It provides interdisciplinary knowledge, advanced methods and qualified data for assessing nuclear safety and the long-term safety of radioactive waste disposal.

In Germany GRS is the leading organisation in the development and application of methodologies and analytical tools for the performance/safety assessment of underground radioactive waste repositories. Together with German and international partner organisations, GRS is involved in a number of international research projects partly co-funded by the EU.

On behalf of the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) GRS is supporting the ministry within the framework of international chemical safety policy.

Contact

Dr. Thorsten Meyer, GRS, Theodor-Heuss-Str. 4, 38122 Braunschweig, Germany

Tel.: +49 531 8012-249, Fax: +49 531 8012-200 E-Mail: thorsten.meyer@grs.de

Prof. Jianlong Wang, INET, Tsinghua University, 100084 Beijing, China.

Tel: +8610-6278 4843, E-Mail: wangjl@mail.tsinghua.edu.cn

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1 Executive Summary

Mercury-contaminated sites potentially represent an important source of mercury emission into the atmosphere due to evaporation of mercury from contaminated land and waters. They constitute an important source for transboundary movement of mercury through hydrological cycles, particularly in large river catchment areas scale and contaminated coastal regions. Contaminated sites in ecosystem-sensitive areas may represent a considerable health and ecosystem risk due to direct and indirect exposure to mercury and its compounds.

The Governing Council (GC) of the United Nation Environmental Project in its 24th session calls for commitments to increase efforts to reduce global releases and risks, increased data collection and analysis as well as strengthening intergovernmental and UNEP partnerships. The GC established an ad-hoc working group to explore viability of voluntary measures and international legal instruments. In decision 24/3 IV the GC identified remediation of contaminated sites as one priority area for increased global efforts. The GC commits to address the remediation of existing contaminated sites affecting public and environmental health as well as to increase knowledge on areas such as inventories.

In response to the GC decisions the German Federal Ministry for the Environment together with German and Chinese partners agreed to organize a workshop on remediation of mercury-contaminated sites in China. Its objective was the exchange of knowledge on characterisation and identification of mercury-contaminated sites, remediation technologies and strategies as well as the development of inventories with respect to mercury.

The topics addressed were:

- Legal Background in Germany, Europe and China
- Register of Contaminated Sites
- Characterisation of Mercury-Contaminated Sites
- Risk Assessment and Risk Management of Harmful Substances
- Remediation Techniques and Strategies
- Remediation of Chemical Production Facilities

Legal Background in Germany and European Perspective

The awareness of contaminated sites being a major environmental problem came up in Germany around 1980 together with some severe cases of soil and groundwater pollution. The regions (Laender) began to register the sites where contamination was suspected: industrial sites, waste disposal sites and military sites. Today, about 290,000 sites are registered as suspected to be contaminated. It is estimated that 10 to 20 % of them will need to be remediated. About 500 million euros are spent every year for the clean-up of contaminated soils and groundwater in Germany.

In 1999, the Federal Government put the Federal Soil Protection Act (BBodSchG) and the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) into force, which established nationally standardised regulations for the registration and remediation of contaminated sites. The purpose of the Soil Act is to protect or restore the functions of the soil on a permanent and sustainable basis. Actions entail the prevention of soil changes which are harmful to the soil, the rehabilitation of the soil and water resources at contaminated sites and precautions against negative soil impacts, such as the disruption of its natural functions and its function as an archive of natural and cultural history.

Since 1999, the individual States have been responsible for the enforcement of Act and Ordinance. Now, the Federal Environment Ministry is preparing an update of the Federal Soil Protection and Contaminated Sites Ordinance. It is to take the experience gained over several years with the implementation of the BBodSchV adequately into account and adapt its technical and methodological requirements to the advanced state of knowledge. In particular, it is necessary to incorporate methodological developments, which have noticeably accelerated with the introduction of soil protection legislation, and the results of a broad range of soil-related research into an updated Soil Protection Ordinance and implementation practice.

In 2006, the European Commission issued a Soil Thematic Strategy and a proposal for a Soil Framework Directive with the objective to protect soils across the European Union. The Strategy is intended to intensify research on soil and to raise public awareness. The Framework Directive sets out common principles, objectives and actions. It requires the 27 Member States to adopt a systematic approach to identify and combat soil degradation, to tackle precautionary measures and to integrate soil protection into other policies. They must set risk reduction targets for those areas and establish programmes of measures to achieve them. They will also have to prevent further contamination, to establish an inventory of contaminated sites on their territory and draw up national remediation strategies.

Register of Contaminated Sites

A successful treatment of contaminated sites requires a systematic and gradual procedure - such as it has proved its worth in Germany for many years. The first step of treatment is the registration of contaminated sites. Registration contains investigation in the sense of collecting information, various steps of assessment and documentation in maps and text. The main target is the complete registration of all abandoned landfills and industrial sites within an area municipality. Normally already existing, but widespread information is collected and systematically analysed. The methods of area-wide registrations are mainly based upon historical sources like documents, plans, aerial photographs and maps. The procedure of area-wide registrations is fairly complex and requires considerable skill. It is important to divide the steps of investigating industrial sites from those which refer to abandoned landfills.

In order to investigate abandoned industrial sites, historical address books, trade indices and license documents as well as historical maps are normally important sources. After the investigation of data, the registered industrial sites must be entered in an up-to-date topographical map of large scale. The most important sources for detecting landfills (and also contaminated sites caused by military action) are historical aerial photos (analysis of time-lapse aerial photos). In order to get all relevant information, aerial photos should be analysed stereoscopically. All information will be stored in a database.

Geographical information systems (GIS) combine spatial data with subject data. This means that e.g. the information „storage building“ contained in the data bank of the Geographical Information System is represented as an area (polygon) exactly as regards its position and contours. That means that the storage building – equally as all other (partial) uses recorded – is represented in the GIS with its contours on the background of a(n) (up-to-date) topographical basic map (or aerial photo) and may be thus exactly localised on the terrain. This graphical information together with the entries into the data bank provide an important basis for planning and carrying out further measures as they may be concentrated on areas showing a high contamination risk owing to their current and/or historical use.

Characterisation of Mercury-Contaminated Sites

Mercury contamination of local, regional, and global environments has become an increasingly studied subject in recent years. Areas where Hg pollution has been most acute include abandoned Hg mines, gold mining areas where Hg was used in the amalgamation process, and industrial sites where Hg has been released as a byproduct of chemical processes. Different from many other heavy metals, mercury undergoes several processes of species transformation, which determine its toxicological potential in natural environments. In all cases, knowledge of the molecular-level speciation of Hg is essential for understanding its potential bioavailability and impact on the environment. Among these transformation processes, the formation of volatile Hg(0) through reduction of Hg^{2+}-compounds and binding of Hg to natural organic matter are the most important processes determining the mobility in the environment. Especially in aqueous systems, the formation of Hg organic complexes such as methylmercury is a key process for the enrichment of Hg in fish and finally in the human food chain. Methods for determining Hg speciation have increased in both number and sophistication over time, ranging from visual identification of Hg phases in ore-grade samples to sequential chemical extractions (SCE), sequential thermal desorption, electron microprobe analysis, and in-situ X-ray absorption spectroscopic analysis. Over the past 15 years, thermal desorption methods have been shown to be a strong tool to determine solid-phase inorganic Hg compounds in contaminated soils and sediments. In combination with aqueous leaching and chemical methods to determine dissolved Hg species, both methods allow far-reaching risk assessment of contaminated areas.

Guizhou province is recognized as a heavily Hg-polluted area in China due to both the special geochemical background and human activities. Two key anthropogenic Hg emission sources in Guizhou were coal combustion and metals smelting, which dominantly contributed to the high levels of Hg in local ecosystems and high fluxes of Hg deposition. The annual Hg emission from anthropogenic sources ranged between 22.6 and 55.5 t, which was about 6.3-10.3% of current total Hg emissions in China.

Meanwhile, Hg-enriched soil in the province serves an important natural Hg emission source to the ambient air. The local environment of Hg mining and zinc smelting areas are seriously contaminated with Hg. It is demonstrated that rice growing in Hg-contaminated soil can accumulate methylmercury (MeHg) to a level to pose a health threat to local inhabitants whose staple food is rice.

Local inhabitants in Hg mining areas are exposed to Hg through inhalation of Hg vapor and consumption of rice with a high level of MeHg. Rice intake is indeed the main MeHg exposure pathway to local inhabitants in Hg mining areas in Guizhou, which is contrary to the general point of view that fish and fish products are the main pathways of MeHg exposure to humans.

Risk Assessment and Risk Management of Harmful Substances

The German soil protection ordinance encloses trigger-values for the soil-to-human, soil-to-groundwater and soil-to-edible-plant exposure pathways to identify “harmful changes to the soil functions”. Trigger values are used for risk-assessment in the exploratory investigation phase to diagnose the need for further investigations. Because of the hazard-based nature of these values – especially for the soil-to-human pathway – they can release remediation measures in certain cases. The derivation of these values is well documented and the exposure conventions are as realistic as possible concerning the ‘realistically worst case’.

The starting point in the derivation of trigger values for the soil-to-human pathway is the tolerable resorbed doses (TRD) achieved from experimental or epidemiological data. Due to different toxicities, inorganic (especially $HgCl_2$) and organic (especially MeHg) mercury species are discriminated. By calculating a TRD-value, safety factors are required to get a safe distance to the lowest observed adverse effect concentration (LOAEL) and the no-effect level (NOAEL), respectively.

To get a trigger value, information about the background exposure by food, drinking water and air is necessary. The background exposure in Germany by oral ingestion was assessed to be 30-300 ng/kg*d. As a result of special research, the convention of a contingent of 80 % of the TRD by the (food) background was chosen in the case of mercury.

Conventions about the exposure of humans, especially children, to contaminated soil are the second stand for calculation of trigger values (e.g. a soil incorporation rate of 33 mg soil/ kg*d for children). From these data, a primary trigger value for (organic, oral) mercury was calculated with 4.7 mg/kg. From all calculation approaches, this was the most sensitive one. Keeping in mind the ratio of inorganic and organic mercury in the ‘worst case’, the trigger value was fixed with 10 mg/kg for playgrounds. Trigger values for all usages are to be discussed in Germany.

Remediation Techniques

In the past, cleanup was very often based on civil engineering approaches aiming at maximum risk control (excavation/containment) or risk elimination. Groundwater remediation has focused on the removal of contaminated water form the subsurface and treating it at the surface (P&T).

From a technical point of view these approaches are still the fastest way to solve the problem. If there is an urgent need to reuse the sites or to solve a problem this is an advantage. The high costs associated with these methods are a big disadvantage and were prohibitive in many projects. As a consequence, concepts which focus on the control of the groundwater plume or the containment of the source rather than the elimination of the source have received increasing attention during recent years. A lot of active and passive in-situ technologies have been developed that address the contamination of soil and groundwater and avoid the (effects and cost of) excavation and the above-ground environmental impacts but require more time. They have less predictable results and may require long-term monitoring and aftercare.

The remediation strategy developed for a particular site may combine both approaches and several different methods. Different mobility of the components of a mixture of contaminants will require different methods, strategies and priorities of remediation.

Integrated strategies consisting e.g. of P&T (pump-and-treat) for hydraulic control and dissolved plume mass removal combined with source-targeted technologies have been determined to be a most effective long-term solution in many cases and may lead to cost-effective remediation measures specifically suitable to large industrial areas, where the source zones are often poorly defined or hardly accessible.

Selection and integration of technologies should use the most effective contaminant transport mechanisms to arrive at the most effective treatment scheme. To assess the applicability and potential performance of technologies, information is required on the contaminants present and the physical, chemical, and biological properties of the material to be treated.

Treatment technologies capable of contaminant destruction by altering their chemical structure are thermal, biological, and chemical treatment methods. Treatment technologies used for extraction and separation of contaminants from environmental media include soil treatment by thermal desorption, soil washing, solvent extraction, and soil vapour extraction (SVE) and water treatment technologies. Treatment technologies that immobilise the contamination include stabilisation, solidification, and containment technologies, such as placement in a secure landfill or construction of treatment walls. No immobilisation technology is permanently effective, so some type of maintenance is desired.

Some technologies can be applied ex-situ (after contaminated soil or groundwater has been removed for the treatment) or in-situ (without removing the contaminated media). Ex-situ treatment may be performed on-site using mobile or transportable treatment systems or off-site fixed treatment facilities.

The processes are frequently combined in treatment trains. A treatment train is a sequential combination of technologies or unit processes which treat recalcitrant matrices more effectively than any single technology could. E.g. soil washing becomes the prelude to chemical or biological treatment.

Remediation of Contaminated Sites – Strategies

In Germany and other European Countries, a large number of regions exist where industrial, military and mining activities during the past century have led to vast contamination in soil, groundwater and surface waters.

Large-scale contaminated sites may severely affect human health, the environment and the economy. Currently some 20,000 of these so-called megasites exist in Europe (including CEE States) with estimated costs for revitalisation measures that exceed the amount of 100 billion euros. The figures clearly demonstrate that revitalisation of megasites demands innovative site investigation and remediation strategies to make it economically feasible.

To streamline site investigations and clean-up decisions, a dynamic framework is needed that allows site managers to achieve defined project objectives. According to the TRIAD approach (approach to decision-making for hazardous waste *site*), which is being recommended by the U.S Environmental Protection Agency, elements such as systematic planning, dynamic work plan, on-site analytical tools need to be integrated in such an approach (EPA, 2005).

In preparation of effective site investigation measures, a series of factors need to be considered. These include technology selection, identification of potential exposure pathways, hot-spot detection, assessment of risks for human health and the environment, design of a conceptual site model (CSM), calculation of clean-up levels, as well as estimation and evaluation of costs for site improvement, operation, and maintenance. Some of the factors are of particular relevance in developing an appropriate remediation strategy for large-scale contaminated sites, among them the CSM and the delineation of contaminant sources in the subsurface.

The CSM is one of the primary planning tools that can be used to support the decision-making process managing contaminated land and groundwater on a large scale. The CSM organises available information about a site in a clear and transparent structure and facilitates the identification of data and information gaps. Once the CSM is established, additionally needed data can be gathered and integrated in the CSM, followed by a revision of the CSM and a refinement of decision goals, if required. Thus, the CSM matures and allows an improved understanding of the site characteristics, such as contamination status, receptor profiles, etc., and the re-adjustment of decision criteria.

The detection of hot spots is essential for the design of source removal measures. Particularly on contaminated sites of large extent, the hot spot search would cause enormous costs if it were performed on the basis of soil and/or groundwater samples taken from a regular grid mesh. A more cost-effective approach is the application of geostatistical methods which allow hot-spot identification under definite boundary conditions (probability of hitting or missing hot-spots, maximum size of hot-spots that would be hit, a grid of samples based on finding a hot-spot of a defined size with a distinct probability).

Remediation of the chemical production facility of Marktredwitz

For more than 200 years, products containing inorganic and organic mercury were processed in the chemical production facility in Marktredwitz (Chemische Fabrik Marktredwitz – CFM), the oldest chemical manufacturing facility in Germany. The plant caused serious environmental pollution before it was closed down in 1985.

On the premises of the chemical production facility, the concrete and the brick-structures of the buildings as well as the subsurface soil and soil- and groundwater were severely contaminated with mercury (up to 5000 mg/kg in subsurface soil and up to 200 mg/l in soil water). For the protection of the nearby river (Kösseine), a vertical groundwater barrier was installed; for the decontamination of the site, technical facilities and buildings were demolished. Soil excavation of material containing more than 10 mg mercury per kg and a groundwater pump-and-treat system were employed until 1996.

About 55,000 metric tons of contaminated debris and soil were treated in an off-site soil treatment facility and cleaned up to concentrations of mercury below 50 mg/kg by soil washing and vacuum distillation. The treated soil was deposited in a mono-landfill. 35,000 metric tons of excavated soil were landfilled directly. Another 5,000 metric tons containing chemical wastes and treatment residuals from the manufacturing process were deposited in a subsurface landfill.

Soil sampling and analysis were done in the nearby city centre in order to characterise the contamination in this area. Mercury content up to 180 mg/kg soil was determined. Furthermore, water, sediment, air, dust and food samples were analysed for mercury. Based on specific exposure scenarios, the epidemiological threat for residents living in the municipal area was estimated.

Consequentially, in gardens with more than 33 mg mercury per kg soil (limit value from risk assessment for housing areas with gardens), soil excavation and backfilling with clean soil was done. Human bio-monitoring (sampling of blood and urine) was performed as well.

Mercury-contaminated effluents were discharged into the rivers Kösseine and Röslau without any pre-treatment for more than 200 years. Analyses of water and sediment showed that for more than 15 km downstream of the CFM, river bed sediments were contaminated with up to 700 mg mercury per kg and flood plains contained up to 170 mg mercury per kg agriculturally used soil. Highest concentrations in river sediments were measured in backwaters from weirs; from these zones, about 16,000 metric tons of river sediments were removed. Forage (grass) from the flood plains was regularly analysed and reassessed for mercury content. A bio-monitoring programme has been installed in order to monitor the effects of the site remediation on the aquatic ecosystem. A long-term risk assessment for the groundwater predicted no adverse effects.

2 Introduction

Mercury-contaminated sites pose a serious risk to human health and the environment. The state of knowledge about the threat of mercury for human health and the environment is assessed and known. These findings are included in UNEP GC decision 22/4. Specific knowledge concerning sites contaminated with mercury is lacking, just as the extent to which sites contaminated with mercury are adding to global, regional or local negative effects on the environment. Especially, site-specific (i.e. soil-specific) and contamination-specific properties influence the extent of the risk for human health or the environment.

Mercury-contaminated sites potentially represent an important source of mercury emission into the atmosphere due to the evaporation of mercury from contaminated land and waters. They constitute an important source for transboundary movement of mercury through hydrological cycles, particularly in the large river catchment areas and contaminated coastal regions. Contaminated sites in ecosystem-sensitive areas may represent a considerable health and ecosystem risk due to direct and indirect exposure to mercury and its compounds.

The Governing Council (GC) of the United Nation Environmental Programme called in its 23th session for the reduction of risks posed by mercury. Improved information on mercury, also through collaborative efforts to inventory global mercury uses and releases, should be provided.

The Governing Council in its 24th session called for a commitment to increase efforts to reduce global releases and risks, increased data collection and analysis as well as strengthening intergovernmental and UNEP partnerships. The GC established an ad-hoc working group to explore the viability of voluntary measures and international legal instruments. In decision 24/3 IV the GC identified the remediation of contaminated sites as one priority area for increased global efforts. The GC commits to address the remediation of existing contaminated sites affecting public and environmental health as well as to increase knowledge on areas such as inventories. The GC requests to analyse information on the extent of site-based contamination as well as associated environmental and public health risks. Environmentally sound mitigation options and associated costs should be provided and the extent of the contribution of contaminated sites to global releases should be assessed. The established Open Ended Working Group (OEWG) composed of governments, regional economic integration organisations and stakeholder representatives are to review and assess options for enhanced voluntary measures and new or existing international legal instruments. At the first meeting of the OEWG in Bangkok in November 2007, remediation of contaminated sites was one priority area to prevent mercury contamination from spreading. Therefore the following topics among others were addressed:

Prevention of mercury contamination from spreading

- Development of guidelines for the identification and surveying of sites possibly contaminated with mercury
- Provision of information on contaminated sites
- Performance of risk assessments for setting priorities for action
- Quarantine of sources of contamination and contaminated areas to prevent further contamination
- Installation of barriers, covers, collection basins or other technologies to minimise the spreading of mercury contamination in affected media

Remediation of contaminated sites

- Development of guidelines for the identification of sites contaminated with mercury.
- Adoption and enforcement of legislation requiring environmental remediation of mercury contamination
- Development and enforcement of mechanisms for monitoring contaminated sites
- Establishment of proper management of water and land resources to prevent enhanced transport and bioavailability of mercury
- Development of guidelines for choosing BAT or BEP remediation technologies based on site-specific criteria
- Development of a cost-effective technology for remediation

Increase knowledge of inventories

- Creation of a mercury register and keeping of national inventories of all mercury stockpiles and production sources
- Improvement of emission inventories

In response to the GC decisions, the German Federal Ministry for the Environment together with German and Chinese partners agreed to organise a workshop on the remediation of mercury-contaminated sites in China. Its objective was to exchange knowledge on the characterisation and identification of mercury-contaminated sites, remediation technologies and strategies as well as the development of inventories with respect to mercury.

The topics addressed were:

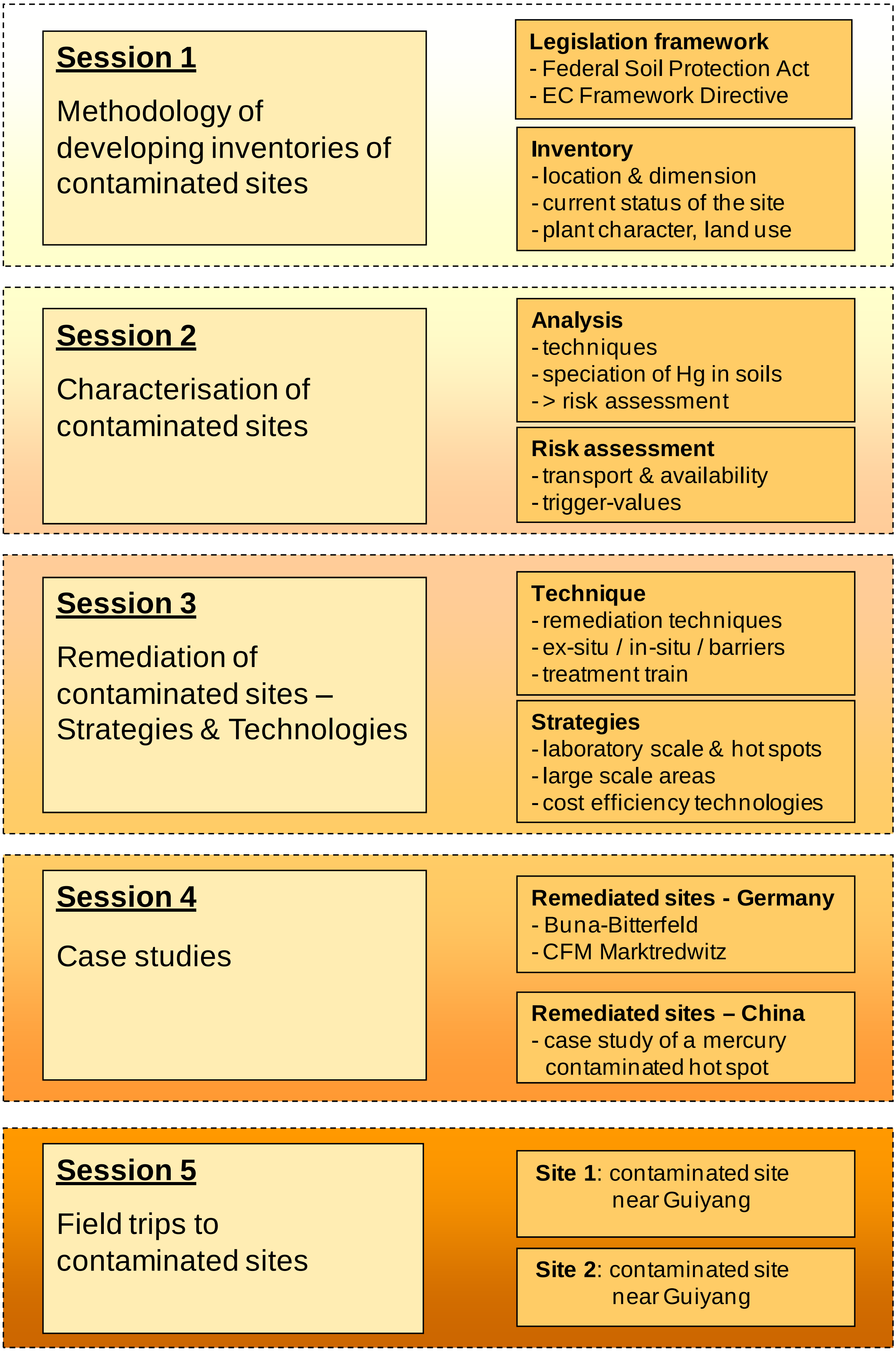
1. Legal framework
    - Federal Soil Protection Act of Germany / Comparison with China
    - Soil Framework Directive of the European Commission

2. Methodology of developing inventories of contaminated sites
    - identification of contaminated sites
    - determination of concentrations/loads of mercury in these areas
    - determination of the actual risk to environmental and human health
    - development of priority lists: cost/benefit considerations

3. Remediation of contaminated sites
    - methods for the characterisation of identified sites
    - analytical methods for fast and reliable determination of mercury
    - remediation technologies
    - remediation strategies

4. Case studies (with on-site visits)
    - cleaning-up of contaminated industrial and mining areas in Germany / Europe
    - examples of identified sites in China (e.g. industrial facilities, mining areas)

The workshop was divided into 5 sessions, which reflected the topics addressed. In the following figure the structure of the workshop is depicted.



Session 1

Methodology of developing inventories of contaminated sites

Legislation framework
- Federal Soil Protection Act
- EC Framework Directive

Inventory
- location & dimension
- current status of the site
- plant character, land use

Session 2

Characterisation of contaminated sites

Analysis
- techniques
- speciation of Hg in soils
- -> risk assessment

Risk assessment
- transport & availability
- trigger-values

Session 3

Remediation of contaminated sites – Strategies & Technologies

Technique
- remediation techniques
- ex-situ / in-situ / barriers
- treatment train

Strategies
- laboratory scale & hot spots
- large scale areas
- cost efficiency technologies

Session 4

Case studies

Remediated sites - Germany
- Buna-Bitterfeld
- CFM Marktredwitz

Remediated sites – China
- case study of a mercury contaminated hot spot

Session 5

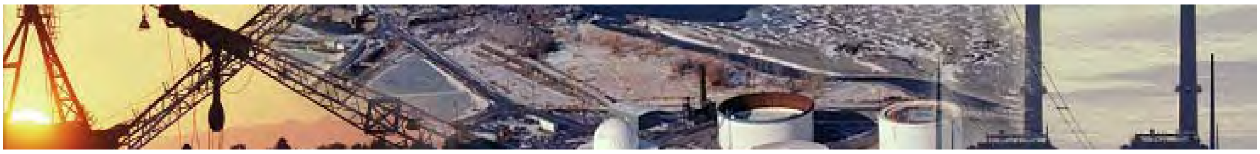
Field trips to contaminated sites

Site 1: contaminated site near Guiyang

Site 2: contaminated site near Guiyang

Figure 1 **Workshop structure**

3 Workshop Presentations



Management of contaminated sites in Germany and Europe - Legislation, Experiences, Tendencies

Jörg Frauenstein, Federal Environment Agency, Wörlitzer Platz , D-06844 Dessau-Roßlau, Germany

Andreas Bieber, Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Robert-Schuman-Platz 3, D-53175 Bonn, Germany

Introduction

In 2007, more than 270.000 sites suspected to be contaminated were registered in Germany. To handle this huge number of sites, a stepwise risk assessment procedure was developed to filter out the sites where there is urgent call for action because of their risks for humans and the environment. In the past 20 years, considerable efforts have been made to clean up and redevelop contaminated sites. Public funding to research as well as to industry has contributed significantly to the development of soil treatment technologies at a high standard. The technologies used are best demonstrated for the treatment of typical industry-originated substances. Current research and development efforts are rather concentrated on the setting up of cost-efficient clean-up techniques and strategies.

At first, the main remediation strategy had been focused on soil decontamination, but nowadays the approaches move to a broader concept. Land remediation not only involves clean-up of soil and groundwater but encompasses the whole process of land development for its reuse, i.e. the entire process which makes the site fit for the purpose of future uses. The remediation process will become more complex and interdisciplinary in which the actual clean-up procedure must contribute by effective technologies at reasonable prices. Regarding a request to the Federal States "Länder" Germany spend each year about 500 Million € public money for investigation and remediation for ownerless sites (coming from "Länder"- budgets) besides the expenditures from responsible polluters, remediation and topic related research programmes. The given statistical information in table 1 are always showing a recent status, which will be updated at least once a year by a joint “Länder” working group. Especial regarding the numbers for finalised risk assessment and remediation a cumulative dimension is shown. So these numbers representing a summation of investigation and measures done so far and depending from the implementation of registers on the “Länder”-level covering former waste disposal and industrial sites only.

German Policy for the management and remediation of contaminated land

Background and Legal framework

The purpose of the Soil Act is to protect or restore the functions of the soil on a permanent and sustainable basis. Actions entail the prevention of soil changes which are harmful to the soil; the rehabilitation of the soil and water resources at contaminated sites; and precautions against negative soil impacts, such as the disruption of its natural functions and its function as an archive of natural and cultural history.

Based on the subsidiary rule, the Soil Act has also effects where sectoral legislation does not cover impacts on soil. Relevant sectoral legislation includes:

- Certain provisions of the Closed Substance Cycle and Waste Management Act;
- Transport of hazardous materials;
- Fertilizer and plant-protection law;
- Genetic Engineering Act (Gentechnikgesetz);
- Federal Forest Act and the Länder forest law;
- Land Consolidation Act (Flurbereinigungsgesetz);
- Construction; modification; maintenance and operation of transport routes and provisions governing traffic and transport;
- Construction-planning law and building regulations;
- Federal Mining Act (Bundesberggesetz);
- Federal Pollution Control Act.

The Soil Act does not apply to installations, activities, devices or equipment, nuclear fuels and other radioactive substances and to investigations for the recovery, transport, storage, treatment and destruction of warfare agents.

According to the Federal Soil Protection Act, harmful impacts on soil functions are defined as hazards implicating considerable disadvantages or nuisances for individuals or the general public.

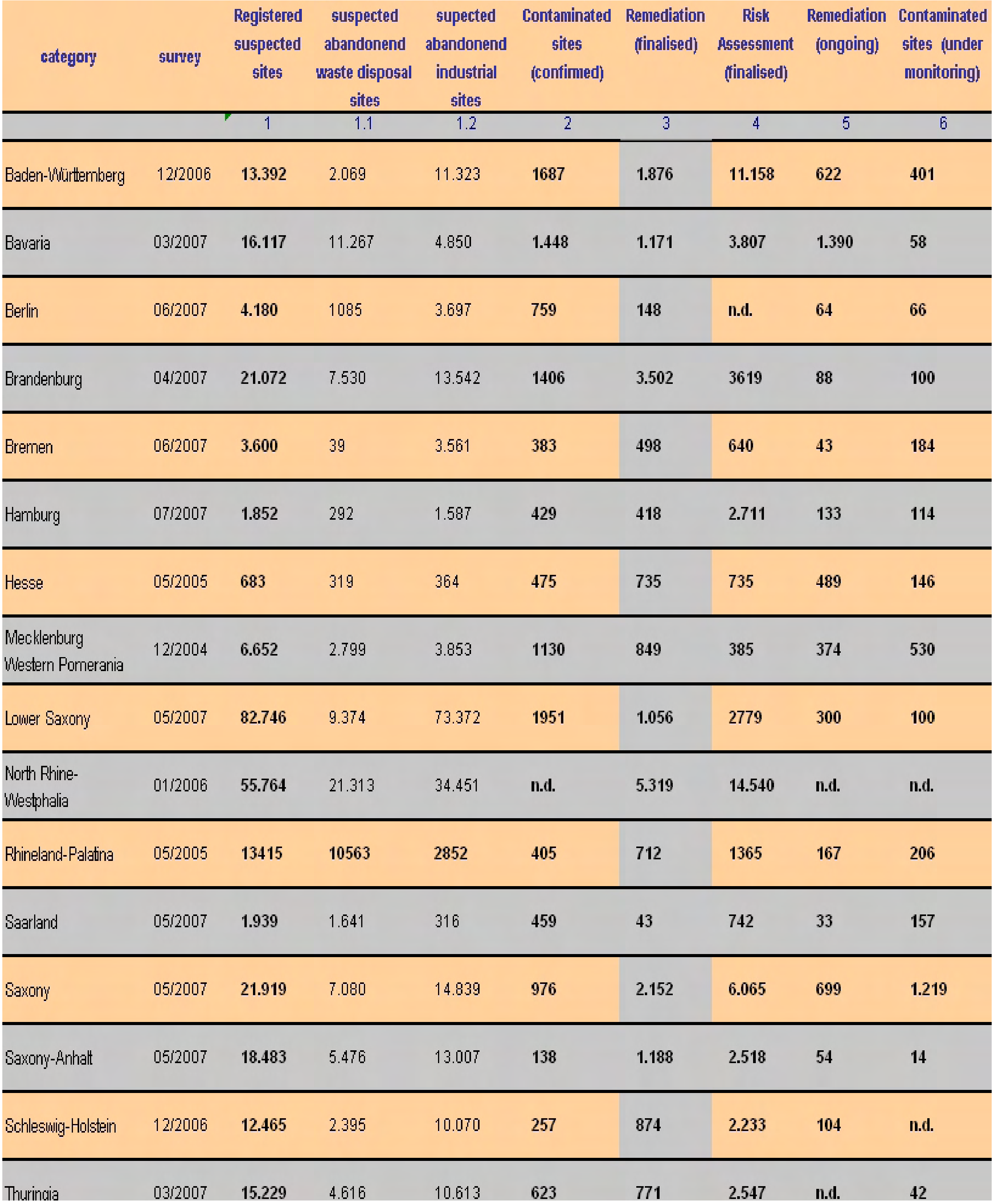
The management of contaminated land and groundwater was a one of the key pressures for a federal law. In 1999, the Federal Government of Germany put the Federal Soil Protection Act (BBodschG) and the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) into force, which established nationally standardised regulations for the registration and remediation of contaminated sites. Since then, the individual States have been responsible for the enforcement of Act and Ordinance.

One important focus of the act is to prevent soil contamination and to regulate the clean-up of abandoned contaminated sites. The Federal Soil Protection and Contaminated Sites Ordinance supplements the Act and specifies requirements in respect of site investigation, sampling strategy and laboratory approach, evaluation and remediation. The laboratory approach and the methods for soil analysis are furthermore determined according to German Industry Standards (DIN) and European Standards (CEN).

This legislation has established a national assessment framework for the evaluation of soil quality in relation to the “Soil-Man”, “Soil-Plant” and “Soil-Groundwater” paths of action.

Planned amendments in legal framework

The purpose of the amending ordinance is to update the Federal Soil Protection and Contaminated Sites Ordinance which entered into force in July 1999. It is to take the experience gained over several years with the implementation of the BBodSchV adequately into account and adapt its technical and methodological requirements to the advanced state of knowledge. In particular, it is necessary to incorporate methodological developments, which have noticeably accelerated with the introduction of soil protection legislation, and the results of a broad range of soil-related research into an updated Soil Protection Ordinance and implementation practice. Planned amendments in detail:



category	survey	Registered suspected sites	suspected abandonend waste disposal sites	supected abandonend industrial sites	Contaminated sites (confimed)	Remediation (finalised)	Risk Assessment (finalised)	Remediation (ongoing)	Contaminated sites (under monitoring)
		1	1.1	1.2	2	3	4	5	6
Baden-Württemberg	12/2006	13.392	2.069	11.323	1687	1.876	11.158	622	401
Bavaria	03/2007	16.117	11.267	4.850	1.448	1.171	3.807	1.390	58
Berlin	06/2007	4.180	1085	3.697	759	148	n.d.	64	66
Brandenburg	04/2007	21.072	7.530	13.542	1406	3.502	3619	88	100
Bremen	06/2007	3.600	39	3.561	383	498	640	43	184
Hamburg	07/2007	1.852	292	1.587	429	418	2.711	133	114
Hesse	05/2005	683	319	364	475	735	735	489	146
Mecklenburg Western Pomerania	12/2004	6.652	2.799	3.853	1130	849	385	374	530
Lower Saxony	05/2007	82.746	9.374	73.372	1951	1.056	2779	300	100
North Rhine-Westphalia	01/2006	55.764	21.313	34.451	n.d.	5.319	14.540	n.d.	n.d.
Rhineland-Palatina	05/2005	13415	10563	2852	405	712	1365	167	206
Saarland	05/2007	1.939	1.641	316	459	43	742	33	157
Saxony	05/2007	21.919	7.080	14.839	976	2.152	6.065	699	1.219
Saxony-Anhalt	05/2007	18.483	5.476	13.007	138	1.188	2.518	54	14
Schleswig-Holstein	12/2006	12.465	2.395	10.070	257	874	2.233	104	n.d.
Thuringia	03/2007	15.229	4.616	10.613	623	771	2.547	n.d.	42

Table 1: Inventory - Germany (last update September 2007 provided by the joint “Länder” working group)

Scope of application and definitions

Based on ordinance authorisations in soil protection and waste legislation, requirements for the utilisation of soil and other materials will be defined in an Ordinance on the utilisation of mineral waste. Within the same process, the application and introduction of materials onto or into soil will be regulated in an extension of Article 12 BBodSchV.

Investigation of suspect sites and sites suspected of being contaminated

The requirements on investigation/analysis methods will be updated. This requires a fundamental revision of Annex 1 to the BBodSchV. As regards investigation methods, the revision aims to take advances in knowledge and developments into account and, secondly, provide the possibility to replace, at least partially, the static reference to methods by a dynamic one, which would obviate the need for a formal amendment of the ordinance in future.

In addition, revisions are necessary for the areas of sampling, soil gas measurement and leachate forecast. In this revision, the requirements for sampling and soil gas measurement must be defined more clearly and amended to reflect advances in knowledge. The provisions on leachate forecasting have to be revised in a practicable way on the basis of the results of research carried out under the eponymous funding priority of the Federal Ministry of Education and Research.

Measurement uncertainty is a prime factor when evaluating the results of relevant investigations. Information on this will be formulated and use instructions will be included in the Annexes to the Ordinance to enable a more reliable interpretation of measurement results.

Assessment of suspect sites and sites suspected of being contaminated

The trigger and action values in Annex 2 to BBodSchV will be reviewed in terms of their timeliness, particularly with respect to their human toxicological basis. Values for additional substances will be added on a moderate scale.

In so doing, the following aspects in particular will be taken into account:

- toxicological relevance,
- frequency of occurrence at contaminated sites and in cases of known soil contamination,
- a sound data base for derivation of values,
- availability of a suitable method of detection.

Furthermore, the requirements for the soil–plant pathway will be supplemented by values for additional organic pollutants, a group of substances which so far has been given too little consideration.

For the soil–human being pathway, trigger values for antimony, cobalt and thallium and for select explosive-typical compounds will be added.

For the soil–groundwater pathway, a harmonisation of trigger values with the marginal thresholds of the Joint Water Commission of the Federal States (Länderarbeitsgemeinschaft Wasser, LAWA) was considered for a select spectrum of substances. Points under discussion are the adoption of marginal thresholds as trigger values for the boundary area between the water-unsaturated and water-saturated zones, the introduction of additional trigger values for evaluating the leachability of pollutant source material, and the integration of transport processes into the assessment on a case-by-case basis.

Remediation, protective and restrictive measures

The issue is whether and how natural attenuation processes should be taken into account in the regular procedure for dealing with contaminated sites. Since major research programmes on this subject have currently not yet been completed, it will not be regulated comprehensively in the BBodSchV; instead, the Ordinance will include provisions that open up the possibility to take natural attenuation processes into consideration.

Accidents

A procedure different from the regular procedure will be incorporated into the Ordinance as “exemption” in the case of accidents, i.e. in the warding off of apparent harmful soil changes or immediate danger.

Precautions

Compliance with precautionary requirements in respect of substance inputs to soil is evaluated on the basis of precautionary values. The inclusion of the soil–soil organisms pathway into the derivation of precautionary values has proved promising and responds to the concern of precautionary soil protection. Here, it has been recommended that additional precautionary values should be included and that the soil-soil organisms pathway should be taken into account in their derivation.

Large-scale federal remediation projects

After Germany’s reunification the properties and thus the financial responsibility for contaminated sites of the former GDR were handed over to the Federal Government.

The often massive contamination on those properties represented a substantial risk for private investors so that there was an urgent need to eliminate such obstacles. In order to encourage investments at contaminated sites, in 1992 the Federal Government and the New States drew up an Administrative Agreement on the financing of contaminated site remediation. Under this Agreement, the Federal Government and the States established 22 large-scale projects whereby the financing of the remediation is shared by the Federal Government (75%) and the New States (25%). The total costs were more than 3 billion Euros.

The large-scale projects comprise industrial complexes, e.g. the huge chemical industry at Leuna, Buna and Bitterfeld-Wolfen, former mining areas, refineries, steelworks and dockyards.

The particularly hazardous situations at the project sites result from interacting factors:

- serious and widespread contamination from abandoned industrial sites and from unsecured or insufficiently secured disposal sites with partly unknown pollutant mixtures

- regionally significant changes in the groundwater systems due to modified water management in former mining areas
- disposals of hazardous substances and radioactively contaminated material from adjacent mining areas.

The aims of the remediation measures in these large scale projects are:

- immediate measures for averting dangers
- remediation and reclamation of landscapes degraded by industrial use or mining
- groundwater protection to guarantee drinking water abstraction
- maintenance of industrial sites including their infrastructure.

Remediation and redevelopment of former mining areas

Germany has a mining tradition that dates back hundreds of years. While potash and rock salt resources together with hard coal and lignite are still extracted, mining of copper, uranium and other metals has stopped. The remediation of former lignite mining areas was and is still one of the main environmental rehabilitation tasks in Germany.

Main tasks in the remediation of mining sites averting dangers arising from former mining activities, e.g. stabilising slopes, reclamation of mining sites, restoring a balanced water regime, eliminating hazards emanating from groundwater and soil contamination by earlier industrial use.

Lignite mining rehabilitation goes beyond the scope of the Federal Soil Protection Act. Most of the former mining sites and suspected contaminated sites are subject to the Federal Mining Act, which came into force in the New States in 1990. Article 55 of the Federal Mining Act requires mine-owners to rehabilitate abandoned mining sites. It has to be ensured that no risks arise from land formerly used for mining purposes and takes the public interest into account.

According to the Administrative Agreement mentioned above under chapter 4 the ownership of the mines passed into the hands of the Federal Government, which became responsible for mining site remediation. The cost sharing ratio between Federal Government and States is similar to the large scale projects.

Until the end of 2007 a total budget of approximately 7.8 billion Euros will be spend for the lignite remediation programme only. The current prolongation of the agreement, which will be in effect from 2008 to 2012, provides for a total budget of nearly 1 billion Euros to finance the costs of remediation measures. The measures are primarily aimed at improving the self regulating groundwater balance and at the rehabilitation of infrastructure in these regions.

Another focus in mining rehabilitation lies on former uranium mining. The financial responsibility belongs to the Federal Government only. The remediation programme will continue until 2015 with an expected budget of 6.2 billion Euros. Two-thirds of necessary actions are finalised so far.

Remaining tasks in the remediation of uranium mining sites are long-term water treatment, environmental monitoring and maintenance and after care for remediation related installations and constructions.

Recent national Research programmes related to contaminated land management, supported by the Federal Ministry of Education and Research

SAFIRA II — Revitalization of Contaminated Land and Groundwater at Megasites — (2006-2012)

SAFIRA II addresses the development and demonstration of a new interdisciplinary approach for a cost-effective and sustainable development-oriented management of megasites. SAFIRA II integrates available and emerging technical and non-technical methodologies and serves in specific the following objectives:

- The development, implementation, and operation of an integrated decision support and management system.

- The integration of socio-economic approaches.

- The preparation of an open platform for innovative technologies and methods.

A major goal of SAFIRA II is to make the technological and methodological innovations available to others and to promote the integrated management system. As in previous SAFIRA projects, the new SAFIRA II infrastructure shall attract other research institutes and further research funding (e.g. in the framework of national and EU-wide research tenders).

SAFIRA II shall serve as the nucleus for inter- and cross-disciplinary activities towards developing sustainable solutions for the management of contaminated land and groundwater at large scales. Very good prospects for establishing a joint platform for targeted research activities related to megasites are already assured by the involvement of external partners from the very beginning of the SAFIRA II project. An important part of the project is therefore the continuous dissemination and exploitation of results and products to the scientific as well as the non-scientific sector.

SAFIRA II offers the unique opportunity to contribute significantly to solve the European megasite problem. It will be the only research platform of this dimension that enables researchers to test the technical and non-technical aspects of new management concepts under real-world conditions.

A major focus of the SAFIRA II research platform is to provide support for megasites located in the new EU Member States, the Accession States and other Eastern European countries. Due to severe financial limitations and consequently very limited reliable data, the conditions at most of the megasites in these countries are considered at least critical in terms of potential health and environmental risks. However, even with additional funding provided by the EU, the majority of the problems encountered cannot be solved based on presently available concepts and technologies often developed for smaller scale problems.

Basic concept

An integrated management system for contaminated land and groundwater needs to balance two conflicting goals. It has to maintain full accountability for all environmental and health risk-related decisions while systematically integrating the preferences of all stakeholders (developers, neighbors, etc.) into the political decision-making on land-use and remediation (acceptability). If stakeholder decision making would lead to any dilution of accountability of the responsible authorities, legal procedures must be installed to protect and control for potential policy failures. On the other hand, if the decisions of responsible authorities do not reflect the total quality requirements of all involved stakeholders (under changing neighborhood and economic conditions), decision making tools and processes must be devised to achieve benchmark values of stakeholder acceptability for any combined land-use and remediation strategy.

Against this background, and based on the experience in previous projects, as well as under consideration of the narrow legal boundaries for an institutionalized stakeholder-decision making process in many European countries (particularly in Germany and in Eastern European countries), a decision support system (DSS) will be that reflects the "differentness" of the two above mentioned goals (pillars) and related tasks.

Innovation through integration

More than 25 years of intensive research worldwide have lead to some significant advancement in understanding some major processes controlling the release, spreading and fate of contaminants in the subsurface. Numerous technologies have been developed which can be used to (partly) de-contaminate the soil or the groundwater either in-situ or ex-situ at various costs. All this has certainly helped to better assess the risks and the possible remediation costs associated with contaminated sites. However, a lot of this knowledge has never made its way to real world sites. One of the reasons is that most of the research projects within this field are funded and organized to optimize only individual sectorial aspects, e.g. the contaminant removal efficiency of a specific technology or the risk assessment for a given receptor. However, decisions at real world sites are generally made based on a variety of factors, technical and non-technical. Consequently, adequate decision support systems have to integrate this variety as well as the extensive scientific knowledge gathered over the years.

The above-stated is probably true for all contaminated sites – however, for megasites it is essential in order to make the problem at all approachable. SAFIRA II therefore specifically recognizes and addresses the issue of "Innovation through Integration" for better solutions to the megasite problem. Integration is endeavoured on different levels by the integration of natural and social sciences, the integrated utilization of technical tools as well as the visualization and dissemination of scenarios, decision options and research findings.

The ambition of integrated megasite management is directly linked to the ambition of integrated modelling. Megasite management requires the provision of computation tools (models) that quantitatively describe the fate and transport of contaminants in all relevant compartments (i.e. vadose zone, groundwater, surface water). The models are an indispensable means for risk assessment and the comparison of different management i.e. remediation strategies at megasites for their effects. Due to the size of the problem (megasites typically cover areas > 10 km^2) and the fact that contaminant transport has to be described in multiple compartments, there is a need for new (scalable) modelling approaches and techniques. It is well known that performance of technical measures in the subsurface is uncertain, and so are the predictions. This is especially true for source treatment (depletion) technologies. The development of appropriate approaches for the quantification of the uncertainty inherent in the modelling results will be another focus of the research.

As the management of a megasite will follow a tiered procedure, fit-for-purpose models of different type and characteristics (e.g. degree of abstraction) will have to be provided, addressing the specific requirements and goals of the respective management step. GIS-based interfaces linking socio-economic boundary conditions to fate and transport models, the integration of efficient heuristic optimization schemes, high performance computing, user-friendly graphical user interfaces, and 3-D interactive visualization tools are further needs to be met. It is planned to make use of catchment scale reactive models that are currently under development. These models (or parts of it) will form the basis of the software development to be carried out within the framework of SAFIRA II.

Some integrative technical innovation highlights have already been identified as being crucial for the implementation of the integrated management approach. These highlights are outlined hereafter.

Technical highlights

Integrated plume delineation and source strength assessment for improved site evaluation: Integral investigation – a reverse perspective.

Integrated source delineation and clean-up strategies for accelerated remediation: In-situ clean up – expedited partial source removal.

Integrated high performance water treatment techniques for simultaneous treatment of a wide variety of complex contaminant mixtures in groundwater: Complex contaminant mixtures – the "treatment train" approach.

Integrated semiactive and passive remediation strategies: Enhancing degradation rates – "the compartment change" approach.

Integrated monitoring techniques for risk assessment, compliance control, and optimization of measures: Compliance monitoring – minimal invasive and reliable.

RUBIN — The German permeable reactive barrier network (2000-2009)

The focus of RUBIN´s missions and goals is to meet current R&D needs pertaining to the practical set up and long-term operation of PRBs as a prospective remediation technology in a large-scale, coordinated initiative. Especially a bundle of technical, operational, economic, ecological, toxicological, administrative and legislative issues as well as issues comprising long-term performance and stability are addressed and investigated. Therefore, RUBIN is scheduled to plan, design, implement, monitor and evaluate pilot and full-scale PRB projects in Germany in order to check and assess as thoroughly and precisely as possible applicability, performance and limits of PRBs in a broad technical scope combined with an intensive, simultaneous scientific backup. The network also covers novel innovative approaches to be utilized for eliminating recalcitrant compounds from contaminated groundwater by means of innovative reactive materials and novel barrier design and construction methods.

Although a growing number of demonstration sites for PRBs, predominantly involving treatment of chlorinated ethenes by granular iron metal, have proven successful in principle in North America, so far, PRBs have not been fully accepted and therefore established as new general remediation technologies in Europe. The lack of general acceptance and missing incentives to implement PRBs in full scale and in a wide scope are due to, among other things, still insufficient or missing comprehensive reliable information on long-term aspects, e.g. longevity, long-term effect and performance, and, associated with these items, the overall rentability. In Germany, 9 pioneering PRB projects (full and pilot scale) have been implemented revealing promising preliminary results, e.g., in Bernau (built 2001), Bitterfeld (1999), Denkendorf (2000), Edenkoben (1998, 2001), Karlsruhe (2000), Oberursel (2002), Reichenbach (2000), Rheine (1998) and Tübingen (1998), all revealing interesting design and engineering features. Therefore, the German BMBF decided to evaluate and assess the performance of PRBs as well as other material issues to a greater extent and in a broader scope by means of RUBIN.

Conclusions

According to the national as well as the international development and the analyses of overall findings at various PRB sites worldwide, some general conclusions have temporarily been drawn in Germany so far: PRBs with a specifically directed ground water flow such as “Drain-and-Gate“ or “Trench-and-Gate“ look promising, because the hydrology is passively manipulated and controlled, therefore, regarding the flow towards the reactor, it is well understood in principle. Furthermore, PRBs equipped with ISV (EC-PRBs) which were inserted into accessible shafts look promising, because control/maintenance concerning the reactive material can be relatively readily exerted, if needed.

Finally, PRBs employing activated carbon (AC) look promising, because it is a well-established reactive (sorptive) material, deployed in a variety of other clean-up processes. It can be advantageously combined with other materials like ZVI in PRBs, and it can treat a variety of different ground water contaminants, even when encountered in complex mixtures and in difficult ground water environments (high hardness, high sulfate etc), both successfully and economically. Moreover, positive findings at several CRB sites worldwide, especially at the Rheine PRB (CRB = no ground water control) and re ISV/Shaft Reactors plus Drainage (EC-PRBs = very high ground water control), equipped with GAC or particularly effective ZVI such as ReSponge, imply that both these systems seem to have a promising future. However, “classical“ F&G systems are apparently losing ground, because they may exert unpredictable influence on the ground water flow regime, even if a thorough modelling was implemented. If a malfunction occurs, e.g., by clogging of the reactive material or bypassing ground water, they often permit neither extended nor cheap investigation, control and/or intervention/repair regarding the particular damage, due to intrinsic hindrance re “active repair” related to their special design. EVERY PRB System that ensures a PLUG FLOW of the contaminated ground water towards its reactor(s)/reactive zones may be successful (Birke et al. 2004). We ought to be not allowed to hold any planning/engineering failure entirely responsible for every malfunctioning PRB (although they do occur). Actual scientific or other unambiguous evidence is needed. Chemical processing engineers and hydrogeologists ought to be consulted to a greater extend than until today in order to clarify current PRB issues.

Extensive data are published in a comprehensive manner in the German compendium and guidance on PRBs in 2006, which is currently issued by the “RUBIN” network/consortium.

KORA — Retention and Degradation Processes Reducing Contaminations in Groundwater and Soil — (2002-2008)

The overall goal of KORA is to investigate natural attenuation (NA) processes for consideration in contaminated land management. The task of the KORA funding priority is the exploration of intrinsically working natural retention and degradation processes in the subsoil on sites of different industrial branches, each with their own typical contaminants. KORA is aimed at developing technical and legal instruments which will facilitate the evaluation and customised use of these processes in the risk assessment and remediation of contaminated soils and groundwater

For this purpose, more than 60 projects of KORA will be carried out in different ways at currently 24 contaminated sites. It would not be possible to meet these common goals without a continuous discussion among the members of KORA and with external experts, authorities, and end users. Regular workshops and status meetings will provide for the communication that is essential for interdisciplinary cooperation; they will also ensure that a concrete result will be obtained at the end of the funding period even from the tax payer’s point of view: a firm basis for the use of natural attenuation processes in the assessment of hazards and in the treatment of contaminated sites.

The funding priority is focused on the results of international research, especially from the U.S. The research contains investigations of biological, (hydro-) geological and chemical processes in soil and groundwater under different environmental conditions and delivers insight into legal issues and acceptance of official bodies and the general public.

Design of KORA

The over 60 projects of this R&D-funding priority are investigating a wide range of sites using different methods. KORA is separated in eight Thematic Networks (TN) with different fields of research. The first six Thematic Networks are analysing effects of natural attenuation in direct dependence of certain industrial contaminations. TN 7 develops software for modelling and problem-related forecasting and TN 8 contains the parts legal aspects, acceptance and economic assessment.

TN 1: Refineries, fuel tanks, fuel/mineral oil (contaminants: TPH, BTEX, MTBE)

TN 2: Gas works, coking plants, coal tar processing (PAH, BTEX, coal tar, heterocyclics)

TN 3: Chemical industries, metal processing (chlorinated solvents)

TN 4: Landfills, abandoned waste disposal sites (household waste, chemical waste, ammonia)

TN 5: Former ammunition works (nitroaromatics)

TN 6: Mining and sediments (acidic water, heavy metals, DDT, HCH)

TN 7: Prognosis, modelling

TN 8: Evaluation, legal issues, acceptance by official bodies and the public

The KORA Management is charged with actively supporting all participants in the funding priority. They should promote the collaboration of the individual thematic networks to present a joint recommendation handbook and compile this using the knowledge and experience gained in the funding priority. Furthermore, the general public should be kept informed about the results of the funding priority through appropriate public relations work.

REFINA — Reduction of greenfield development and for promoting sustainable land management — (2004-2008)

The REFINA research programme is intended to define the necessary research lead in close cooperation with the municipal sector, with companies and competent Federal Government and federal state authorities and also with NGOs. The focal points are:

- Development of exemplary model concepts of innovative land management for selected regions and types of area
- Analysis, methods and evaluation for a sustainable land use
- Recycling and revitalization of derelict areas that were previously used and are contaminated in part (land recycling)
- Development of new yardsticks for evaluating soil quality and the need for the protection of selected areas
- Regional and national trend analyses of regional development and its assessment
- Further development of the tools for sustainable land management, taking into consideration the legal, economic and institutional conditional framework as well as
- Dissemination of knowledge by developing new information and communication structures.

The research activities should contribute to solving the following questions:

- How can land consumption be reduced and decoupled from economic growth?
- How can planning processes be organized to realize a resource-conscious land use?
- How can the reuse of former industrial, traffic or settlement areas be increased?
- Which case examples have to be chosen to prove the efficiency and sustainability of new strategies and solutions for a resource-conscious land use?
- How can social acceptance and perhaps a change of human behaviour be achieved with regard to sustainable land use and protection of soil?

As a result of the announcement of REFINA 838 institutions with 141 project proposals have applied for funding. Important topics are, among others:

- the rehabilitation of abandoned industrial sites/contaminated deposits
- land recycling of inner-city industrial areas
- the conversion of military sites
- the improvement of regional planning
- the restructuring of shrinking cities

Research projects with a funding volume of 20 million Euros and a total volume of 30 million Euros are planned for land management and soil protection measures. Research funding is provided in the form of grants to the amount of 50 to 100 % according to the EU funding framework conditions.

As a result of REFINA, best-practice examples are to be presented by cities and local authorities and scientific fundamentals of land management further developed.

The implementation of the research programme running until 2008 will be accompanied and annually evaluated by an advisory council with representatives from several federal states, government departments and associations.

European Soil Framework Directive

In September 2006, the European Commission presented a Thematic Strategy for soil protection and a Proposal for a Directive establishing a framework for the protection of soil.

The Strategy sets out a series of actions aiming at defining a comprehensive strategy with the overall objective of protection and sustainable use of soil, by preventing further soil degradation, preserving its functions and restoring degraded soils to a level of functionality consistent at least with current and intended use. The Strategy is intended to be partly implemented through the proposed Directive which contains the following elements:

- integration into sectoral policies;
- precautionary measures;

- prevention of contamination;
- measures to limit or mitigate sealing;
- identification of risk areas for erosion, organic matter decline, compaction,
- salinisation, landslides;
- identification of contaminated sites;
- programmes of measures;
- national remediation strategy;
- awareness raising, reporting and exchange of information.

The SFD is an important chance to regulate soil protection on the same level like water and air. It was not possible, at this stage, to attain the qualified majority needed to reach political agreement on a draft directive establishing a framework for the protection of soil.

The draft Directive aims at filling this gap by establishing a common strategy for the protection and sustainable use of soil, based on the principles of integration of soil concerns into other policies, preservation of soil functions within the context of sustainable use, prevention of threats to soil and mitigation of their effects, as well as restoration of degraded soils. The SFD should link to other EU regulations with consequences for national soil contamination policies, especially the Directive 96/61/EC (on Integrated Pollution Prevention and Control-IPPC), Directive 2003/105/EC (on the control of major-accident hazards involving dangerous substances – Seveso II), Directive 2004/35/CE on environmental liability with regard to the prevention and remedying of environmental damage).

The current SFD proposal leaves an important “policy vacuum“ for locally contaminated groundwater. If the soil is relatively clean (no significant risks for current of approved use of the land) there can still be a groundwater contamination plume. The risk of soil contamination for the groundwater may no longer be present, which implies that no further action is required according to the SFD.

From the point of view of the Groundwater directive the plume may not significantly affect groundwater quality in a (large) groundwater body. The Groundwater directive does not require action either in this case. Another situation: Soil remediation takes away significant risks for human health and the environment. This means that soil related sources of groundwater contamination are “cleaned up” but the groundwater pollution itself may remains in place as the SFD only addresses soil. The Groundwater directive seems to imply that action for groundwater is only necessary if the local contamination is a threat for the good status of the whole groundwater body.

German regulations in comparison to the proposed Soil Framework Directive (SFD)

The German Soil protection act includes accurate definitions for suspected sites and contaminated sites. The identification of contaminated sites according to the SFD is as well based on their significant risk to human health or the environment (Art. 10,1.). However the term “site” seems more vague compared to the German term “property”.

The Federal States (Länder) may regulate the details for the identification and inventory of suspected contaminated sites and contaminated sites. In practice all Federal States are keeping such inventories. This is in line with Art. 10,2 of the SFD. The identification of suspected contaminated sites depends on concrete causes for suspicion. The German “Länder” use branch and waste catalogues, which contain branches relevant to suspected contaminated sites. We think that potentially soil-polluting activities (Art. 11,2.) as listed in Annex II of the SFD do not meet practical requirements as long as they are not established on concrete suspicion.

Following the German Law the competent authorities should take appropriate measures to determine the facts of relevant matter if there are essential points for the existence of contaminated sites. If the trigger values are exceeded, the authority should take measures necessary to determine whether a contaminated site exists. This regulation generally complies with Art. 11,3. of the SFD in that the competent authorities shall measure the concentration levels of dangerous substances at the identified site. Both procedures are similar although the SFD does not set forth concentration levels which can be used for single case assessment.

Art. 12 of the SFD refers to a soil status report which the owner or the prospective buyer has to provide to the responsible authority if a site is to be sold on which a potentially polluting activity listed in Annex II is taking place or has taken place due to national registers. This request does not exist in German regulations although similar instruments are developed more and more under private law when buying and selling real estates.

In Germany the party who caused the contamination on a site, the universal successor, the relevant property owner as well as the occupant of the relevant real property, all of them as joint and several debtors shall be obliged to remediate the contaminated sites and any water pollution caused by contaminated sites. This duty is similar to Art. 13,1 of the SFD which refers to the duty for remediation of listed contaminated sites by the Member States. Thus the “polluter pays principle” is essential in both regulations.

The German definitions concerning remediation measures, such as decontamination measures, securing containment measures and protection and restriction measures correspond largely with Art. 13,2. of the SFD.

Funding mechanisms for remediation measures (in case the responsible person for the pollution cannot be identified or cannot be held liable (Art.13,3. (SFD)) are not regulated by the German Soil Protection Act. In general the Federal States cover the cost of remediation for such contaminated sites. However the designated setup of a national finance instrument for the remediation of orphan sites offers a chance for remediation, which can be started without wasting time. The request for a National Remediation Strategy according to Art. 14 SFD is not known to the German Law. But components of such a National Remediation Strategy, for instance general verbal remediation targets, can be derived from the existing law: contaminated sites have to be remediated in such a way that no hazards, considerable disadvantages or considerable nuisances for individuals or the general public may occur in the long term. Detailed remediation targets however can only be derived on a case by case basis.

Prioritisation of sites to be remediated, timetables and funds to be allocated by the authorities for remediation activities are not covered by German legislation. Containment of sites or natural recovery of pollution, which may need monitoring, already part of German remediation practice.

However, due to a couple of still open key points within the draft of SFD and expected problems for the implementation there is no unanimous position among involved parties on the federal as on the state level. The Federal Environment Ministry is communicating constructive proposals to find a national consensus, which might be accepted as well as in the EU.

Status Quo - Outlook

The draft Soil Framework Directive aims at filling this gap by establishing a common strategy for the protection and sustainable use of soil, based on the principles of integration of soil concerns into other policies, preservation of soil functions within the context of sustainable use, prevention of threats to soil and mitigation of their effects, as well as restoration of degraded soils. Soil protection has not been subject to a specific legislative instrument at Community level so far.

The previous Portuguese EU-Presidency did a lot to reach a seminal political progress. However it was not possible on the 2842nd Deliberation of the Environment Council (20th of December 2007) to attain the qualified majority needed to reach political agreement on a draft directive establishing a framework for the protection of soil. AT, DE UK, NL, FR could not accept the text tabled.

Existing bottlenecks:

- Priority area approach: not only cover the agricultural land, also include forest land as well as residential, industrial, recreational and coastal land - criteria and the procedures must be available and practicable
- Identification and inventory of contaminated sites and Soil status report: main difficulties remain concerning the degree of flexibility given to Member States to identify contaminated sites by following a step-by-step approach and arriving at an inventory of contaminated sites; the degree of obligations and the methodology attached to those steps, including chemical analysis of soils; the degree of flexibility given to Member States to use results of identification of contaminated sites obtained under national provisions before transposition; and scope and nature of the annex.
- Non-compliance to subsidiarity principles
- Expected increase on bureaucracy

Under the perspective of German “Länder” points of concern are:

- identification and adjustment of priority areas including action programmes
- enlargement for the inventory of contaminated sites
- adoption of the soil status report

- comprehensive obligations to report
- national remediation strategy requirement linked with the given timeline

Nevertheless, among most member states several communities express the crucial interest to come forward with a European Soil Framework quickly. Within the Common Forum (the network of contaminated land policy makers and advisors from national ministries in EU member states and EFTA countries), it was announced that France will pick up the SFD back on the political agenda for the upcoming EU-Presidency. In addition, the Czech Republic will go further in case the goal will not reach within 2008.

Reflecting the statement given by the French Minister during the Deliberation of the Environment Council, we expect that the technical discussion about content will shift the political arguments against a European Soil Framework.

Further Information

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety: *http://www*.bmu.de

Federal Environment Agency: http://www.umweltbundesamt.de/

Legal Documents (Soil Protection Act and Federal Soil Protection and Contaminated Sites Ordinance) and other information will be found at the contaminated sites information site of the Federal Environmental Agency (English version)
http://www.umweltbundesamt.de/altlast/web1/estart.htm

Environmental Information of German Authorities: *http://www.portalu.de*

EUGRIS — Portal for Soil and Water Management in Europe: *http://www.eugris.info/*

2842nd Deliberation of the Environment Council, media clip:
http://ceuweb.belbone.be/archivevideo.php?sessionno=1413&lang=EN

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SAFIRA II, Dr. Martin Bittens, Helmholtz Centre for Environmental Research-UFZ

RUBIN, Dr. Volker Birke, Leuphana University of Lüneburg

REFINA, Uwe Wittmann, Maike Hauschild, PTJ, Berlin.

Register of Contaminated Sites

Harald Mark,

MSP GmbH, Germany

Introduction

A successful treatment of contaminated sites requires a systematic and gradual procedure - such as it has proved its worth in Germany for many years. The first step of treatment is the registration (recording) of contaminated sites.

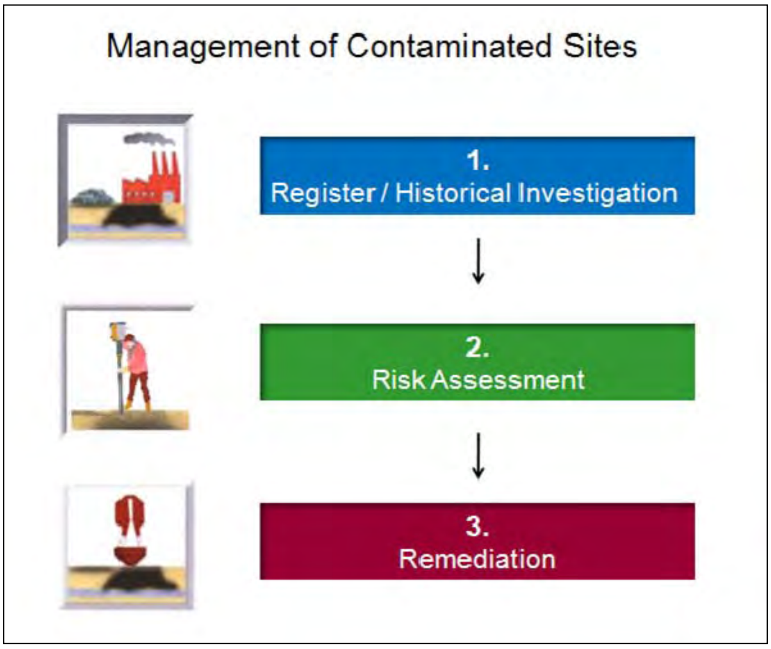


Fig. 1: Treatment of contaminated sites as a multi-stage process

In Germany the biggest mistakes were made, when remediation took place without the steps of recording and risk assessment.

Object of recording is**:**

- conducting area-wide investigations of industrial sites and waste disposal sites and their compilation in a list;
- the assessment of the industrial sites and waste disposal sites investigated with regard to identifying sites suspected of being contaminated;

- conducting extensive site-related investigations;
- assessment of the results of investigations in the sense of a first risk assessment and further measures resulting from it.

Content and target of the investigations are**:**

- classification of specific case groups of industrial sites and waste disposal sites or individual cases of areas suspected of being contaminated,
- determination of the position and spatial extension of the potentially contaminated areas and
- collection and processing of all further information relevant to environment on the individual areas

Investigations do, as a rule, not involve local investigations exceeding a potential site inspection. Boring, sounding, chemical-physical investigations etc. are basically left to the subsequent stages. The data and findings gathered are filed in registers and files and updated and represented on maps by the competent authorities.

The investigations made by the authorities follow basically two aims:

- detection and localizing of possibly all industrial sites and waste disposal sites situated in the area of responsibility of an authority (area-wide investigations).
- compilation of all detailed information required for the individual treatment (site-related investigations).

Before the background of the target of the investigations, namely to record and document uses and events which may play a (restrictive) part in planning a follow-up use normally the following object categories have to be investigated:

- Buildings and plants and their use: An essential object of recording is always the stock of buildings and plants as it has developed in the course of the history of use. To assess uses with regard to a potential pollution risk all uses – independent of their relevance to environment – are recorded and reflected in the maps of the results.
- Sewerage system and sewage plants: As far as existing, the sewerage system is recorded and represented on maps. An important target of research is to record the (formerly) existing sewage plants.

- Waste disposal sites: Furthermore, sites will have to be determined where material has been deposited. In most of the cases, it will not be possible to determine the deposited material, however, waste disposal sites have to be recorded as deposits or backfills:
- Storage areas: Storage areas will be recorded as a further object category. They are defined as areas where piece goods or bulk material (partly not to be specified in a more detailed way) have been stored.

Methods and sources of recording contaminated sites

Basically there are available only a few information sources, if any at all, providing **directly**

- the partial areas of a site which are possibly contaminated,
- the contamination concerned
- when or in which period potential damage was inflicted.

In practical site-related investigation four methods have proved to be especially efficient:

1. archive research with evaluating the unprinted and printed documents obtained in public archives and company archives and in official (old) registries,
2. multi-temporal mapping, i.e. the evaluation of maps and aerial photos of various subjects and times of origin, especially
    - the evaluation of first editions and continuation of official topographic maps of a scale of 1:25,000 and larger and
    - the interpretation of aerial photos available from aerial, route and other navigation,
3. questioning of contemporary witnesses
4. site inspection to understand the actual situation.

As a rule, it is not sufficient to apply only one of the methods mentioned. In German practice notably the combination of the 1st and 2nd methods has proved successfully, whereas questioning of contemporary witnesses is to be recommended only if after completing archive research/evaluation of documents and records and multi-temporal mapping still obvious gaps will exist. If possible, the findings of recording should be supplemented by a site inspection.

Archive research and evaluation of documents and records

In the course of the history of use of a site, from today’s point of view, necessarily more or less comprehensive documents and records with directly or indirectly usable information relevant to environment have been compiled. As typical examples of such documents and records there should be mentioned:

- operating licences,
- applications for permissions for the construction and reconstruction of buildings and plants,
- respective layouts and plant layouts at specific times of industrial site development, furthermore
- production and other plant reports and
- damage information relating to accidents including war damage.

The evaluation of this documentation – frequently compiled over decades – as a rule, will supply important information on

- the historical building and plant stocks and their functions (fig. 2),
- potential accidents/leakage and other singular events such as military actions,
- manufacturing methods (relevant to contaminated sites) and other industrial procedures and sequences of work
- ownership systems (and their change).

To efficiently find documents and records it is basically to be recommended to adopt an approach deriving from the official regulations relating to the transmission of documents and records. Document stocks considered to be worth archiving are usually arranged and stored according to the provenance and site principle, i.e. according to sites where they have been compiled. Accordingly, there has to be, first of all, reconstructed which operations are of relevance to contaminated sites (mostly) without being indicated by the titles of the records. Subsequently, there has to be determined which authorities or company departments have been dealing with a process possibly relevant to contaminated sites.

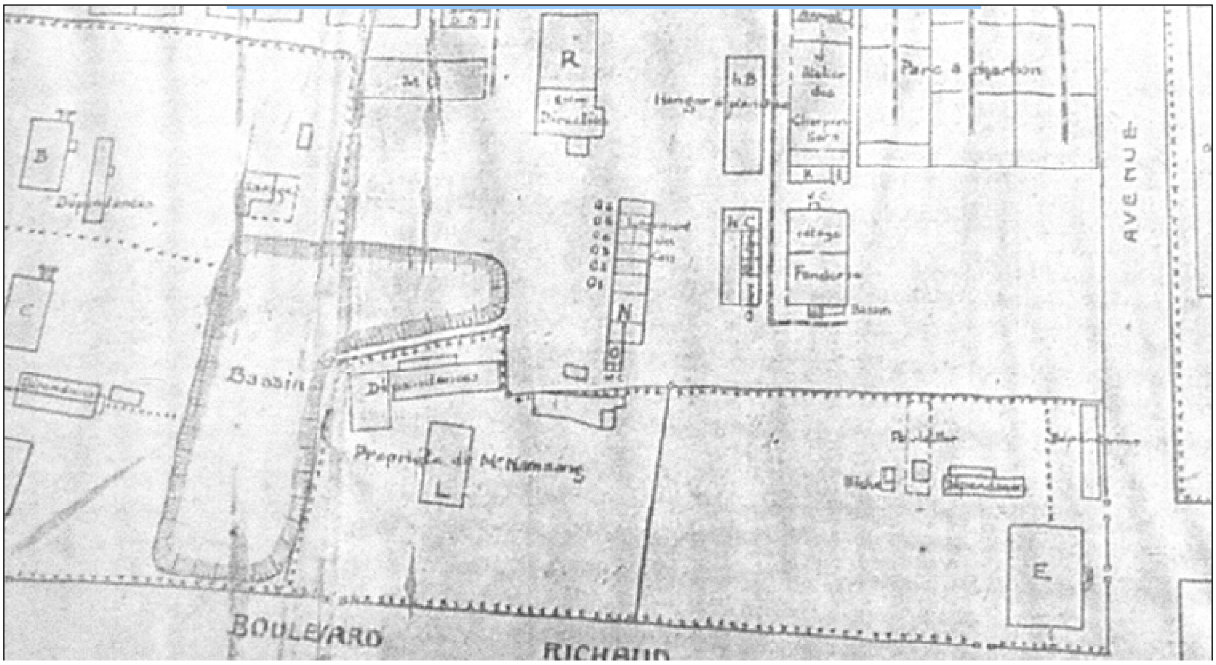


Fig. 2: Part of a site-plan of a textile company in Vietnam from 1928

Then the archives or information offices competent for storing the records of the sites concerned will have to be found.

In this connection, attention shall be paid to the fact that administrative competences on the decision-making level as well as in the regional subordination (administrative reforms) (may) have changed. Furthermore, documents with information relevant to contaminated sites may not only be available on one level but, by the parallel transmission of specific records/documents, on a few archive levels.

Site-related investigations will normally start with finding the relevant records on local level. Which archive or official (old) registry shall be, here, consulted preferably is scarcely generally binding but ultimately to be decided only depending on the case-specific basic conditions. If a company archive will exist for the site under investigation and access to it will be provided the research should be started there at any rate.

If in research on local level obvious gaps in transmitting documents will appear the competent archives on regional or national levels will have to be considered in further stages.

Multi-temporal evaluation of maps and aerial photos

The multi-temporal mapping involves a combined analysis of maps (in particular official topographic, yet also other maps) and aerial photos with the evaluation of these area reproducing information carriers - taking place not only on one time level but – multi-temporally – in several periods.

The information value of topographical maps is distinctly lower than that of aerial photos – mainly due to a generalization. The larger the scale is the more suitable is the map for recording. The most suitable scale is the scale 1: 5,000, followed by the scales 1: 10,000 and 1:25,000.

However, aerial photos are essentially more substantial than maps and document a site with all details without generalizing exactly the condition and appearance at the time of taking the photo (Fig. 3). Information relevant to contaminated sites provides aerial photos notably of fills and deposits, the supplementation and checking of the building and plant stocks resulting from the evaluation of the plant layout.

Fig. 3: Aerial photo and topographical map of the same region (in Vietnam). (Source: Information Centre of Natural Resources and Environment, Vietnam)

In many phenomena of use the identification of objects is possible without causing problems owing to visual properties such as object shape (layout/front view), object size (length, width, height), position and arrangement on the terrain or towards other objects. Thus, among former industrial plants e. g. tanks, cooling towers and other prominent plants with unmistakable building and structural properties visible on aerial photos, as a rule, may be easily identified. However, some buildings and plants appear on the aerial photos so non-specifically that – owing to their position and arrangement – they may be only indirectly identified in their functions or with a respective uncertainty or not at all. In investigating and mapping former industrial sites the interpretation of aerial photos has to be regarded rather as a method supplementary to the evaluation of the plant layouts or – depending on the records and plans – also the other way round. The combined application of both methods is imperative to reach good results of research of the plant and building stock as often aerial photos document plant (units) not to be found in plant layouts. On the other hand, aerial photos show frequently that buildings shown in plant layouts have partly not left their “stage of planning”, i.e. have never been built. As compared with aerial photos plant layouts are so important because – as mentioned above – an assignment of the functions of (historical) buildings and plants is only seldom possible solely on the basis of aerial photos.

However, aerial photos are frequently the only source to record potential waste disposal sites. Waste disposal sites may be identified on the aerial photo by various features. On a black-and-white aerial photo they stand out by a lighter or darker grey shading – independent of a. o. material properties and incidence of light. On an aerial colour photo possibly colour properties of a waste disposal site or its surrounding facilitate its identification (fig. 4).

Fig. 4: Waste disposal in an aerial photo (Source: Information Centre of Natural Resources and Environment, Vietnam)

The contours of waste disposal sites are mostly irregular and not always clearly definable. As a matter of fact, many types of waste disposal sites in their original state show carrying-over seams of a few meters which render impossible sharp fencing even on the terrain.

The three-dimensional character of former waste disposal sites should be detected by means of optical instruments rather than through hard shadows. Using stereoscopes is obligatory for identifying former waste disposal sites. The multi-temporal evaluation of aerial photos allows to map various dumping phases and – if existing – to identify also a change of material.

Questioning

If questioning should bring useful results it has to be ensured that the persons questioned have founded special and also respective site knowledge. In addition, they should have a sufficiently reliable memory and, not last, they should be ready to give unreservedly information about processes and facts relevant to environment.

Though, in actual cases, it is in general, not very difficult to find contemporary witnesses meeting largely this requirement profile, if knowledge about facts actual longer ago has to be obtained by questioning finding of suitable interview partners may absolutely prove to be a problem.

The results of questioning contemporary witnesses – even if prepared and carried out in a professional way – shall be always assessed critically. In fact, questioning may impart absolutely new, basic knowledge on uses of the site relevant to environment and thus contribute to supplementing the data stock of a site-related investigation. This, however, applies predominantly to uses and events of a more recent date.

Site inspection

In conclusion of a site-related investigation a detailed inspection of the site under investigation is to be recommended. Such a site inspection serves, on the one hand, the documentation of the actual state (a. o. by photos) and, on the other hand, it serves the aim of supplementing the findings of research by considering the following aspects:

- mapping of perceptible contamination; to investigate and assess soil pollution the use of a folding spade may be useful. However, there should be checked in advance whether a ground photo will be required (protective measures, waste disposal etc.);

- subsequent investigation of relevant units of a plant (separator etc.) to be neither recognized on the aerial photo nor indicated in plant layouts;
- assessment and classification of waste disposal sites still visible with regard to their material composition;
- clarification of building and plant functions so far uncertain.

In addition, type and state of sealing and further parameters relevant to the assessment and depending on the individual case may be collected. Ideally site inspection is carried out accompanied by a person knowing the site and, if necessary, then in combination with questioning of contemporary witnesses.

If the advantage of a site inspection for supplementing the findings of the research and the documentation of the actual state is undisputed, its importance to site-related investigations is often overestimated. It need not be further commented that site inspections may, as a rule, supply information on a very small part of the history of use of a site, namely notably on the condition of the terrain after the plant was closed down.

Changes of the building and plant stock, overgrown waste disposal sites and backfills are only a few exemplary categories not to be investigated by site inspections. In site inspections industrial safety measures shall be always paid attention.

Assessment of the results of investigation

The results of investigation shall be always assessed differently with regard to their relevance. This means specifically that some areas of a site under investigation show a higher contamination risk than others. That is why it is important for planning all further measures to make a special assessment of the results of investigation and to distinguish between the investigated areas as to the extent of the risk. The investigated areas shall be distinguished according to the following pattern:

- high contamination risk
- medium contamination risk
- small contamination risk
- no contamination risk (as all uses are recorded, among others, of course, also such uses which are not connected with a contamination risk).

- contamination risk not to be classified (if the available information is not sufficient to assess the contamination risk)

Data from relevant literature provide the basis for the special assessment of the results of the investigation. Furthermore, the assessment shall be based on experiences made with comparable sites. In assessing the risk the following factors shall be considered:

- type of use
- period of use
- material potential
- risk restricting measures.

The elementary components of the register: GIS and database

A register of contaminated sites is an area-wide information system basically consisting of two components (Fig. 5):

- **geometrical data**: refer to the position of a site relevant to environment on a large-scale map, its exact limits and – if necessary – details of respective uses
- **site data**: are data assigned to the site, informing on geographical details (such as co-ordinates), legal facts (such as owners) and aspects relevant to environment (such as industrial plants, accidents).

Area and site information is linked with each other through indices and is constantly updated. Formerly registers of contaminated sites were always arranged in parts of maps and records compiled and continued manually. Today registers of contaminated sites are compiled and continued by means of a data bank and GIS software. The digital „register of contaminated sites“ allows a comparatively faster access to individual data and is easier to be continued at lower costs.

A „functioning“ register of contaminated sites requires that

- all sites (of a regional corporate body) relevant to environment have been recorded and localized,
- detailed information on the respective sites is available.

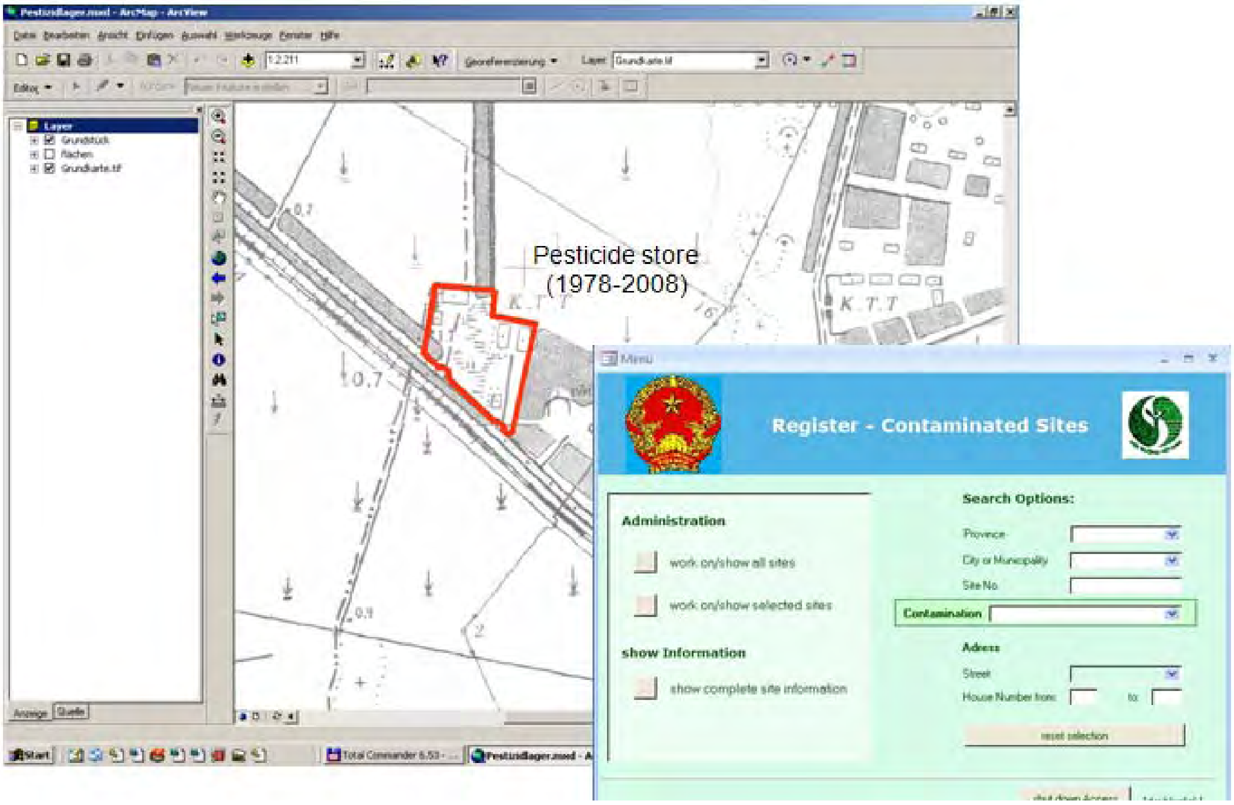
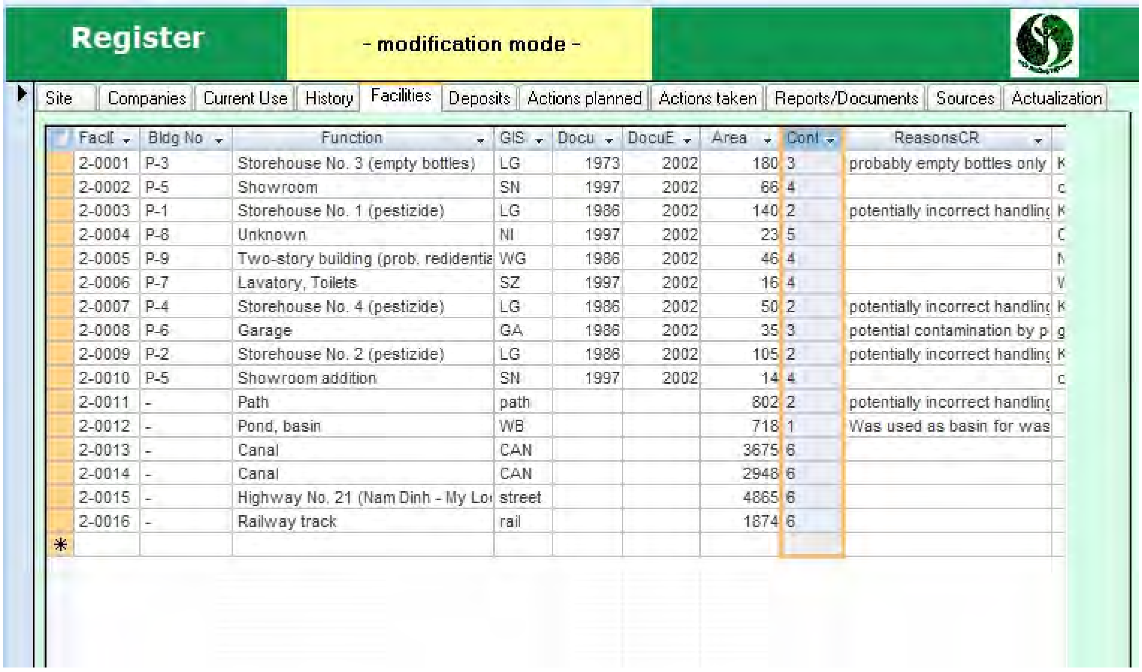


Fig. 5: Schematic representation of the principle of the register of contaminated sites: geometric data and site data

The database contains some data fields, like the exact localization, the owners, the current use and benchmark data of the historical development of the site. The most important class of information is the actual and former use of the buildings and facilities of the site. Fig. 6 shows as an example the function of each building of a pesticide store as well as the time of use. These data are directly linked with the Geographical Information system.

Fig. 7 shows all the buildings of a pesticide store in different colors, which refer to their special function.



FacII	Bldg No	Function	GIS	Docu	DocuE	Area	Conl	ReasonsCR	
2-0001	P-3	Storehouse No. 3 (empty bottles)	LG	1973	2002	180	3	probably empty bottles only	K
2-0002	P-5	Showroom	SN	1997	2002	66	4		c
2-0003	P-1	Storehouse No. 1 (pestizide)	LG	1986	2002	140	2	potentially incorrect handlin	K
2-0004	P-8	Unknown	NI	1997	2002	23	5		C
2-0005	P-9	Two-story building (prob. redidentia	WG	1986	2002	46	4		N
2-0006	P-7	Lavatory, Toilets	SZ	1997	2002	16	4		V
2-0007	P-4	Storehouse No. 4 (pestizide)	LG	1986	2002	50	2	potentially incorrect handlin	K
2-0008	P-6	Garage	GA	1986	2002	35	3	potential contamination by p	g
2-0009	P-2	Storehouse No. 2 (pestizide)	LG	1986	2002	105	2	potentially incorrect handlin	K
2-0010	P-5	Showroom addition	SN	1997	2002	14	4		c
2-0011	-	Path	path			802	2	potentially incorrect handlin	
2-0012	-	Pond, basin	WB			718	1	Was used as basin for was	
2-0013	-	Canal	CAN			3675	6		
2-0014	-	Canal	CAN			2948	6		
2-0015	-	Highway No. 21 (Nam Dinh - My Lo	street			4865	6		
2-0016	-	Railway track	rail			1874	6		
*									

Fig. 6: Database with information about the facilities within a site (pesticide store)

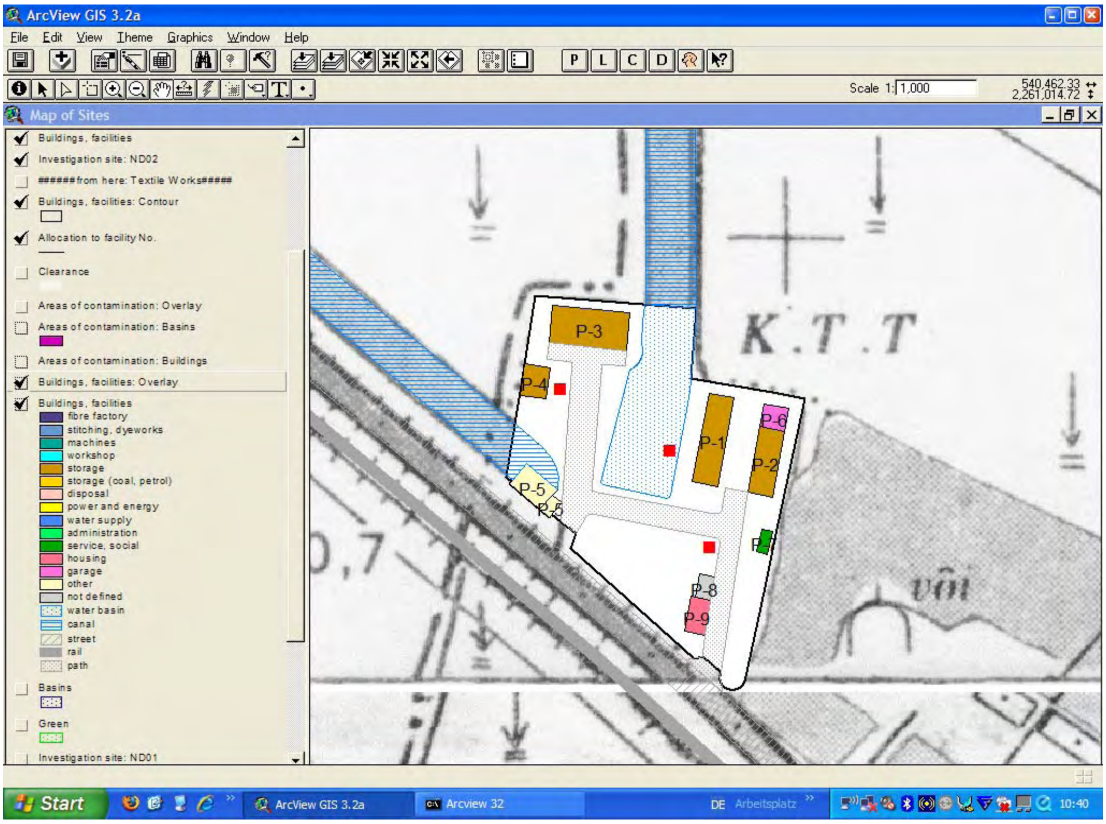


Fig. 7: GIS-data linked with the database

Conclusions

The practical use of applying the register of contaminated sites is multifarious providing notably advantages for the areas environmental protection/health and economy:

- The investigation data provide the basis for decision-making on further measures of site-related environmental management. Only if it is known whether and where on a site uses suspected of causing contamination have taken place follow-up stages of sampling and analyzing may be planned purposefully.
- But with the recording data especially grave environmental impacts may be recognized already early and respective emergency measures may be initiated. Thus, the health of the population concerned will be immediately improved.
- Preparing of digital maps and plans in the framework of recording forms also the basis for planning all further measures not only of specific treatment of contaminated sites but also for other fields of environmental management (monitoring data etc.).
- In Germany the planned approach has proved to be a most low-cost alternative. Thus, making costly wrong decisions owing to lack of site information will be largely avoided. In Germany the principle is applicable: that money which is invested in data collection will be repeatedly saved later on owing to reliable decisions being made on the basis of a solid data stock.

Characterization of Mercury Contaminated Sites
– The Role of Speciation Analyses –

Harald Biester,

Technical University of Braunschweig, Germany

Introduction

Mercury contamination of local, regional, and global environments has become an increasingly studied subject in recent years. Areas where Hg pollution has been most acute include abandoned Hg mines, gold mining areas where Hg was used in the amalgamation process, and industrial sites where Hg has been released as a byproduct of chemical processes (e.g., the electrochemical separation of chlorine from sodium salt at chlor-alkali plants) Kim et al., 2003). Different from many other heavy metals mercury undergoes several processes of species transformation, which determine its toxicological potential in natural environments. In all cases, knowledge of the molecular-level speciation of Hg is essential for understanding its potential bioavailability and impact on the environment. Among these transformation processes, the formation of volatile Hg(0) through reduction of Hg^{2+}-compounds and binding of Hg to natural organic matter are the most important processes determining the mobility in the environment (Fig. 1a,b). Especially in aqueous systems the formation of Hg organic complexes such as methylmercury is a key process for the enrichment of Hg in fish and finally in the human food chain. Methods for determining Hg speciation have increased in both number and sophistication over time, ranging from visual identification of Hg phases in ore-grade samples to sequential chemical extractions (SCE) (Revis et al., 1989, Sakamoto et al., 1992, *6-8*), sequential thermal desorption (Biester et al., 1997, 1999, 2000), electron microprobe analysis (Barnett et al., 1997), and in-situ X-ray absorption spectroscopic analysis (Kim et al., 2000). Over the past 15 years thermal desorption methods have been shown to be a strong tool to determine solid phase inorganic Hg compounds in contaminated soils and sediments. In combination with aqueous leaching and chemical methods to determine dissolved Hg species both methods allow far reaching risk assessment of contaminated areas (Biester et al., 1997a,b, 1999, 2000, Sladek et al., 2002, Gustin-Sexauer et al., 2002). This overview shows several examples of the application of a thermal Hg desorption techniques combined with aqueous leaching to detect Hg species in soils and sediments of contaminated industrial sites and a former Hg mining area.

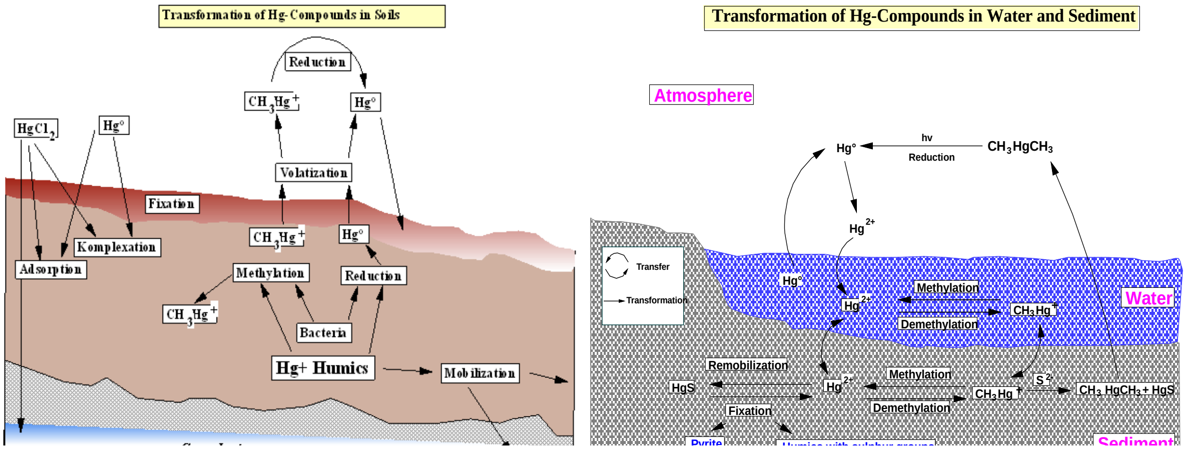


Figure 1: Formation and transformation processes of Hg compounds in soils and sediments

Methods

Mercury thermo desorption techniques area based on the comparatively low thermal stability of many Hg compounds and the release of volatile Hg(0) during their thermal breakdown. Samples are continuously heated up to 700 °C in an inert gas atmosphere and released Hg(0) is simultaneously determined by atomic absorption spectroscopy. Figure 2 shows a schematic view of the analytical setup, a detailed description of the method is given elsewhere.

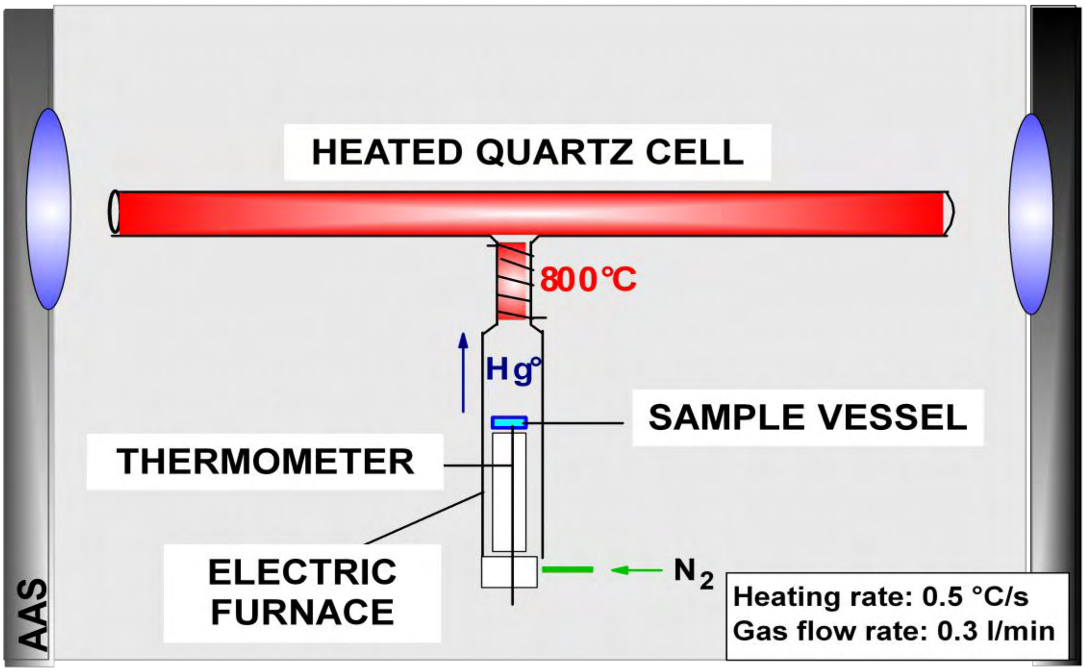


Figure 2: Scheme of the Hg thermo desorption (after Biester et al., 1997a)

Case studies 1: Chlor-alkali plants

Besides coal burning and waste incineration, one important industrial source of Hg emissions are chlor-alkali plants (CAP) using metallic Hg for the electrolytical production of chlorine. The environmental impact of Hg emissions from CAPs has been demonstrated in several studies (e.g. Lodenius and Tulisalo, 1983, Baldi and Bargagli, 1984, Maserti and Ferrara, 1991, Gonzales, 1991, Biester et al., 2002a,b). Several studies have shown that most Hg emitted from chlor-alkali plants is dispersed over long distances, and only small amounts are deposited in the vicinity of the sites (Jernelöv and Wallin, 1973; Högström *et al.*, 1979). Nevertheless, it has been reported that soils surrounding chlor-alkali plants show Hg concentrations up to 75 times the background (EPA 1997). However, the dynamics of atmospherically deposited Hg in soil, especially the fate of Hg(0) have been long only poorly understood. A multi-site study on Hg deposition in the vicinity of CAPs has shown that less than 2 % of the emitted Hg remains in local soils and the rest are subject to long range transport (Biester et al., 2002a). Based on Hg thermo desorption analyses it could be shown that Hg in these soils predominately exists in a matrix-bound form such as Hg organic matter complexes and that Hg(0) is in most cases absent (Fig. 3). However, samples containing unbound Hg(0) always show large amounts of Hg bound to organic matter, which results from oxidation of Hg(0) to Hg^{2+} complexation to organic matter (Fig. 4).

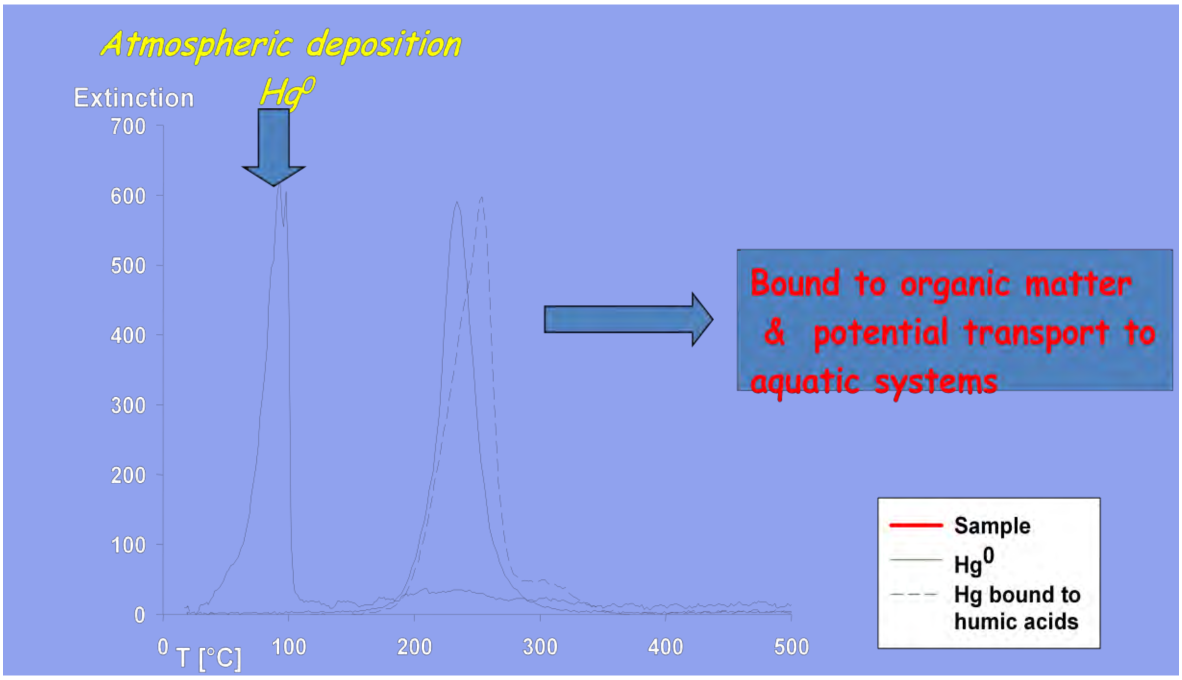


Figure 3: Mercury thermo desorption curves of a typical soil samples taken near a chlor-alkali plant (Biester et al., 2002b).

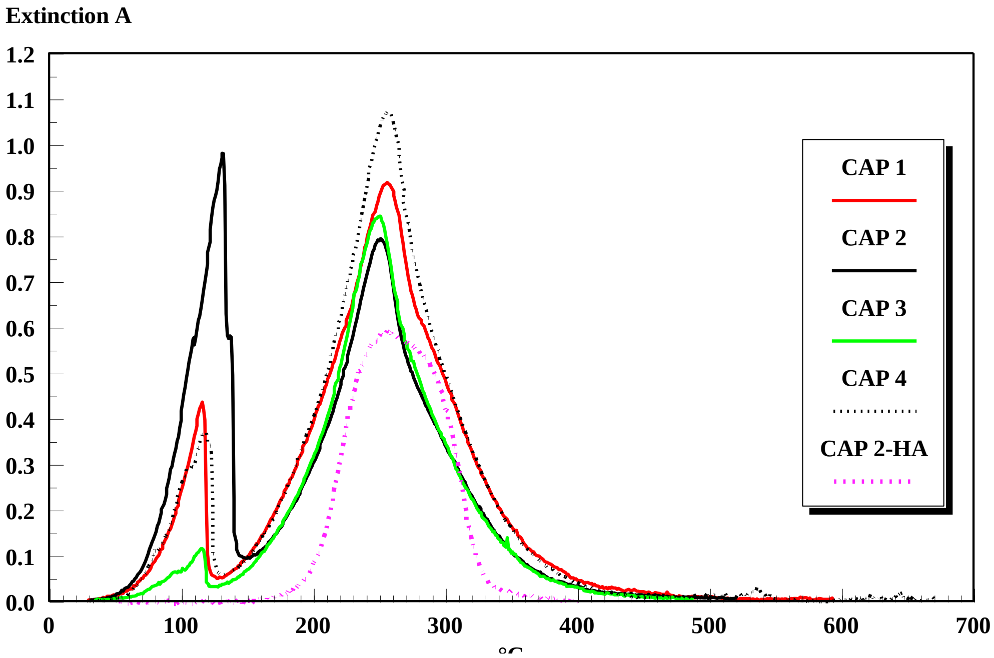


Figure 4: Mercury thermo desorption curves of soil sample contaminated by direct spilling of Hg(0) on a chlor-alkali plant and extracted humic acids showing both Hg(0) and Hg bound to organic matter.

The important process of Hg(0) oxidation and coupling to organic matter in contaminated systems was also observed in a Hg(0) contaminated sewer system. Here, Hg(0) introduced by a electric rectifier workshop was rapidly oxidized and bound to humic acids (HA). Further microbial decomposition of the organic matter and reducing conditions in the sewer sediments caused the formation of metacinnabar (HgS) or organo-Hg-sulfides (Fig. 5).

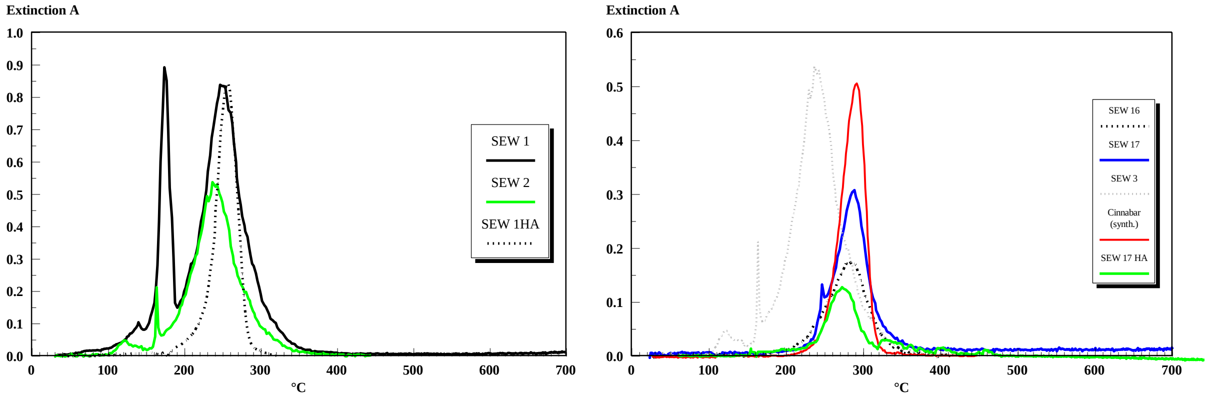


Figure 5: Mercury thermo desorption curves of sewer sediment samples showing Hg(0) and in-situ formed organically bound Hg (extracted humic acids HA).

Conclusions

The shown examples indicate that Hg(0), which is the most important Hg species emitted from CAPs 70%., is not preserved in soils surrounding the plants. It is assumed that the major Hg compound deposited near the plants is Hg(II), which is in accordance with model calculation of Hg deposition near CAPs. Hg(0), initially deposited to the soils, is re-emitted within a short time or oxidized to Hg(II) and adsorbed to soil components suggesting that most Hg(0) emitted from the plant is directly or indirectly subject to long range transport.

Case study 2: Wood Preservation sites

The antiseptic effect of mercury(II)chloride ($HgCl_2$) has been known since the 18th century and was widely applied by the wood preservation industry. The process of kyanizing, named after John Kyan who patented this process in England 1832, consists of steeping wood in a 0.67% mercuric chloride preservative solution to prevent the wood from decay (Schöndorf *et al.*, 1999). On these wood impregnation sites, the improper storage of treated wood or leakage of dip basins often led to a severe contamination of the environment, especially of soils and groundwater. The following examples demonstrate how species transformation processes of Hg in the aquifer can change mobility and dispersion of Hg in contaminated groundwater.

Site description

Wooden telegraph poles, trellis support poles for vineyards, and sleepers for railway tracks were treated with $HgCl_2$ solution against fungal attack at a former wood impregnation plant in Southern Germany. The site covered an area of almost 9 ha and during the 60 years of operation (1904-1965) an estimated amount of 10-20 tons of Hg has been released into the local soils and the aquifer (Schöndorf *et al.*, 1995). Currently a residential area of 8 ha, the site is contaminated with up to 11000 mg/kg Hg and a groundwater plume with a maximum Hg concentration of 230 µg/L and a width of 100 m persists 1.3 km down gradient (Fig. 6).

The aquifer consists of highly permeable sand and gravels and has a groundwater gradient of 0.7 to 1%. This results in a hydraulic conductivity of 3×10^{-3} ms^{-1} and a high flow velocity of 3 – 10 m/d. The base of the aquifer consists of weathered gravels of low permeability, which form the aquitard (Schöndorf *et al.*, 1999).

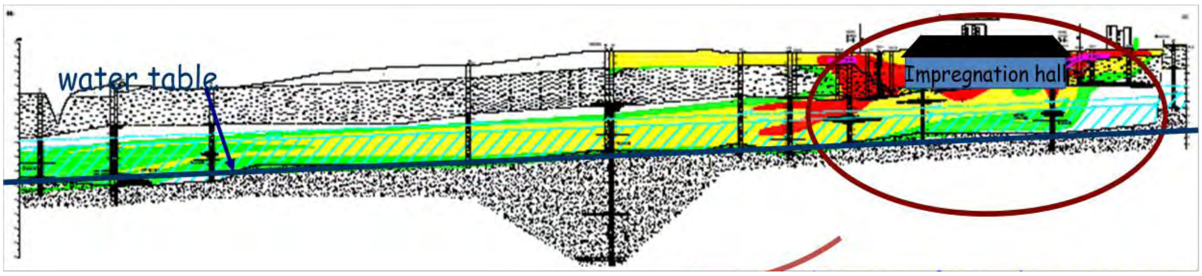


Figure 6: Location of the former distribution of the contaminant plume and locations of ground water wells.

Seepage modelling for this site estimated that due to high Hg concentrations in soil and low seepage fluxes there will be a continuous Hg release from the unsaturated soil zone into the aquifer for at least the next few hundred years.

Methods

During the past 10 years 28 groundwater wells were installed which fully penetrate the shallow groundwater down to the base of the aquifer. The most important observation during this time was that Hg concentrations in the contaminant plume dropped rapidly at a distance of about 800 m from the contamination source to values near background concentrations Figure 7. Up to now the reasons for the strong decrease in Hg concentration and the constant contamination plume are mostly unknown. The following results of soluble Hg species analyses indicate that Hg species transformation might be a possible explanation.

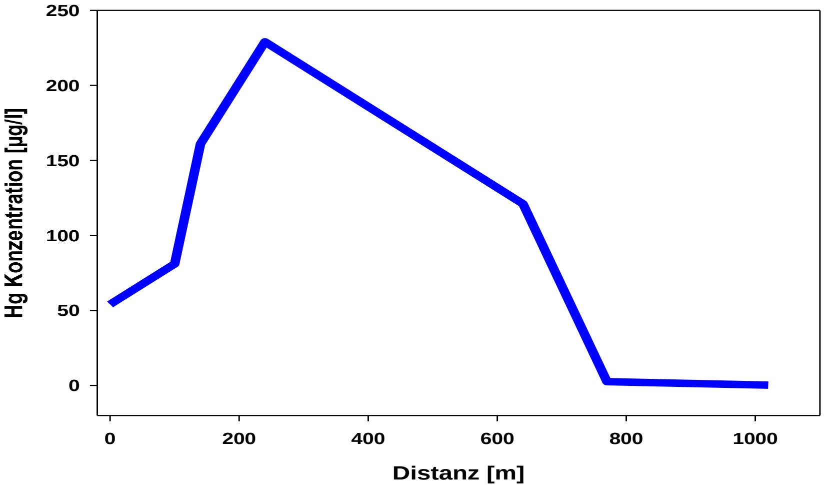


Figure 7: Hg concentration in groundwater with distance from the contaminant source

Investigation on Hg species in groundwater were performed during a period of 1 year at monthly intervals. Speciation of soluble Hg species in groundwater is based on differentiation of operational defined species (Fig. 8, modified after Brosset, 1987 and Meili *et al.* 1991).

A scheme of the speciation procedure to distinguish between reactive (easily reducible) soluble Hg compounds and non-reactive (non-educible) soluble organic complexes is given in Figure 8.

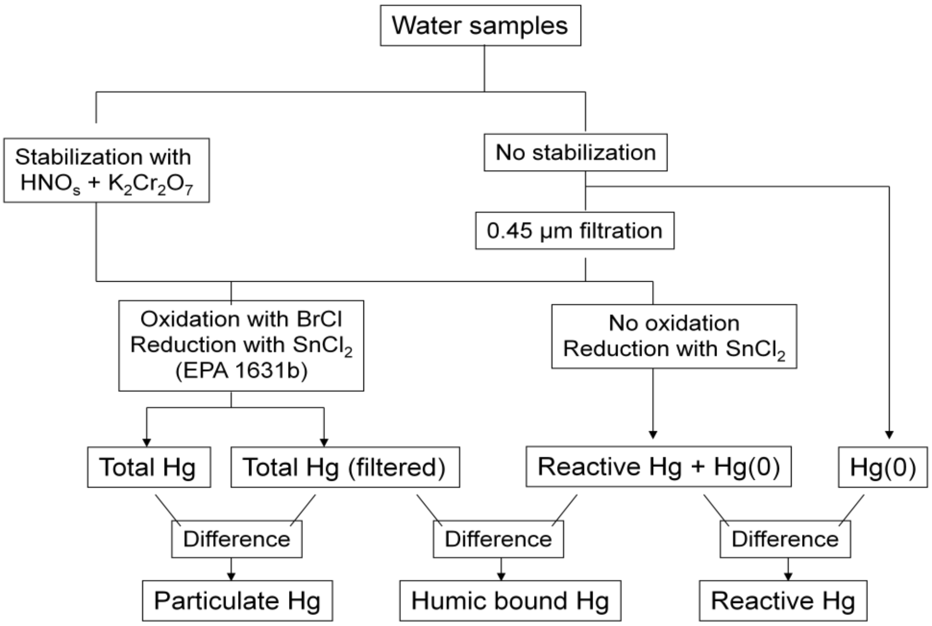


Figure 8: Analytical procedure for the determination of soluble Hg species in water modified based on the method by Brosset (1987) and Meili *et al.*(1991).

Results

The results of Hg speciation measurements in groundwater indicate that reactive Hg compounds are the dominant form of Hg in groundwater and that only a very small portion of the Hg appears to be bound to organic complexes. This indicate that most Hg in the aquifer is likely to be transported in its original form, which is $HgCl_2$ leached from the contaminated soils. As solubility of $HgCl_2$ is high (70 g/L) the sharp decrease of Hg concentrations in the aquifer could not be explained by the dominant species of soluble Hg, as no changes of the predominant Hg species in groundwater could be observed with distance from the contaminant source.

However, Hg thermo desorption analyses of the aquifer material indicate formation of considerable amounts of Hg(0) in the solid phase (Fig. 9). It has been concluded that the formation of Hg(0) in groundwater is due to a change in redox conditions when $HgCl_2$ is leached from the soil into the groundwater. Redox-pH measurements in groundwater and calculation of the stability of inorganic Hg compounds in the groundwater indicate that both $HgCl_2$ and Hg(0) could be stable under the given conditions in the aquifer (see Fig. 10). It has been assumed that the reduction of $HgCl_2$ to Hg(0) could be the main reason for the decrease of Hg concentrations in groundwater. This process would decrease the solubility of Hg from 70 g/L ($HgCl_2$) to 60 µg/L (Hg(0)), which is a factor of ~10^6 lower. Similar observations could be made in comparable $HgCl_2$ contaminated aquifers (Bollen et al., 2007)

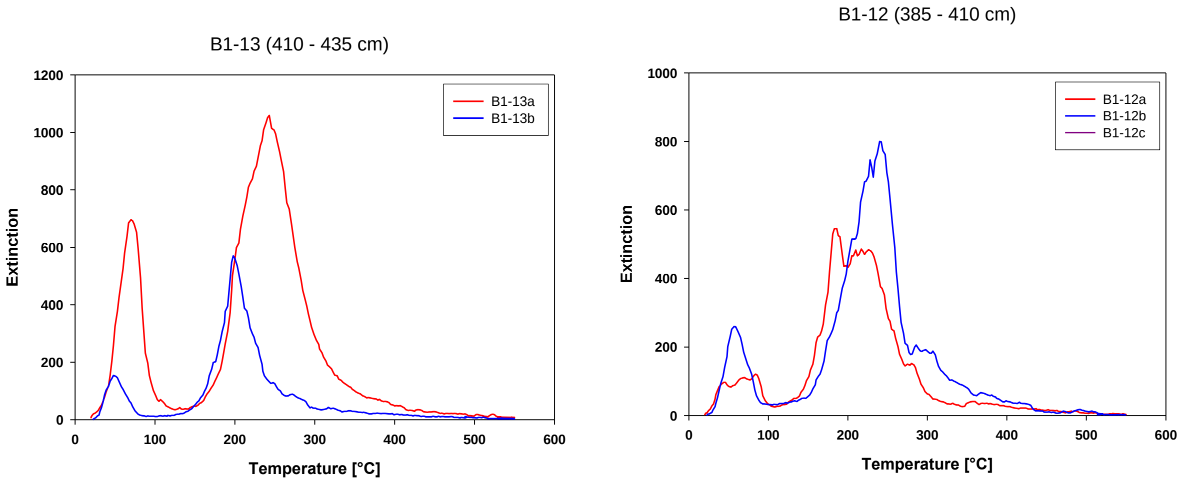


Figure 9: Hg thermo-desorption curves of aquifer material. Peaks at temperatures below 100 °C indicate the formation of Hg(0) through the reduction of $HgCl_2$ (Bollen et al., 2007).

In addition to the formation of Hg(0) the occurrence of HgS in some aquifer samples indicates the precipitation of Hg^{2+} as insoluble Hg sulfide. However, at the investigated site the formation of HgS seems to be restricted to isolated peat layers in the aquifer, where reducing conditions and free sulfide ions as a result of sulfate reduction occur (Fig. 11).

Conclusions

The presented case study of a Hg chloride contaminated aquifer has shown that Hg species transformation processes such as the formation of Hg(0) or HgS are key processes, which control the dispersion of Hg in groundwater systems. Moreover, it highlights the importance of both solid and liquid phase Hg speciation to evaluate environmental risk and to understand the fate of Hg in such complex contaminated systems. It has to be mentioned here that Hg thermo desorption is the only available analytical method which could directly detect Hg(0) in solid material.

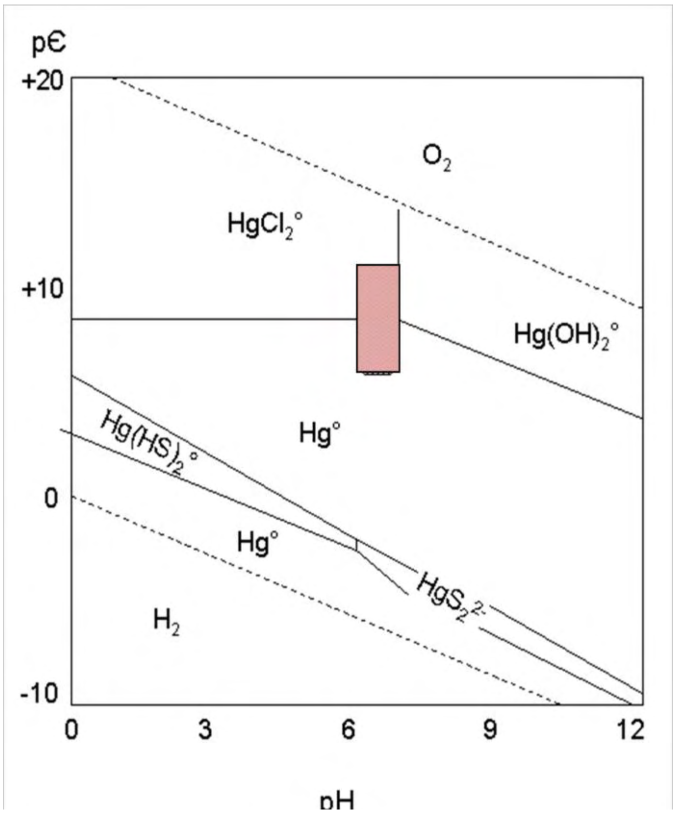


Figure 10: pH-pE stability diagram of the most important naturally occurring inorganic Hg compounds. The red area shows the pH-pE conditions in the investigated aquifer (Schöndorf et al., 1999, Bollen et al., 2007).

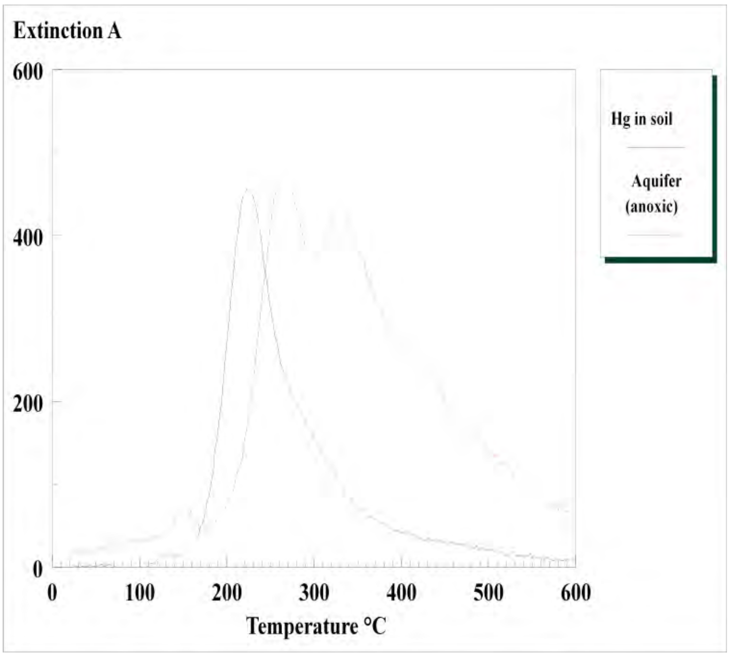


Figure 11: Hg thermo-desorption curves of isolated peat layers in aquifer. Peaks at temperatures above 300 °C indicate the formation of Hg sulfide (HgS).

Case study 3: The mercury mining area of Idrija, Slovenia

Mercury mining areas are comparatively rare. However, due to the high toxicity of many Hg compounds and the release and wide range dispersion of large amount of Hg(0) released during the roasting process into the environment, Hg mining areas are large scale contaminated sites, which often demand development of specific strategies to characterize the risk potential of the different contaminated environmental compartments. Contamination at Hg mining areas such as the Almadén (Spain) or Idrija (Slovenia) mines has affected large areas of tens or hundreds of square kilometers and nearly all environmental media. Due to the different contamination pathways, Hg speciation is of great importance to understand and the fate of Hg in such areas and to predict environmental risk potential. The Idrija mining area is typically for large scale Hg contamination attributed to long term mining activities. In the past 15 years several studies have demonstrated the high grade and widespread contamination of soils in the vicinity of the smelters and the Idrijca river systems, which drains the mining area (Fig. 12) (Biester et al., 2000, Gnamus et al., 2000 and the literature cited therein, Covelli et al., 2001).

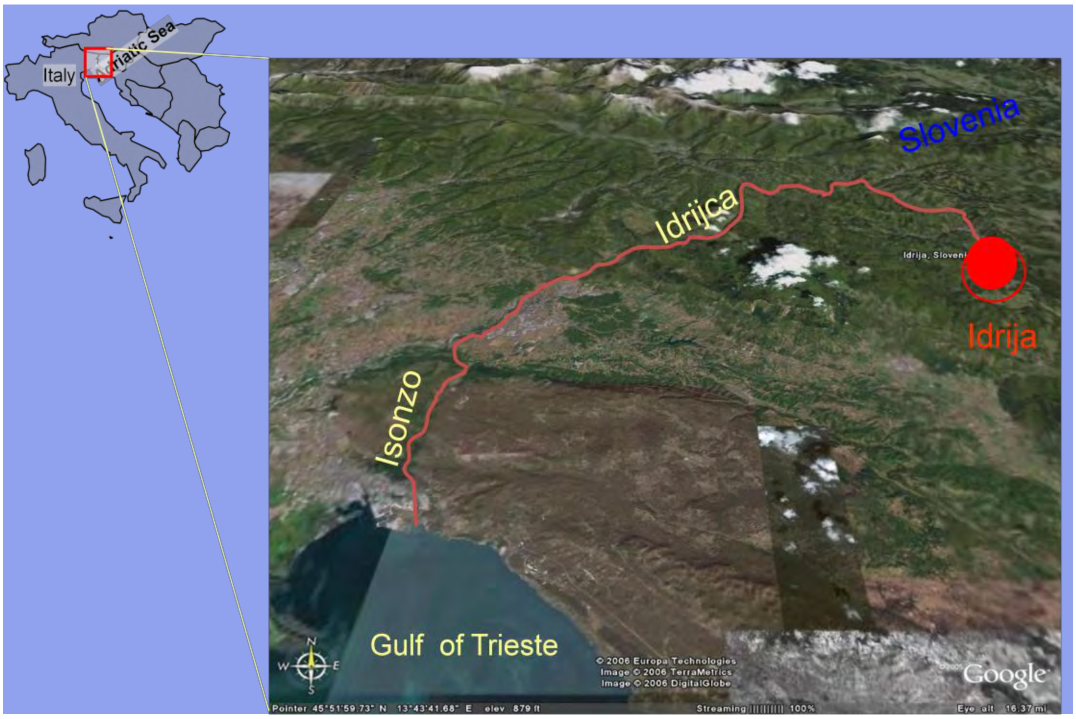


Figure 12: Map of the Idrija mining area, the catchment area of Idrijca river and the Gulf of Trieste, which is the final sink of Hg contaminated material transported by Idrijca river.

Because of the different toxicity and bioavailability of Hg compounds found in mining areas, Hg speciation is of great importance. In most Hg mining areas cinnabar (HgS) is the primary

Hg ore. Due to its very low solubility in water (~ 10^{-54} mol/L) the risk potential of cinnabar to become bioavailable is comparatively low. However, attributed to the emissions of Hg(0) from the roasting plant and the deposition of Hg(0) and Hg(II) to soil, several potentially bioavailable Hg components such as organically bound Hg forms could be found in soils and river sediments.

Figure 13 gives an overview on the main processes of Hg dispersion in the Idrija mining area. It has been estimated that about 45.000 tons of Hg were lost to the environment during ~ 500 years of mining activity. Note that during the most intense mining activity more than 12 kg of Hg(0) were emitted daily from the chimney of the roasting plant. Recent measurement of Hg concentrations and Hg thermo desorption in attic dust have shown that house dust contains high amounts of Hg and that Hg(0), Hg(II) as well as HgS could be found in different proportions depending on the distance from the smelter (Fig. 15) (Gosar et al., 2006).

Figure 15 shows Hg thermo desorption curves of the most important Hg phases occurring in soil, dust and sediments in the mining area. It could be seen that cinnabar in soil and dust is only found in areas close to the smelter, whereas the ecotoxicologically more problematic matrix-bound Hg forms, such as humic acid bound Hg (which could be methylated) are the predominant Hg components found in samples taken more distant from the smelter as a result of long range transport of the emitted Hg(0).

Another important source of Hg pollution has been the dumping of mining residues into the river Idrijca. The aim of this common practice was to get rid of highly contaminated mining residues, which were washed down the river during flood events, mainly in spring after the snow melt. The key question for the risk assessment of the Hg contaminated river system was, to which extend the Hg stored in the river sediments and especially in the Gulf of Trieste could be transformed into highly toxic methylmercury (MeHg). Cinnabar is known to have a low potential to be transformed to MeHg, whereas organically bound Hg or dissolved ionic Hg species mainly derived from soil or tailings are known to be easily methylated in sediments under anoxic conditions and may therefore enter the human foodchain through the enrichment in fish. Besides direct determination of methyl Hg in sediments speciation analyses aim to distinguish cinnabar from non-cinnabar Hg compounds (mainly humic acid bound Hg forms) in sediments.

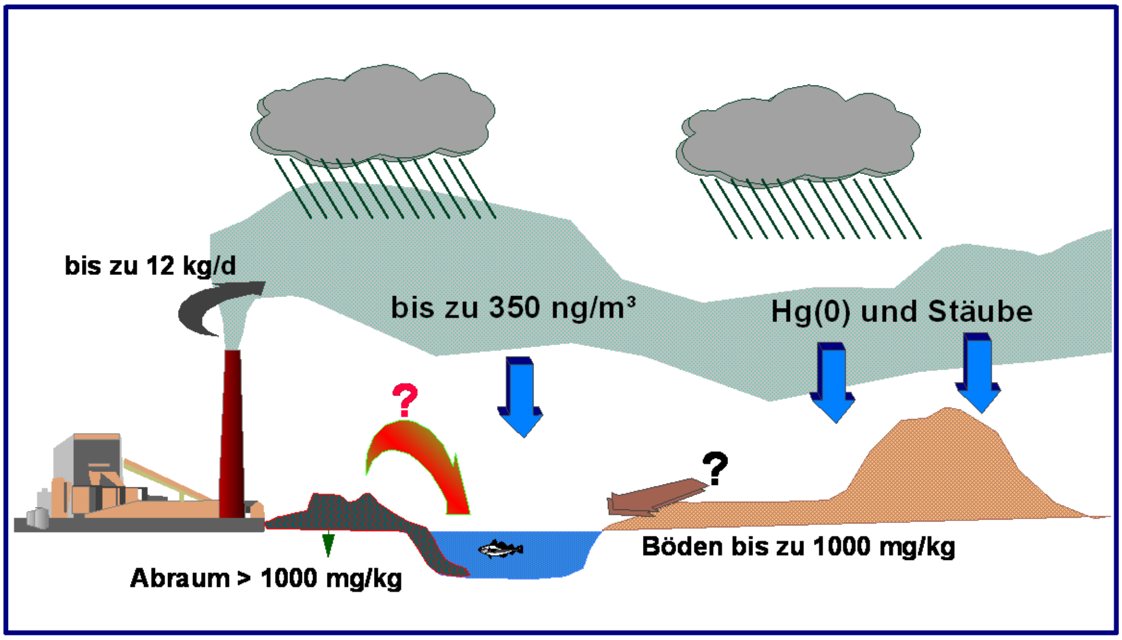


Figure 13: Main pathways of Hg dispersion in the Idrija mining area attributed to smelter emission and dumping of mining residues.

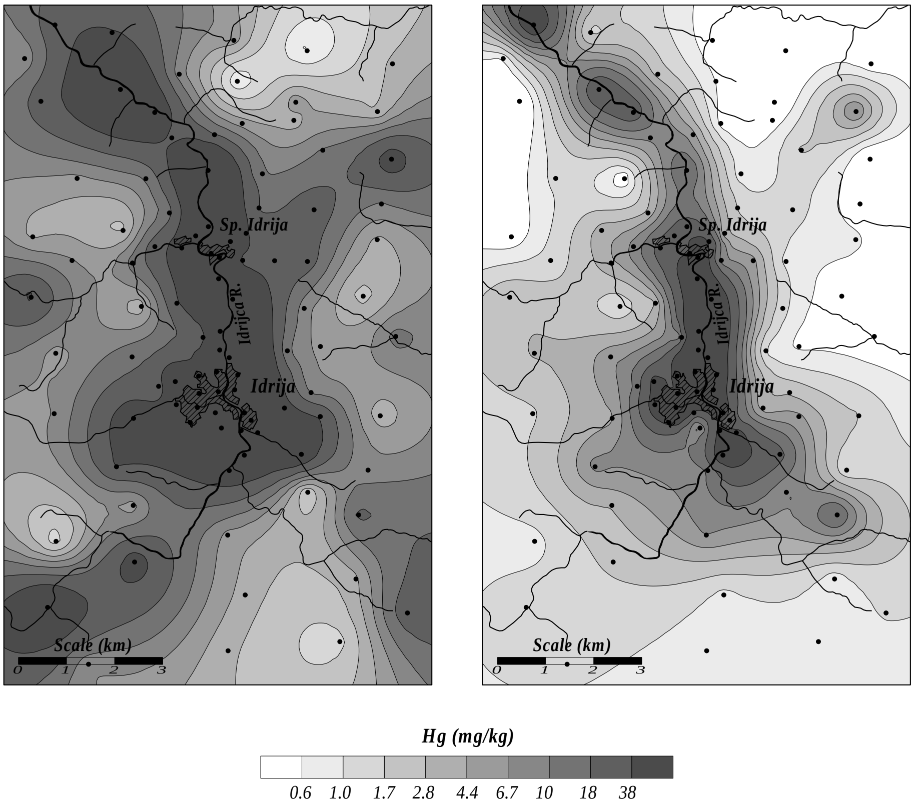


Figure 14: Distribution of Hg concentrations in attic dust (left) and soils (right) in the Idrija mining area (from Gosar et al., 2006).

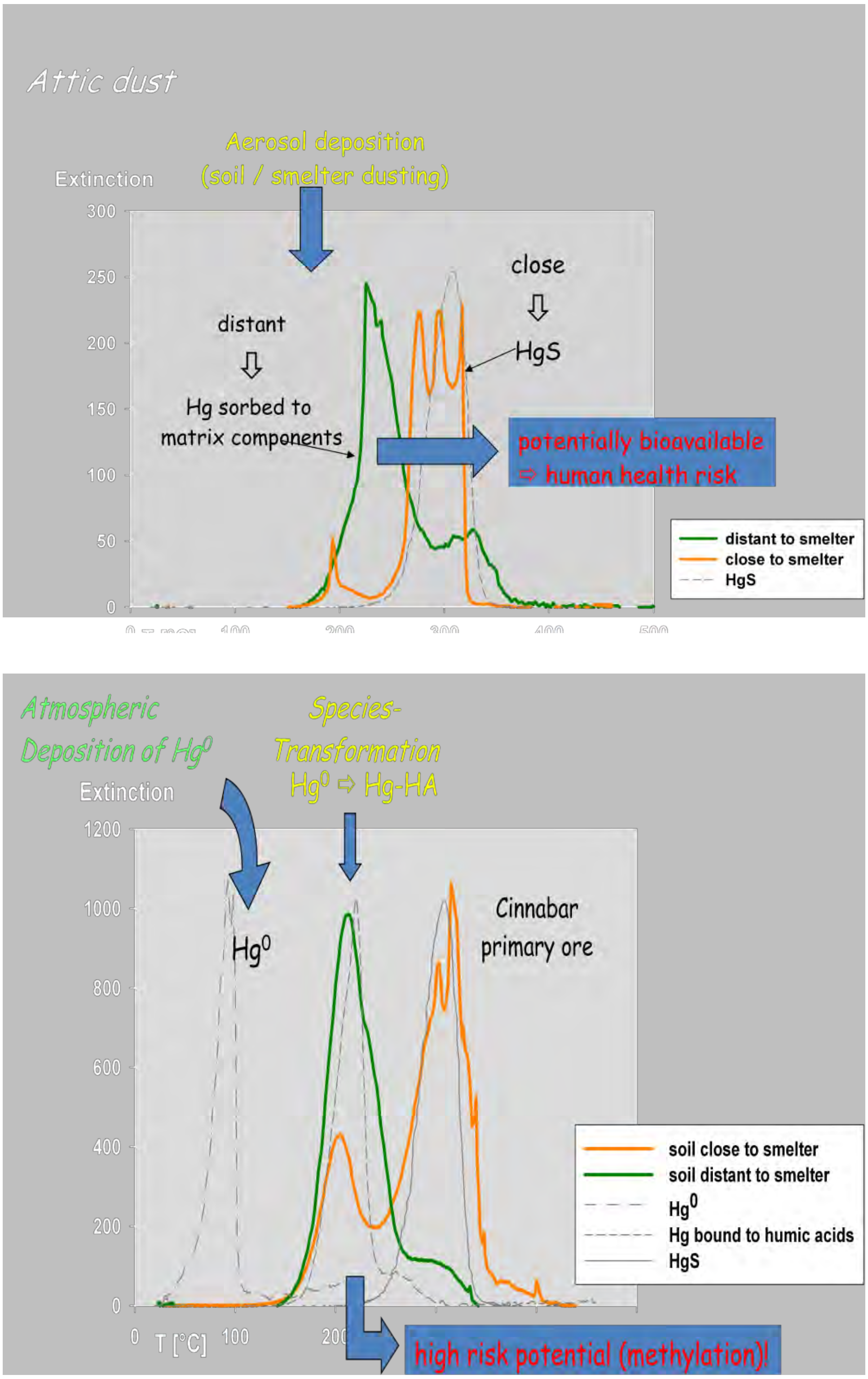


Figure 15: Thermo-desorption curves of Hg in soil and dust samples in the Idrija mining area (from Biester et al., 1999).

The following figures show the results of Hg thermo desorption analyses in sediments from river Idrijca and the Gulf of Trieste. All sediment core analyses clearly indicate that cinnabar is the predominant Hg compound in all samples and that matrix-bound (non-cinnabar) Hg compounds account for less than 20 % of total Hg with the exception of samples taken from old river terraces (Tem 1), which are strongly influenced by atmospheric deposition of Hg(0).

These findings indicate that most Hg in the river sediments is attributed to erosion of tailing material, which over most of the mining history still contains large amounts of cinnabar due to inefficient roasting techniques (Biester et al., 1999).

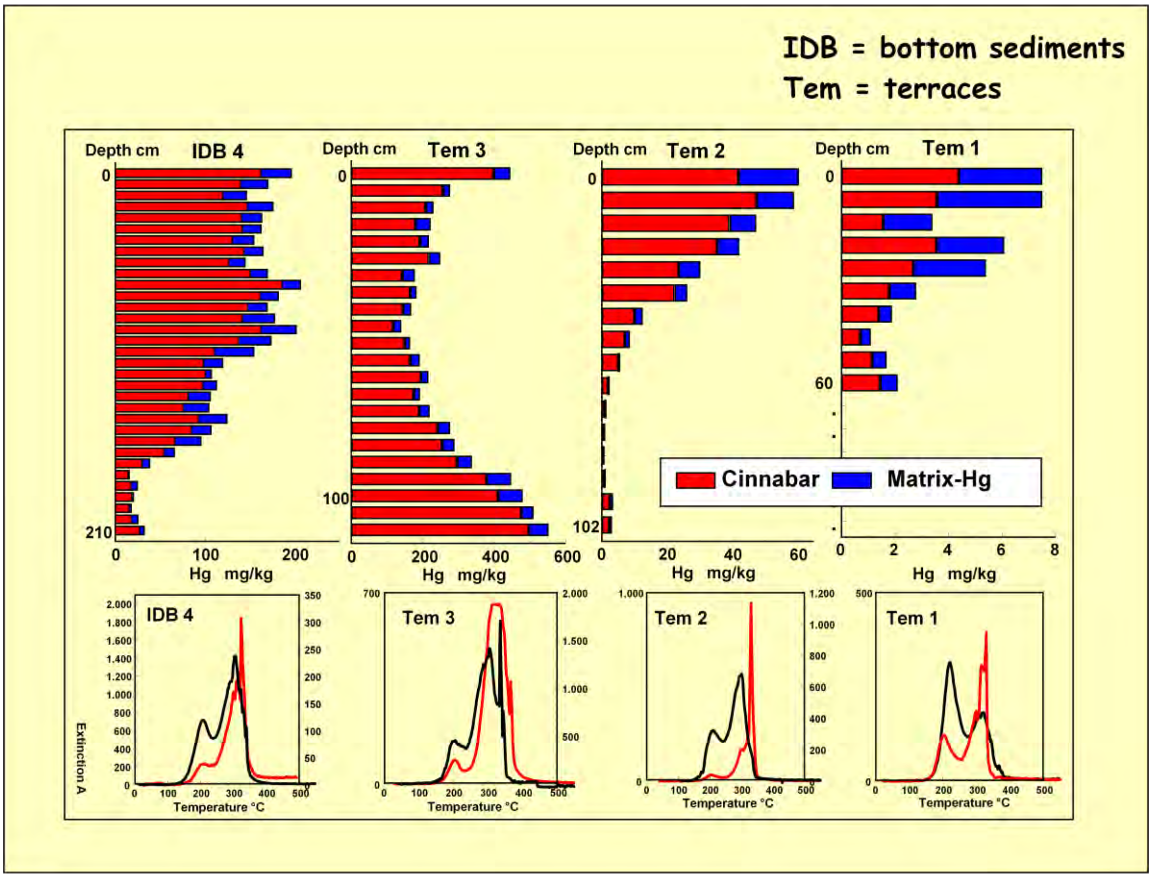


Figure 16: Results of Hg thermo desorption measurements in sediment cores taken at different locations of river Idrijca (Biester et al., 2000).

However, analyses of sediment samples from the Gulf of Trieste indicate that cinnabar is also the predominant Hg species in sediments taken from the river mouth where Hg concentrations are still highly elevated, but samples taken more distant from the coast show predominantly non-cinnabar Hg compounds and only low amounts of cinnabar (Fig. 17). More important, those areas, which show mainly matrix-bound Hg forms, also show highest concentrations of methylmercury despite that total Hg concentrations in those areas are comparatively low.

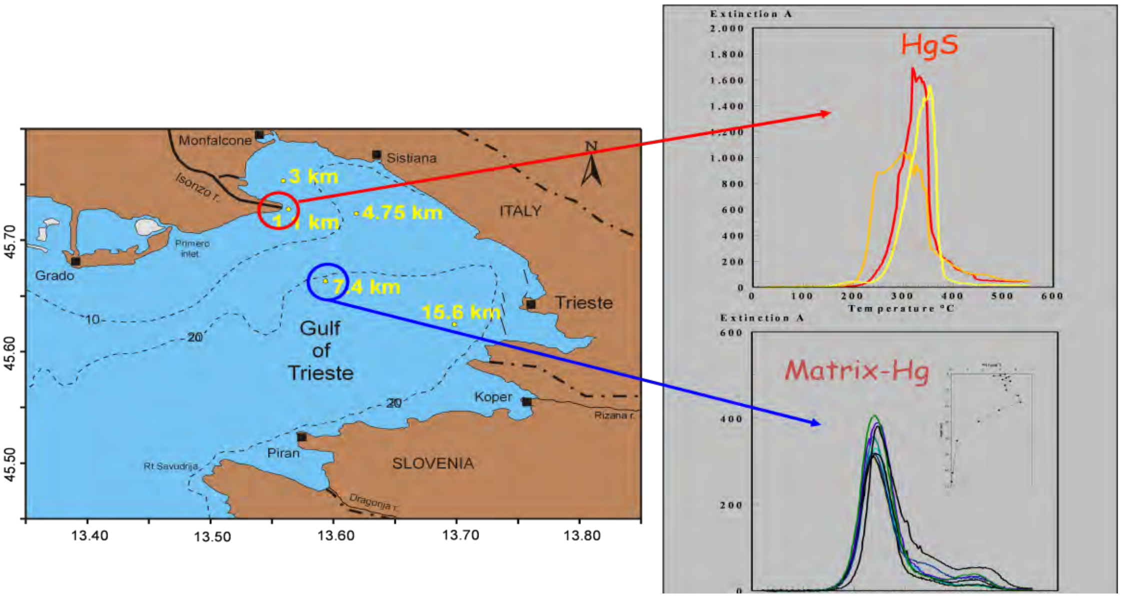


Figure 17: Location of sediment cores taken from the Isonzo (Idrijca) river mouth and in the center of the Gulf of Trieste and predominant Hg binding forms as determined by Hg thermo desorption analyses (Piani et al., 2005).

Comparison of Hg species in sediments with the amount of very fine grained sediments particles (2-16 µm) and the amount of organic carbon in the sediments indicate that matrix-bound Hg compounds show in both cases a very good positive correlation, whereas cinnabar shows a good negative correlation for both parameters (Fig. 18) (Piani et al., 2005).

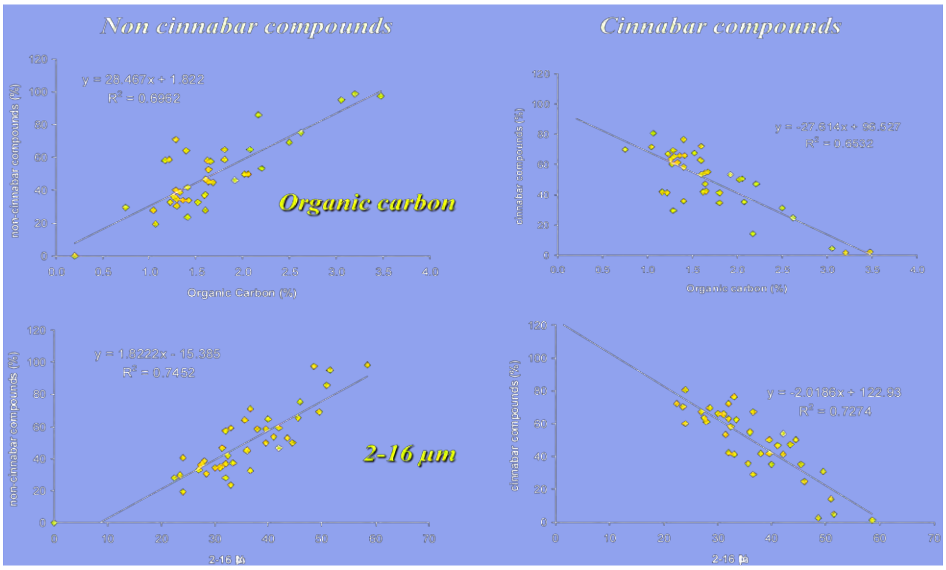


Figure 18: Correlation between non-cinnabar and cinnabar compounds with the amount of fine particles (2-16µm) and the amount of organic matter in sediments of the Gulf of Trieste (Piani et al, 2005).

This findings clearly indicate that the dispersion of different Hg compounds in the river systems depend to a large extend on hydrodynamic conditions. Cinnabar which is mainly associated with coarser particles eroded from the tailings is only transported at high flow regime and deposited where flow velocity decreases (river mouth), whereas non-cinnabar matrix bound Hg compounds including soluble Hg-humic complexes can also be transported at lower flow regimes and are transported far into the Gulf of Trieste where they can potentially be methylated in the sediments.

Conclusions

Several examples of contaminated sites of different scale have been shown where solid phase Hg thermo desorption analyses and determination of operational defined soluble Hg species have been applied to soils, sediments and aqueous samples. It could be demonstrated that both methods are strong tools to detect Hg species and species transformation processes in the environment and that speciation analyses are crucial to evaluate and predict present and future environmental risks of Hg contaminated sites.

References

Baldi F, Bargagli R. (1984) Sci Tot Environ. 39: 15-26

Barnett, M. O.; Harris, L. A.; Turner, R. R.; Stevenson, R. J.; Henson, T. J.; Melton, R. C.; Hoffman, D. P. (1997) Environ. Sci. Technol. 31, 3037-3043.

Biester, H., Gosar, M. Müller, G. (1999) J Geochem Explor. (65)3: 195-204.

Biester, H., Gosar, M., Covelli, S. (2000) Environ. Sci. Technol. 34, 3330-3336.

Biester, H., Müller, G., Schöler, H.F. (2001a) Sci. Tot. Environ., 284/1-3, 191 - 203.

Biester, H., Müller, G., Schöler, H.F. (2001b) Sci. Tot. Environ. , 284/1-3, 177 - 189.

Biester, H., Nehrke, G., (1997b). Fresenius J. Anal Chem. 358, 446-452.

Biester, H., Scholz, C., (1997a) Environ. Sci. Technol., 31, 233-239.

Bloom, N. S.; Pereus, E.; Katon, J.; Hiltner, M. (2003) Anal. Chim. Acta, 479, 233-248.

Bollen, A., Wenke, A., Biester, H. (2007) Water Research,, 42/1-2, 91-100.

Brosset, C., (1987) Water Air Soil Pollut. 34, 145–166.

Covelli, S., Faganeli, J., Horvat, M., Brambati, A., Biester, H. (2001) RMZ – Materials and Geoenvironment, Vol. 48, No. 1 pp. 151-156.

EPA, Mercury Study –Report to Congress Volume III, Fate and Transport of Mercury in the Environment, EPA-452/R-97-005, 1997.

Gnamus, A., Byrne, A., Horvat, M. Environ. Sci. Technol. 2000, 34, 3337-3345

Gonzales H. Water Air Soil Pollut (1991). 56: 83-93.

Gosar, M., Sajn, R., Biester, H. (2001). RMZ – Materials and Geoenvironment, 48, No. 1 pp. 87-94.

Gosar, M., Šajn, R., Biester, H., (2006) Science of the Total Environment. 369, 150-162.

Gustin-Sexauer, M., Biester, H., Kim, C. (2002) Atmospheric Environment, 36: 3241-3254.

Högström U, Enger L, Svedung I. Atmos Environ 1979; 13: 465-476.

Jernelöv A, Wallin T. (1973) Atmos Environ. 7: 209-214.

Kim, C. S.; Brown, G. E., Jr.; Rytuba, J. J. (2000) Sci. Total Environ.,261, 157-168.

Kim, C., Bloom, N., Rytuba, J., Brown, G. Environ. Sci. Technol. 2003, 37, 5102-5108

Lodenius M, Tulisalo E. (1983) Bull Environ Contam Toxicol. 32: 439-444.

Maserti BE, Ferrara R. (1991) Water Air Soil Pollut. 56: 15-20.

Meili, M., Iverfeldet, A., Hankanson, L., (1991). Water Air Soil Pollut. 56,439–453.

Piani, R., Covelli, S., Biester, H. (2005). Applied Geochemistry, 20: 1546-1559.

Revis, N. W.; Osborne, T. R.; Holdsworth, G.; Hadden, C. (1989) Water, Air, Soil Pollut., 45, 105-113.

Sakamoto, H. T.; Tomiyasu, T.; Yonehara, N. (1982) Anal. Sci. 8,35-39.

Schöndorf, T., Egli, M., Biester, H., Mailahn, W., Rotard, W., 1999. Distribution, bioavailibility and speciation of mercury in contaminated soil and groundwater of a former wood impregnation plant. In: Ebinghaus, R. (Ed.), Environmental Science—Mercury Contaminated Sites. Springer, Berlin–Heidelberg, pp. 181–206.

Schöndorf, T., Heinrichsmeier, K., Biester, H., Achstetter, U., 1995. TerraTech 5, 31–35.

Sladek, C., Gustin-Sexauer, M., Kim, C., Biester, H. (2002) Geochemistry, Exploration- Environment-Analysis, 4, 369-375.

Mercury Pollution in Guizhou, Southwestern China - an overview

Xinbin Feng *, Guangle Qiu

State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, PR China

1. Introduction

Mercury (Hg) is a highly mobile heavy metal. Small releases of Hg can result in a significant exposure to wild animals and humans, presenting a global health concern. Hg occurs in several forms in nature. Elemental Hg (Hg(0)) is relatively stable, volatile and has a low solubility in water, thus undergoing long-range transport in the atmosphere. Divalent Hg (Hg(II)), which readily associated with chlorine, sulfur, hydroxyl ions and dissolved organic carbon (DOC), is more common in the environments. Organic compounds of Hg, such as methylmercury (MeHg), are of the greatest concern on human health due to high toxicities.

MeHg is recognized as the most toxic Hg form to humans. It can be generated from ionic Hg in environments by organisms under appropriate conditions such as reducing environments (Grieb et al., 1990; Choi and Bartha, 1994; Ebinghaus et al., 1994). Because of its accumulative and persistent characteristics in biota, MeHg has a strong ability of bioaccumulation in the food chain, resulting in fish tissues more than 106 times higher than ambient water MeHg concentrations (WHO, 1990; US EPA, 1997a). In this sense, an important transformation in Hg cycle is the conversion of inorganic Hg to MeHg.

Guizhou province (N24º30′-29º13′, E103º1′-109º30′; Figure 1) is located in southwestern China with an elevation of 1100 m above sea level and a land area of 176,000 km^2. Its climate represents a typical subtropical humid monsoon with an average annual temperature of 15 °C and a precipitation of 1100-1400 mm. Guizhou is a typically karstic topography. The bedrocks in the province are limestone and dolomite.

From the perspective of the global plate tectonics, Guizhou province is situated in the center of the circum-Pacific mercuriferous belt (Qiu et al., 2006a; Gustin et al., 1999). Therefore, Guizhou is one of the world’s important Hg production centers. So far, at least 12 large and super-large Hg mines have been discovered in the province (e.g. Wanshan, Wuchuan, Lanmuchang, and Danzhai, etc.) and the locations of all Hg mines are shown in Figure 1. The total reserves of cinnabar deposits in the province reached 80,000 tons of metal Hg and represented 80% of the total in China (Qu, 2004). A long-term of 3000 years Hg mining activities have experienced in Guizhou and introduced significant quantities of gangues and mine tailings (calcines), which are uncontrolled stockpiled near the abandoned Hg processing sites and retorts. Between 1949 and early 1990s in the Wanshan Hg mining areas, for instance, approximately 125.8 million tons of calcines and 20.2 billion cubic meters of Hg-contained exhaust gas had been dispersed into the adjacent ecosystems (Liu, 1998). The gangue and calcine piles are continuing releasing Hg to the environment, causing serious Hg contamination. As a result, the crops produced in Hg mining areas contained elevated Hg (Qiu et al., 2008; Feng et al., 2008), posing health threat to the local inhabitants.

Guizhou is one of the major coal production centers and coal consumers in China. Approximately 80% of total energy consumption in the province resulted from coal combustion (Tan et al., 1997; 2000). Currently, more than 50 million tons of coals were combusted annually for both industrial and domestic purposes, and most coals were used without cleaning or flue gas controls (Tang et al., 2007). Due to the special geochemical background, Hg concentrations in coal from Guizhou are elevated compared to coal produced in other provinces in China (Feng et al., 2002). Therefore, a large quantity of Hg is released from coal combustion in Guizhou, resulting in Hg contamination to the ambient air and the local environment.

Guizhou is also an important artisanal Zn smelting center. Large quantities of artisanal Zn smelting workshops were scattered in northwestern parts of the province (i.e. Hezhang, and Weining). Artisanal Zn smelting using indigenous methods experienced at least hundreds years in Guizhou (Figure 1). Hg is an important associate element in zinc ores, and during zinc smelting processes a large quantity of Hg is released to the environment, resulting in serious Hg contamination to the local environment (Feng et al., 2004a, 2006; Li et al., 2008).

In addition, Guizhou has a unique State-owned chemical plant, Guizhou Organic Chemical Plant (GOCP), which used Hg as a catalyst for acetaldehyde production. Drainages released from the GOCP through direct and/or river discharges contributed to significant Hg contaminations to the local ecosystems. The total loss of Hg into environments estimated by the GOCP was about 134.6 tons within 30 years of operation of the company.

Hg pollution problems in Guizhou have drawn a great attention to the scientific communities in China and over the world. A number of studies have been diverted to understand the emission, transport, and cycling of Hg in the environment in Guizhou and the health impacts to humans. This paper is mainly aimed at summarizing the state of art of knowledge on the status of Hg pollution in the environment in Guizhou, China and the status of Hg pollution in the environment in China has been reviewed by Jiang et al. (2006) and Wang and Wong (2007).

2. Anthropogenic Hg emissions in Guizhou

Recent estimates of anthropogenic total Hg emissions to the atmosphere in China suggested that the total anthropogenic Hg emissions in China reached 536 tons in 1999, which constituted about 1/4 of the total emissions over the world (Streets et al., 2005). It is pointed out that Guizhou is one of the most important Hg emission regions. Contributions estimated from the province ranged between 22.6 and 55.5 t yr^{-1}, which was about 6.3-10.3% of current total anthropogenic Hg emissions in China (Wang et al., 2000; Streets et al., 2005; Wu et al., 2006; Zhang and Wong, 2007).

2.1 Emission from coal combustion

Coal combustion is an important source category of anthropogenic Hg emissions to the atmosphere worldwide. Guizhou stands out in coal-related Hg emissions primarily due to high Hg contents in raw coals and numerous combustion facilities without pollution control facilities (Feng et al., 2002; Tang et al., 2007).

An investigation of 48 crude coal samples collected from 4 coal production centers in Guizhou provided a high average Hg concentration of 0.53 mg/kg, ranging from 0.10 to 2.67 mg/kg (Feng et al., 2002). Zhang J. et al. (2004) introduced a wide range of 0.04-10.5 mg/kg Hg in coals from southwestern Guizhou. An extremely high value of 12.1 mg/kg was reported in an anthracite coal sample from Xingren, in southwestern Guizhou (Dai et al., 2006). Coal Hg contents in Guizhou were higher compared with other regions in China, which ranged from 0.02 to 0.44 mg/kg on average (Wang et al., 2000; Streets et al., 2005). High levels of Hg contents in raw coals were predominantly attributed to the high background of Hg in bed rocks in Guizhou, which is in the center of the circum-Pacific global mercuriferrous belt (Gustin et al., 1999). Since the majority of commercial coal produced in Guizhou is not washed to remove heavy metal contaminants, Hg contents in commercial coal should be identical to the crude coal.

Hg emission rates and speciation profiles depend greatly on the combustion and pollution control techniques employed in the facilities. Statistical data for coal consumption suggested that large-scale coal-fired power plants, industrial sectors, and domestic users consumed about 30%, 48%, and 22% of the total coal consumption in Guizhou, respectively. Using a mass balance technique, Tang et al. (2007) estimated that Hg emission factors of a small industrial coal fired boiler without and with flue gas desulphurization (FGD) systems was 66% and 26% of total Hg presented in coal, respectively. Hg emission factors of a large coal-fired power plant with electrostatic precipitators (ESPs) systems was up to 85% of total Hg presented in coal, which could be decreased to 43% in the case of FGD systems employed. Those data suggested that 56% of Hg emission from coal combustion in Guizhou was released as Hg^0, 33% as Hg^{2+}, and 13% as HgP, respectively, which were comparable to the estimated values of China by Streets et al. (2005).

Using above-estimated Hg emission factors, Tang et al. (2007) estimated that the annual emission of total Hg into atmosphere from coal combustion in Guizhou steadily increased from 5.8 t in 1986 to 26.4 t in 2006 (Figure 2). However, Streets et al. (2005) reported an even higher value of 39 t of total Hg in Guizhou in 1999, with 18.2 of Hg^0, 11.1 t of Hg^{2+}, and 9.5 t of HgP, respectively. It is obvious that the coal consumption increased significantly with the rapid economic development. With the implementation of “Go West” policy, more coal fired power plants are planned to be constructed in Guizhou by 2010, and by then the total coal consumption will be doubled compared to the current consumption. New regulations in China will force all newly built coal fired power plants to install both ESP and FGD, which will significantly reduce Hg emission from coal burning (Tang et al., 2007).

2.2 Emission from Zinc smelting

Hg emission from refining of Zn is another important anthropogenic source (Nriagu and Pacyna, 1988; Pai et al., 2000). Most compounds of Hg will be decomposed to Hg^0 at temperatures greater than 700-800 °C (Lindqvist, 1986; Schroeder and Jackson, 1985), thus at high temperatures of Zn smelting (~1000 °C), nearly all of Hg occurring in Zn ores will be converted to Hg^0 and emitted to the ambient air with the exhaust gas.

Zinc ores produced in Guizhou contain high Hg concentrations. Feng et al. (2004a) reported an average Hg concentration of 66.8 mg/kg in sulfide ores from Hezhang. Li et al. (2007) found Hg concentrations in carbonate Zn ores from Weining ranged from 1.06 to 87.1 mg/kg, with an average of 13.4 mg/kg, which was similar to the results found in oxide ores from Hezhang (Feng et al., 2004a). Elevated Hg concentrations in both sulfide Zn ores and oxide Zn ores occurred in those areas were probably contributed to the high-background Hg concentrations in bedrocks in the circum-Pacific global mercuriferrous belt.

Using a mass balance method, Feng et al. (2004a) estimated the average Hg emission factors from artisanal Zn smelting in Hezhang to be 155 and 79 g Hg t-1 of Zn produced from sulfide ores and oxide ores, respectively. Similar to the emission factor from oxide ores in Hezhang, an average Hg emission factor from carbonate ores in Weining was 75 g Hg t-1 of Zn produced (Li et al., 2007). The average Hg emission factor from sulfide ores was almost two times higher than that of oxide ores. However, compared to the value reported in the literature, which was 25 g Hg t-1 of Zn produced in developing countries (Nriagu and Pacyna, 1988), Hg emission factors of artisanal Zn smelting in Hezhang and Weining were significantly higher.

Emission factors of Hg from smelting facilities strongly depend on Hg concentrations in Zn ores and efficiencies of Hg removal by air pollution control equipments. No pollution devices were applied for artisanal zinc smelting activities. The amount of Hg remained in bottom ash from combustion chambers was estimated to be less than 5% of total Hg in Zn ores during artisanal Zn smelting processes (Li et al., 2005).

Using above estimated Hg emission factors, annual Hg emissions from artisanal Zn smelting in Hezhang from 1989 to 2001 were estimated to be a few metric tons (Figure 3). The maximum annual Hg emission was 7.1 t in 2000, which was comparable to the annual Hg emission from coal combustion in Guizhou in 1995 (Feng et al., 2002). It highlights that artisanal Zn smelting is an important regional atmospheric Hg emission source.

2.3 Emission from artisanal Hg mining in Guizhou

Since the beginning of 21st century, all large scale Hg mining activities in Guizhou province have ceased mainly due to lack of profits for the mining companies. However, the market for Hg demand has been increasing since China started to restrict importing Hg from Europe and other regions a few years ago. Consequently Hg prices in the market went up recently, which stimulated the revival of small scale (artisanal) Hg activities using indigenous methods in Guizhou province.

Especially the artisanal Hg mining activities using indigenous method have extensively existed in Wuchuan areas, northeastern Guizhou province, China. Wuchuan is one of the most important Hg production areas in Guizhou province. The large scale mining activities ceased in 2003 because of the increasing environmental concerns. But small scale smelting activities which are classified as illegal and forbidden by the local government are still in operation in this area. The Hg ore (cinnabar) was crushed and then heated to 700-800 °C to produce Hg vapor that condensed in cooling wooden barrel, which contained water (Li P et al., 2008). Because the simple smelting processes are without any environmental protection measures, the Hg emission factors (the proportion of Hg in ore is released to the ambient air) ranged from 6.9% to 32.1% and the annual Hg emission from artisanal Hg smelting activities was up to 3.7 to 9.6 tons in Wuchuan area (Li et al., 2006).

3 Hg emissions from natural sources in Guizhou

3.1 Emission from Hg enriched soil in Guizhou

In Hg mine areas, soil Hg concentrations are usually elevated by 2-4 orders of magnitude compared to the national background value of 0.038 mg/kg mainly due to Hg mineralization processes. Hg emissions from Hg-enriched substrates may, therefore, serve as an important natural emission source in Guizhou.

A field examination of Hg emissions by Wang et al. (2005) showed that in the Lanmuchang Hg mines, Southwestern Guizhou, Hg emission from soil was the main source of Hg in the ambient atmosphere. An average Hg emission flux of 19.9 mg/m^2 per year was obtained and within a total area of ~2.9 km^2, the annual Hg emission reached ~3.54 kg Hg, indicating that soil is a strong Hg emission source to the ambient air. The average Hg emission fluxes from soil in Wanshan Hg mines ranged from 1.42 to 243.7 mg/m^2 per year (Wang et al., 2007a), while the average Hg emission flux reached 1.23 mg/m^2 per year in Wuchuan Hg mines (Wang et al., 2007b).

3.2 Emission from natural soil

Due to high-Hg levels of geological baseline, natural soils in Guizhou are usually enriched in Hg. In-situ total gaseous Hg (TGM) exchange fluxes between air and soil surface were intensively measured in Guiyang and Hongfeng reservoir area (Feng et al., 2005; Wang et al., 2004). Results showed that Hg emission fluxes from natural soil reached 9.64 µg/m^2 per year, which was almost one order of magnitude higher than the value used to estimate Hg emission from the soil in the global mercuriferous belts. The annual Hg emission from natural soil in Guiyang reached 0.41 tons, which constituted an important atmospheric Hg source in the ambient air of Guiyang.

3.3 Emission from natural water

Hg exchange between air and water surfaces is recognized to be of significance in global biogeochemical cycling of Hg (Lindqvist et al., 1991; Mason et al., 1994). Since the Baihua reservoir was seriously contaminated with Hg released from the GOCP (Yan et al., 2008), an annual Hg emission from the reservoir to ambient air is estimated to be 0.75 kg, constituting of 3% of total Hg in water body of the reservoir (Feng et al., 2004b). The Hg emission from water surfaces of the Baihua reservoir is considered to be an important local atmospheric Hg sources.

4. Atmospheric Hg pollution and deposition

4.1 Hg in ambient air

Significant Hg emissions from anthropogenic and natural sources resulted in high levels of atmospheric Hg in Guizhou. An average TGM concentration in ambient air in Guiyang was 11 ng/m^3 in 1996 and 13 ng/m^3 in 1999 (Feng et al., 2002). An investigation on TGM distribution in ambient air in Guiyang from November 2001 to November 2002 showed that an annual average TGM concentration was 8.4 ng/m^3, with a seasonal distribution pattern descending from winter, spring, fall to summer (Feng et al., 2004c). Those values were significantly elevated compared to the global continental background values of the Northern hemisphere which varied from 1.5 to 2.0 ng/m^3 (Schroeder et al., 2001; Ebinghaus et al., 2002a; Lamborg et al., 2002). The seasonal TGM distribution pattern in Guiyang could be attributed to different amount of coal combustion between cold and warm seasons.

In Lanmuchang Hg mine, highly elevated TGM concentrations in ambient air varied from 35.2 ng/m^3 (7.9-353.8 ng/m^3) in cold season to 111.2 ng/m^3 (12.7-468.0 ng/m^3) in warm season (Wang S et al., 2005). Recently, atmospheric Hg levels in ambient air nearby artisanal smelting retorts in Wuchuan exhibited values of 17.8-1101.8 ng/m^3 (Wang S et al., 2007a). The highest value of 12,222 ng/m^3 was measured at an artisanal Hg smelting site at the prevailing wind direction. Even at considerable distance of 5-10 km in a downwind direction from the smelting retorts, high air Hg levels of 50.5-56.3 ng/m^3 were observed as well. A significant correlation (R^2=0.98) between air Hg concentrations and distances from artisanal Hg smelting sites were observed (Wang S et al., 2007b), and the study indicated that air Hg concentrations decreased exponentially with distance between sampling sites and Hg smelting areas.

Air Hg concentrations in Hg mines were much elevated by 2-4 orders of magnitude compared to the values observed in pristine areas in Europe and North America, which was 1.5-2 ng/m^3 (Ebinghaus et al., 2002b; Poissant et al., 2005).

Znic smelting process also resulted in high concentrations of Hg in the ambient air. A study conducted in Weining exhibited a high average air concentration of TGM of 124 ng/m^3 on an average of 24 measurements around a Zinc smelting workshop (Li G et al., 2007).

4.2 Hg deposition

Large Hg emissions can lead to marked Hg depositions (Carpi, 1997; Nadim et al., 2001). Using moss bag technique, Hg deposition fluxes in Guizhou were investigated (Xiao et al., 1998; Tan et al., 2000). Total annual depositions ranged from 336 to 2340 µg/m^2 and the annual wet deposition ranged from 144 to 1404 µg/m^2. The highest annual total Hg deposition of 2340 µg/m^2 was as much as 42 times of the deposition flux measured at a reference site (Tan et al., 2000). Xiao et al. (1998) reported that the annual total Hg deposition to Fanjing Mountain Nature Reserve was 115 µg/m^2, of which the dry deposition was of >50%. Recently, annual wet deposition fluxes of total Hg from five monitoring sites in rural areas of Guizhou were reported to be 34.7 µg/m^2 in 2006 (Guo et al., 2008). Those data in Guizhou were much higher than the value of 9.3 µg/m^2/a reported in North America (NADP, 2007).

An investigation on the precipitation showed that total Hg concentrations in rain ranged from 10.3 to 90.6 ng/L with an average of 33 ng/L in Guiyang in 1996 (Feng et al., 2002). Similar results were found in 2006, which ranged from 7.5 to 149.1 ng/L with an average of 49.2 ng/L (Guo et al., 2008). Since Guiyang is impacted by acid rain caused by coal combustion (Shen et al., 1993), high levels of Hg in precipitation could be contributed to the Hg emission from coal combustion in the region.

5. Hg contamination to the environment from anthropogenic activities

5.1 Hg contamination from zinc smelting

In Hezhang, top soils were sampled along a valley from upwind direction of the artisanal zinc smelting workshops to the downwind direction. It is shown that total Hg concentrations in top soils decreased exponentially with the distance from Zn smelting areas, and dropped dramatically at upwind direction (Feng et al., 2006). This indicated that contaminations of Hg in top soils were mainly derived from the deposition of atmospheric Hg emitted from Zn smelting.

Local surface waters were also seriously contaminated with Hg due to Zn smelting. An average total Hg concentration in surface water in Hezhang reached 138 ng/L and was higher than the values observed in local springs and wells (Feng et al., 2004a). Apart from the deposition of Hg species that emitted from Zn smelting, smelting residues were also the primary source of Hg contamination to the surface water systems.

5.2 Hg contamination from cinnabar mining

Although large-scale state owned Hg mining activities were completely shut down in 2004, large quantities of illegal artisanal Hg mining activities are still operating in Wuchuan. Long-terms of Hg mining and the artisanal Hg mining activities resulted in significant quantities of piles and spoil heaps of calcines, which are dumped in stream banks and flood plains and are continuing to impact the local environments.

5.2.1 Hg levels in mine tailings (calcines)

High concentrations of total Hg in mine tailings, up to 4400 mg/kg, were observed in Wanshan (Qiu et al., 2005). Results from leaching experiments on calcines identified the existence of soluble reactive Hg compounds (Li P et al., 2008a), suggesting that the introduction of Hg-contaminated tailing materials into river systems could release Hg species (i.e. soluble reactive Hg) to water. Studies showed that Hg phases in calcines, which usually include elemental Hg, metacinnabar, and Hg sulfates and chlorides (Kim et al., 2000; 2004), mainly depend on the efficiency of roasting techniques (Gray et al., 2002, 2003, 2004).

MeHg concentrations in calcines ranged from 0.17 to 3.9 µg/kg (Qiu et al., 2005, 2006a). Those data were comparable to the values reported in the Palawan Quicksilver Mine (Gray et al., 2003), but were 10-1000 times lower than the levels of 96-3100 µg/kg found in Nevada and Almadén (Gray et al., 2002, 2004). Qiu et al. (2005) concluded that low MeHg in calcines in Guizhou might be linked with the low microbial activities during sampling campaign in winter.

As both speciation and mobility of Hg in tailing materials are mostly unknown, determining solid phase Hg binding forms and aqueous phase Hg mobility in tailings is essential to estimate the potential for Hg transformation processes and to evaluate the environmental risks.

5.2.2 Hg levels in soil

Mining operations severely enhanced the mobilization of Hg through the smelting activities and the depositions of mine tailings and thus resulted in elevated Hg levels in soils. Hg concentrations in soils from Hg mines varied in wide ranges from background levels to several hundreds mg/kg. At the Wanshan Hg mine, Hg concentrations in surface soils could be as much as 790 mg/kg (Qiu et al. 2005). At a site of 24 km downstream from the Wuchuan mine, soils alongside river banks were still heavily contaminated with Hg and Hg concentration reached 24 mg/kg (Qiu et al., 2006a).

The distribution of Hg in a soil profile impacted by a large scale Hg smelter was investigated in Wuchuan by Qiu et al. (2006a). Results showed that total Hg concentrations were the highest in the surface soil, ranging from 6.5 to 17 mg/kg, and decreased to a low level of 0.48 mg/kg at a depth of 45 cm. This indicated that Hg species deposited onto the soil surface can be transported downward so that anomalous Hg values can extend to depths of about 50 cm.

Elevated MeHg levels as high as 23 µg/kg in soil was found in Wanshan (Horvat et al., 2003). Similar results were reported in soils from Wuchuan, which ranged from 0.69 to 20 µg/kg (Qiu et al., 2006a). However, studies showed that MeHg concentrations in rice paddies were usually higher than those of cornfields (Qiu et al., 2005, 2006a) due to its favorable environment for methylation of Hg (Hines et al., 1999). Hg contaminated irrigating water and the anaerobic conditions most likely contributed to the high concentrations of MeHg in rice paddies. High levels of MeHg in paddies may result in MeHg exposure to humans through the food chain.

Although soils from Hg mining areas have elevated levels of MeHg, no significant correlation between MeHg and total Hg were found as shown in Figure 4. However, ratios of MeHg to total Hg were lower in Hg mining areas compared to the background sites in un-mineralized areas. This might be because an enzyme-catalyzed microbial demethylation reaction breaks the Hg-C bond to produce Hg(II) and CH_4 (Summers, 1986), thus preventing high concentrations of MeHg from accumulating in these soils (Hines et al., 1999).

5.2.3 Hg levels in surface water

Total Hg concentrations in surface water emanating from calcines in Wanshan were reported to be up to 10,580 ng/L (Horvat et al., 2003). Concentrations of total Hg in surface water collected from Wanshan, Lanmuchang and Wuchuan varied from 24.8 to 7020 ng/L (Feng et al., 2003; Qiu et al., 2006a, b). A geochemical study showed that the drainages from calcines piles had pH value of 10.6-11.8, containing high dissolved Hg concentrations of 300-1900 ng/L (Zhang G. et al., 2004). This indicated that the reaction between water and calcines increased the concentrations of Hg in mine drainage and was an important process, which controls the release and transport of Hg from mining sites into the streams.

A positive correlation between total Hg and suspended substances in surface water samples was shown in Figure 5. This suggested that Hg associated with particulate material was an important vector for Hg migration from the abandoned Hg mine sites (Horvat et al., 2003; Qiu et al., 2006a, b). In temperate climates, the source of mass loading was from Hg mine tailings and the transport of Hg from mining sites occurred primarily in particulate forms (Qiu et al., 2006a). Besides the atmospheric Hg deposition and the influx of soil-derived Hg, most of Hg found in streams is attributed to the erosion of tailings material. Hence, the secondary sources of the toxic forms of Hg can be transported to great distances from the original sources.

The fate of Hg transported downstream is controlled primarily by the biogeochemical conditions which affect the mobility of Hg. Studies revealed that the high concentrations of MeHg in downstream watersheds were associated with significant quantities of inorganic Hg emitted from those abandoned Hg mines (Horvat et al., 2003; Qiu et al., 2006a). The relationship between total MeHg and dissolved MeHg in surface water was shown in Figure 6. This significant positive correlation indicated that the dissolved fraction dominated MeHg levels in stream waters from the Hg mining areas.

Hg concentrations in waters in Hg mining areas were much higher than those found in other aquatic systems that had been investigated in other parts of Guizhou (Jiang et al., 2004; Hou et al., 2004; He et al., 2006). Aquatic systems are of great interest due to the possibility of Hg transformation and accumulation in the food chain. Moreover, these contaminated stream waters are used by the local farmers to irrigate the rice paddy fields, which could result in further Hg contamination to soil compartment. The chemical speciation, fractionation and availability of Hg in sediments could be useful to understand the fate of Hg within the systems and thus need to be investigated.

5.2.4 Hg levels in plants

Only a few studies were conducted to evaluate the environmental impacts and the potential hazards related to Hg contamination in plants (Table 1). In Hg mining areas, a significant amount of Hg can be concentrated in the foliar portion of the plants, which confirmed the Hg uptake of plants via absorption of atmospheric Hg by leaves (Ericksen et al., 2003). Levels of Hg up to 18 mg/kg occurred in green cabbages (B. oleracea) grown in Hg-contaminated soils in Lanmuchuang Hg mining area (Qiu et al., 2006b), where atmospheric Hg concentrations were elevated mainly due to Hg emissions from Hg enriched soil (Wang et al., 2005).

Moss obtaining nutrients through atmospheric route can be used as a bio-indicator of air pollution of Hg (Carpi et al., 1994; Calasans and Malm, 1997; Fernández et al., 2000). A significant amount of Hg can be concentrated in mosses in Hg mining areas, reaching up to 95 mg/kg (Qiu et al., 2005; Li P et al., 2008b). Qiu et al. (2005) clearly demonstrated that a significantly positive correlation between atmospheric Hg concentrations and total Hg concentrations in moss. The elevation of Hg concentrations in moss samples collected in Wanshan and Wuchuan Hg mining areas indicated that Hg mining activities have resulted in serious Hg contamination to the ambient air.

Though inorganic Hg species predominated in most of Hg-enriched plants, high levels of MeHg in rice (Oryza sativa L.) grown in Hg mining areas were reported (Horvat et al., 2003; Feng et al., 2008; Qiu et al., 2006a, 2008). It is demonstrated that total Hg concentrations in almost all agriculture crops exceeded the national guidance limit for foodstuff other than fish that is 20 µg/kg for food and 10µg/kg for vegetables recommended by the Chinese National Standard Agency (Feng et al., 2008). However, it is clearly demonstrated that only rice could assimilate and accumulate MeHg in its edible portion in a high level, and MeHg concentration in rice can be as high as 174 µg/kg (Qiu et al., 2008). The Hg contaminated water (Horvat et al., 2003; Feng et al., 2003) for irrigation the soil and the anaerobic conditions created by the seasonal flooding during rice growing period may contribute to the high methylation ability in paddy soils. Qiu et al. (2005) observed MeHg concentrations in soil samples from rice paddy field were generally higher than those in cornfield in Wanshan Hg mining area. However, the mechanism of rice tissue to uptake MeHg probably through its roots is still unclear.

5.3 Hg contamination from the GOCP and other plants

The GOCP, which used Hg-based technology till 1997, is located at the upper reaches of the Baihua reservoir. The GOCP went into operation in 1980, and about 160 tons of Hg had been consumed since then. From 1980 to 1985, drainages from the GOCP were directly discharged to the environment without any treatment, which seriously contaminated the surrounding environments with Hg, especially the Baihua reservoir.

High average concentrations of total Hg in water samples from the Baihua reservoir were found up to 73.4 ng/L (Yan et al., 2005). Data reported by Yan et al. (2008) showed that the highest total Hg concentration of 39 mg/kg in sediments was obtained in the upstream of the Baihua reservoir, which is located immediately downstream of the GOCP. However, high Hg concentrations and strong variations with depth were observed in the sediment cores collected in a downstream part of the Baihua reservoir. Two strong peaks could be distinguished at 14 cm and 22 cm in the sediment cores, respectively. In more recent sediments, however, concentrations of Hg decreased toward surface of the sediment, which corresponding the reducing discharging Hg from the company. The study testified an exceedingly high Hg level in the historical records provided by sediment cores.

Yasuda et al. (2004) demonstrated that the paddy fields downstream of GOCP receiving the waste water from GOCP were seriously contaminated with Hg. The average total Hg concentration was 15.73 ± 42.98 mg/kg, which were significantly elevated compared to the average value of 0.11 ± 0.05 mg/kg in the control area nearby (Yasuda et al., 2004). Horvat et al. (2003) reported that Hg concentrations in soil in Quingzhen is the highest close to the GOCP but the levels reached background concentrations at a distance of several km. Even though the major source of Hg in this area is inorganic Hg. It was observed that active transformation of inorganic Hg to organic Hg species (MeHg) takes place in water, sediments and soils. The concentration of Hg in rice grains can reach up to 87.8 μg/kg of total Hg of which 41.4 μg/kg was in MeHg form, and the percentage of Hg as MeHg varied from 32.9 to 52.8% (Horvat et al., 2003).

Recently, an investigation on the spatial and temporal distribution of MeHg in the Hongfeng reservoir, which was impact by a coal-fire power plant, showed that MeHg concentrations significantly increased from 0.053 to 0.92 ng/L in hypolimnion in summer season, suggesting strong MeHg productions in water column. The outflow of reservoir was rich in MeHg, which was 5.5 times higher than those of the inflow (He et al., 2006, 2008). This study indicated that MeHg-enriched water from the anoxic hypolimnia in the reservoir can be a potential MeHg contamination source to the downstream ecosystems.

6. Hg exposure pathways and human health risk

The human health risk assessment of Hg exposure in Hg mining areas was conducted by several studies. In Wuchuan, the average hair total Hg and MeHg for smelting workers were 69.3 and 2.32 mg/kg, respectively, and were significantly higher than those in a control group, which were 0.78 mg/kg for total Hg and 0.65 mg/kg for MeHg, respectively. (Li P et al., 2008c). Urinary Hg levels ranged from 22.6 to 4577 mg/kg creatinine for the exposed workers and from 1.0 to 17.4 mg/kg creatinine for the unexposed subjects (Sakamoto et al., 2007; Li P et al., 2008c). Total Hg concentrations in urine and hair showed a significant correlation in the exposed group (r=0.62), indicating an adhesion of Hg vapor to hair (Sakamoto et al., 2007). Total tremor intensity and frequency-specific tremor intensities at 1-6 and 10-14 Hz of the exposed workers were significantly higher than the unexposed subjects (Iwata et al., 2007). Studies clearly demonstrated that symptoms included finger and eyelid tremor, gingivitis and typical dark-line on gums were observed in six workers (Li P et al., 2008). These indicated that physical impairments were occurred and the workers were heavily exposed to Hg vapor during the process of cinnabar roasting.

Feng et al. (2008) reported that concentrations of total Hg and MeHg in hair samples collected from residents from three villages in Wanshan Hg mining area ranged from 0.6 to 58.5 mg/kg and 0.2 to 5.6 mg/kg, respectively. However, hair Hg levels in samples from a control site were quite low, ranging from 0.32 to 1.7 mg/kg in total Hg and 0.26 to 1.1 mg/kg in MeHg, respectively. As mentioned above, MeHg tends to accumulate in rice, which is a staple food for the local residents, and MeHg-contaminated rice consumption could represent a social and economic problem. Recent experiments on rats' 20-day exposure to rice from Wanshan revealed an inducible lipid peroxidation in rat's brain, liver, and kidney tissue, exhibiting an increase of c-jun mRNA (Cheng et al., 2005, 2006). A study of 98 persons from Wanshan showed a significant correlation ($r=0.65$, $p<0.01$) between hair MeHg concentrations and daily MeHg intake through rice consumption (Feng et al., 2008). Official statistical data showed that for the rural populations in Guizhou, the amount of fish and rice consumed per person per year varied from 0.22 to 0.31 kg, and from 140 to 153 kg, respectively (Bureau, 2006). Hence, rice provides more caloric input than fish and other single food. This indicated that rice is an important MeHg exposure route for residents in Wanshan and the main human exposure to MeHg via food consumption is rice rather than fish. Generally, the inhabitants in Wanshan Hg mining area are exposed to Me-Hg to a certain level. However, they are not under a serious health risk. Hair MeHg concentrations of the inhabitants in Wanshan Hg mining area were much lower than the thresholds for onset of neurological symptoms in human body recommended both by WHO (1990) and National Research Council (2000). Nevertheless, some female participants may exceed the tolerable intake levels of MeHg for pregnant women established by US EPA (1997b). Thus, rice intake in Hg mining areas in Guizhou may pose a health-risk of MeHg exposure to local habitants.

7. Summary

Coal combustion and metals smelting (i.e. Hg and Zn smelting) were two key sources for Hg pollution in environments in Guizhou. High values of Hg deposition fluxes were found even in rural areas in the province. Residents in the vicinity of smelting areas could be exposed to high levels of Hg vapor through the inhalation due to high levels of Hg vapor in the ambient air. In Hg mining areas, rice consumption is a main exposure pathway of MeHg to the local populations. Though a number of studies are summarized in an effort to understand Hg pollution status in Guizhou, these studies showed an important knowledge gap concerning identification and quantification of Hg compounds, which are known to be dominant components of Hg chemistry (Ullrich et al., 2001). In addition, an accurate assessment of molecular-level speciation of Hg contained in environmental compartments, which is a main parameter governing Hg mobility, toxicity, and bioavailability (Brown et al., 1999), is necessary to determine for the remediation actions that should be taken. There is also an urgent need for the better understanding of the fate of Hg in the atmosphere, as well as in aquatic ecosystems. Moreover, long-term effects of consuming MeHg-contaminated rice should be scrutinized to assess the risk of human exposures.

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References:

Brown GE Jr, Foster AL, Ostergren JD. Mineral surfaces and bioavailability of heavy metals: a molecular-scale perspective. Proceedings of National Academy of Sciences of USA. 1999; 96:3388-3395.

Bureau, G.S. Guizhou Statistical Yearbook 2005;Guiyang, 2006.

Calasans C, Malm O. Elemental Hg contamination survey in a Chlor-alkali plant by the use of transplanted Spanish moss, *Tillandsia usneoides* (L.). Science of the Total Environment 1997; 208:165-177.

Carpi A. Mercury from combustion sources: a review of the chemical species emitted from their transport in the atmosphere. Water Air Soil Pollution 1997; 98:241-254.

Carpi A, Weinstein LH, Ditz DW. Bioaccumulation of mercury by *Sphagnum* moss near a municipal solid waste incinerator. Air Waste 1994; 44:669-672.

Cheng JP, Yuan T, Wang W, Jia J, Lin X, et al. Mercury pollution in two typical areas in Guizhou province, China and its neurotoxic effects in the brains of rats fed with local polluted rice. Environmental Geochemistry and Health 2006; 28:499-507.

Cheng JP, Wang WH, Qu LY, Jia JP, Zheng M, et al. Rice from mercury contaminated areas in Guizhou province induces c-jun expression in rat brain. Biomed Environ Sci 2005;18:96-102.

Choi SC, Bartha R. Environmental factors affecting mercury methylation in estuarine sediments. Bull Environ Contam Toxicol 1994;53:805-812.

Dai S, Zeng R, Sun Y. Enrichment of arsenic, antimony, mercury, and thallium in a Late Permian anthracite from Xingren, Guizhou, Southwest China. Int J Coal Geol 2006;66:217-226.

Ebinghaus R, Kock HH, Temme C, Einax JW, Lowe AG, et al. Antarctic springtime depletion of atmospheric mercury. Environ Sci Technol 2002a;36:1238-1244.

Ebinghaus R, Kock HH, Coggins AM, Spain TG, Jennings SG, et al. Long-tern measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. Atmos Enviorn 2002b;36:5267-5276.

Ebinghaus R, Hintelmann H, Wilken RD. Mercury-cycling in surface waters and in the atmosphere. Species analysis for the investigation of transformation and transport properties of mercury. Fresenius J Anal Chem 1994;350:21-9.

Ericksen JA, Gustin MS, Schorran DE, Johnson DW, Lindberg SE, et al. Accumulation of atmospheric mercury in forest foliage. Atmos Environ 2003;37:1613-1622.

Feng X, Li P, Qiu G, Wang S, Li G, Shang L, Meng B, Jiang H, Bai W, Li Z, Fu X. Methylmercury exposure through rice intake to inhabitants in Wanshan mercury mining area in Guizhou, China. Environmental Science and Technology, 2008, 42, 326–332

Feng X, Li G, Qiu G. A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous methods in Hezhang county, Guizhou, China: Part 2. Mercury contaminations to soil and crop. Sci Total Envrion 2006;368:47-55.

Feng X, Wang S, Qiu G, Hou Y, Tang S. Total gaseous mercury emissions from soil in Guiyang, Guizhou, China. J Geophys Res 2005;110:D14306, doi:10.1029/2004JD005643.

Feng X, Li G, Qiu G. A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous methods in Hezhang county, Guizhou, China-Part 1: mercury emission from zinc smelting and its influences on the surface waters. Atmos Environ 2004a;38:6223-6230.

Feng X, Yan H, Wang S, Qiu G, Tang S, et al. Seasonal variation of gaseous mercury exchange rate between air and water surface over Baihua reservoir, Guizhou, China. Atmos Environ 2004b;38:4721-4732.

Feng X, Shang L, Wang S, Tang S, Zheng W. Temporal variation of total gaseous mercury in the air of Guiyang, China. J Geophys Res 2004c;109:D03303, doi:10.1029/2003JD004159.

Feng X, Qiu G, Wang S, Shang L. Distribution and speciation of mercury in surface waters in mercury mining areas in Wanshan, Southwestern China. J Phys IV France 2003;107:455-458.

Feng X, Sommar J, Lindqvist O, Hong Y. Occurrence, emissions and deposition of mercury during coal combustion in the province Guizhou, China. Water Air Soil Pollut 2002;139:311-324.

Fernández JA, Aboal JR, Carballeira A. Use of native and transplanted mosses as complementary techniques for biomonitoring mercury around and industrial facility. Sci Total Environ 2000;256:151-161.

Gray JE, Hines ME, Higueras PL, Adatto I, Lasorsa BK. Mercury speciation and microbial transformations in mine wastes, stream sediments, and surface waters at the almadén mining district, Spain. Environ Sci Technol 2004;38:4285-4292.

Gray JE, Greaves IA, Bustos DM, Krabbenhoft DP. Mercury and methylmercury contents in mine-waste calcine, water, and sediment collected from the Palawan Quicksilver Mine, Philippines. Environ Geol 2003;43:298-307.

Gray JE, Crock JG, Lasorsa BK. Mercury methylation at mercury mines in the Humboldt River Basin, Nevada, USA. Geochem Explor Environ Anal 2002;2:143-149.

Grieb TM, Driscoll CT, Gloss SP, Schofield CL, Bowie GL, et al. Factors affecting mercury accumulation in fish in the Upper Michigan Peninsula. Environ Toxicol Chem 1990;9:919-930.

Guo Y, Feng X, Li Z, He T, Yan H. Distribution and wet deposition fluxes of total and methyl mercury in Wujiang River Bassin, Guizhou, China. Atmospheric Environment 2008;(in review).

Gustin MS, Lindberg S, Marsik F, Casimir A, Ebinghaus R, Edwards G, Hubble-Fitzgerald C, Kemp R, Kock H, Leonard T, London J, Majewski M, Montecinos C, Owens J, Pilote M, Poissant L, Rasmussen P, Schaedlich F, Schneeberger D, Schroeder W, Sommar J, Turner R, Vette A, Wallschlaeger D, Xiao Z, Zhang H. Nevada STORMS project: Measurement of mercury emissions from naturally enriched surfaces, J. Geophys. Res., 1999; 104: 21,831– 21,844.

He T, Feng X, Guo Y, Qiu G, Li Z, et al. The impact of eutrophication on the biogeochemical cycling of mercury species in a reservoir: A case study from Hongfeng Reservoir, Guizhou, China. Environ Pollut 2008;(in press)

He T, Feng X, Li Z, Qiu G, Bai W, et al. Buildup of methyl mercury in a seasonal anoxic reservoir and impact on downstream. J Lake Sci 2006;18:565-571. (in Chinese)

Hines ME, Bailey EA, Gray JE, Rytuba JJ. Transformations of mercury in soils near mercury contaminated sites in the USA. 5th International Conference on Mercury as a Global Pollutant, Proceedings, Vol. 1, CETEM, Rio de Janeiro, 1999;471.

Horvat M, Nolde N, Fajon V, Jereb V, Logar M, et al. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. Sci Total Environ 2003;304:231-256.

Hou Y, Feng X, Qiu G, Yan H. Distribution of different species of mercury in Baihua Lake, Guizhou Provinc. J Lake Sc 2004;16:125-132. (in Chinese)

Iwata T, Sakamoto M, Feng X, Yoshida M, Liu XJ, et al. Effects of mercury vapor exposure on neuromotor function in Chinese miners and smelters. Int Arch Occup Environ Health 2007;80:381-387.

Jiang H, Feng X, Dai Q, Wang Y. Preliminary study on speciation and distribution of mercury in Wujiang River. Environ Chem 2004;23:556-561 (in Chinese).

Jiang G-B, Shi J-B., Feng X. Mercury pollution in China- an overview of the past and current sources of the toxic metal. Environ Sci Technol, 2006, 40: 3672-3678.

Kim CS, Rytuba JJ, Brown Jr GE. Geological and anthropogenic factors influencing mercury speciation in mine wastes: an EXAFS spectroscopy study. Appl Geochem 2004;19:379-393.

Kim CS, Brown Jr GE, Rytuba JJ. Characterization and speciation of mercury-bearing mine waste using x-ray adsorption spectroscopy. Sci Total Environ 2000;261:157-168.

Lamborg CH, Fitzgerald WF, Torgersen T. A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients. Geochim Cosmoschim Acta 2002;66:1105-1118.

Li G, Feng X, Qiu G, et al. Environmental mercury contamination of an artisanal zinc smelting area in Weining county, Guizhou, China. Environmental Pollution, 2008, doi:10.1016/j.envpol.2007.11.012..

Li G, Feng X, Qiu G. Preliminary study on mercury emission from artisanal zinc smelter using indigenous method in Hezhang county of Guizhou province. Acta Scientiae Circumstantiae 2005;25(6):836-839 (In Chinese with English abstract).

Li, P., Feng, X., Qiu, G., Wang, S., 2006. Mercury emission from the indigenous method of mercury smelting in Wuchuan mercury mining areas, Guizhou Province. Environ. Sci. 27, 837-840(In Chinese with English abstract).

Li P, Feng X, Shang L, Qiu G, Meng B, et al. A preliminary study on mercury pollution from artisanal mercury smelting activities in Tongren, Guizhou, China: Part 1. Mercury contaminations to the local environment. 2008a; (submitted to Applied Geochemistry)

Li P, Feng X, Qiu G. The preliminary study of mercury pollution in Wuchuan Hg mining area, Guizhou Province. Environ Chem 2008b;(in press)

Li P, Feng X, Qiu G, Li Z, Fu X, et al. Mercury exposures and symptoms in smelting workers of artisanal mercury mines in Wuchuan, Guizhou, China. Environmental Research, 2007, doi:10.1016/j.envres.2007.08.003.

Li P, Feng X, Qiu G, Wang S. Mercury emission from the indigenous method of mercury smelting in Wuchuan mercury mining areas, Guizhou Province. Environ Sci 2006;27:837-840. (in Chinese)

Lindqvist O, Johansson K, Aastrup M, Anderson A, Bringmark L, Hovsenius G, et al. Mercury in the Swedish environment-recent research on cause, consequences and corrective methods. Water Air Soil Pollut 1991;55:1-261.

Lindqvist O. Fluxes of mercury in the Swedish environment: contributions from waste incineration. Waste Manage Res 1986;4(1):35-44.

Liu JY. The influence of environmental pollution on eco-agriculture systems in Guizhou province. Guizhou Environ Prot Sci Technol 1998;4:40-44 (in Chinese).

Yasuda Y, Matsuyama A, Yasutake A, Yamaguchi M, Aramaki R, Xiaojie L, Pin J, Yumin A, Li L, Mei L, Wei C, Liya Q, Mercury distribution in farmlands downstream from an acetaldehyde producing chemical company in Qingzhen City, Guizhou, People's Republic of China. Bulletin of Environmental Contamination and Toxicology 2004; 72(3): 445-451.

Mason RP, Fitzgerald WF, Morel MM. the biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochimica Cosmochimica Acta 1994;58:3191-3198.

Nadim F, Perkins C, Liu S, Carley RJ, Hoag GE. Long-term investigation of atmospheric contamination in Connecticut. Chemosphere 2001;45:1033-1043.

NADP. National atmospheric deposition program 2006 annual summary. ISWS Data/Case Study 2007-01 and NADP Data Report 2007-01, 2007;pp 1-16. (http://nadp.sws.uiuc.edu/lib/data/2006as.pdf)

National Research Council. Toxicological effects of methylmercury; National Academy Press, Washington, DC, 2000.

Nriagu JO, Pacyna JM. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 1988;333:134-139.

Pai P, Niemi D, Powers B. A North American inventory of anthropogenic mercury emissions. Fuel Processing Technology 2000;65-66:101-105.

Poissant L, Pilote M, Beauvais C, Constant P, Zhang H. A year of continuous measurements of three atmospheric mercury species (GEM, RGM and Hgp) in southern Quebec, Canada. Atmos Environ 2005;39:1275-1287.

Qiu G, Feng X, Li P, Wang S, Li G, et al. Methylmercury accumulation in rice (Oryza sativa L) grown at abandoned mercury mines in Guizhou, China. J Agric Food Chem 2008;(in press).

Qiu G, Feng X, Wang S, Shang L. Environmental contamination of mercury from Hg-mining areas in Wuchuan northeastern Guizhou, China. Environ Pollut 2006a;142:549-558.

Qiu G, Feng X, Wang S, Xiao T. Mercury contaminations from historic mining to water, soil and vegetation in Lanmuchang, Guizhou, southwestern China. Sci Total Environ 2006b;368:56-68.

Qiu G, Feng X, Wang S, Shang L. Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China. Appl Geochem 2005;20:627-638.

Qu L. A study on the prevention and remedy of Hg-contamination in Guizhou, Guizhou Press, Guiyang, 2004.

Sakamoto M, Feng X, Li P, Qiu G, Jiang H, et al. High Exposure of Chinese mercury mine workers to elemental mercury vapor and increased methylmercury levels in their hair. Enviornmental Health and Preventive Medicine 2007;12:66-70.

Schroeder WH, Steffen A, Lawson G, Strachan W. Mercury measurements at Alert, in Synopsis of Research Conducted Under the 2000/2001 Northern Contaminants Program, edited by Kalhok S, pp. 130-135, Indian and North. Affairs Can., Ottawa, Ontario.

Schroeder WH, Jackson RA. An instrumental analytical technique for speciation of atmospheric mercury. Intern J Environ Anal Chem 1985;22:1-18.

Shen Z, Wu Y, Xiao H, Bai C, Huang M. Some basic features of cloudwater chemistry in the southwest area of China. Scientia Atmospherica Sinica 1993;17:87-96. (in Chinese).

Streets DG, Hao J, Wu Y, Jiang J, Chan M, et al. Anthropogenic mercury emissions in China. Atmos Environ 2005;39:7789-7806.

Summers AO. Organization, expression, and evolution of genes for mercury resistance. Annual Reviews Microbiology 1986;40:607-634.

Tan H, He J, Liang L, Lazoff S, Sommer J, et al. Atmospheric mercury deposition in Guizhou, China. Sci Total Environ 2000;259:223-230.

Tan H, He J, He T. Dry and wet deposition of elemental mercury by moss bag near a mercury mine. Environ Sci 1997;18:71-72. (in Chinese)

Tang S, Feng X, Qiu J, Yin G, Yang Z. Mercury speciation and emissions from coal combustion in Guiyang, southwest China. Environ Res 2007;105:175-182.

Ullrich SM, Tanton TW, Abdrashitova SA. Mercury in the aquatic environment: a review of factors affecting methylation. Crit Rev Environ Sci Technol 2001;31:241-293.

US EPA. EPA 452/R-97-005; U.S. EPA Office of Air Quality Planning and Standards and Office of Research and Development: Washington, DC, 1997a.

U.S. EPA. Mercury study report to the congress; EPA 452/R-97-0003; U.S. Environmental Protection Agency: Washington, DC, 1997b.

Wang Q, Shen W, Ma Z. Estimation of mercury emission from coal combustion in China. Environ Sci Technol 2000;34:2711-2713.

Wang S, Feng X, Qiu G, Fu X, Wei Z. Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou, China. Atmos Environ 2007a;41:5584-5594.

Wang S, Feng X, Qiu G, Shang L, Li P, et al. Mercury concentrations and air/soil fluxes in Wuchuan mercury mining district, Guizhou province, China. Atmos Environ 2007b;41:5984-5993.

Wang S, Feng X, Qiu G, Wei Z, Xiao T. Mercury emission to atmosphere from Lanmuchang Hg-Tl mining area, Southwestern Guizhou, China. Atmos Environ 2005;39:7459-7473.

WHO. Methylmercury, Environmental Health Criteria 101, Geneva, 1990.

Wu Y, Wang S, Streets DG, Hao J, Chan M, et al. Trends in Anthropogenic mercury emissions in China from 1995 to 2003. Environ Sci Technol 2006;40:5312-5318.

Xiao Z, Sommar J, Lindqvist O. Atmospheric mercury deposition on Fanjing Mountain Nature Reserve, Guizhou, China. Chemosphere 1998;36:2191-2200.

Yan H, Feng X, Shang L, Dai Q, Wang S, et al. The variation of mercury in sediment profiles from a historically mercury-contaminated reservoir, Guizhou province, China. Science of the Total Environment 2008;(in review).

Yan H, Feng X, Jiang H, Qiu G, Li G, et al. The concentrations and distribution of mercury in aquatic ecosystem of Baihua Reservoir. Chinese J Geochem 2005;24:377-381.

Zhang G, Liu CQ, Wu P, Yang Y. The geochemical characteristics of mine-waste calcines and runoff from the Wanshan mercury mine, Guizhou, China. Appl Geochem 2004;19:1735-1744.

Zhang J, Ren D, Zhu Y, Chou C, Zeng R, et al. Mineral matter and potentially hazardous trace elements in coals from Qianxin Fault Depression Area in southwestern Guizhou, China. International Journal of Coal Geology 2004;57:49-61.

Zhang L, Wong MH. Environmental mercury contamination in China: Source and impacts. Environment International 2007; 33:108-121.

Table 1: Total Hg and MeHg concentrations in plant samples collected from Guizhou Hg mining areas

Sample types	**THg (mg/kg)**			**MeHg (µg/kg)**			**Sources**
	Min	Max	Mean	Min	Max	Mean	
Moss	0.98	95	16	0.19	20	4.0	Qiu et al., 2005
	2.1	182	39				Li P et al., 2008b
Rice	0.0091	0.55	0.159	4.2	18	11.2	Qiu et al., 2006a, 2008
	0.019	1.12	0.228	1.6	174	22.8	
	0.011	0.57	0.149	8.0	144	38.8	Horvat et al., 2003
	0.010	0.19		3.3	27.6		Feng et al., 2008
			0.133				Cheng et al., 2006
Corn			0.065				
	0.089	0.57	0.20	0.28	1.3	0.71	Qiu et al., 2006a,b
Tobacco	0.20	0.76	0.48	0.83	1.9	1.4	
Cole	0.47	0.69	0.57	0.57	0.83	0.71	
Cabbage	0.12	18	2.5	0.65	5.5	3.2	
Potato			0.018				Cheng et al., 2006
Capsicum			0.18				

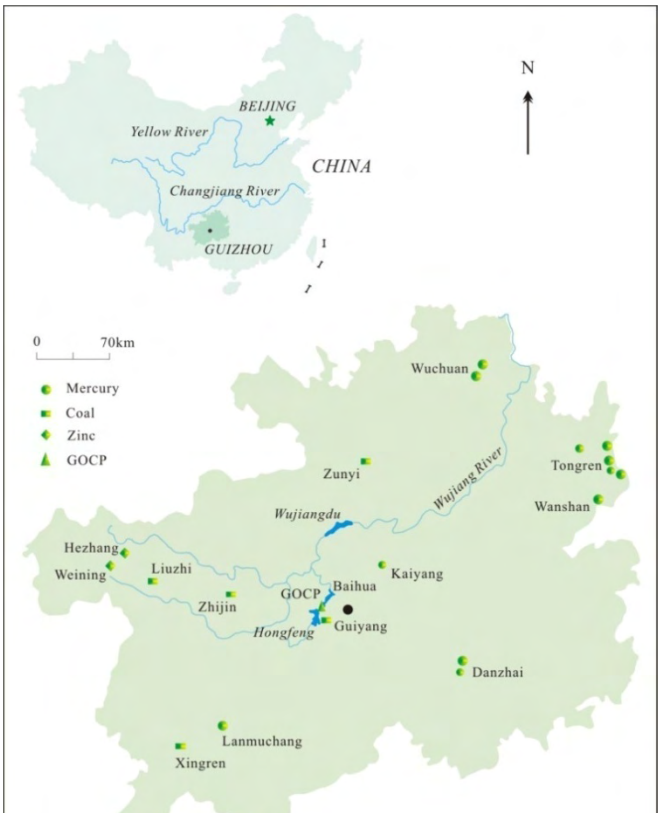


Figure 1. Map of Guizhou and typical anthropogenic Hg emission sources

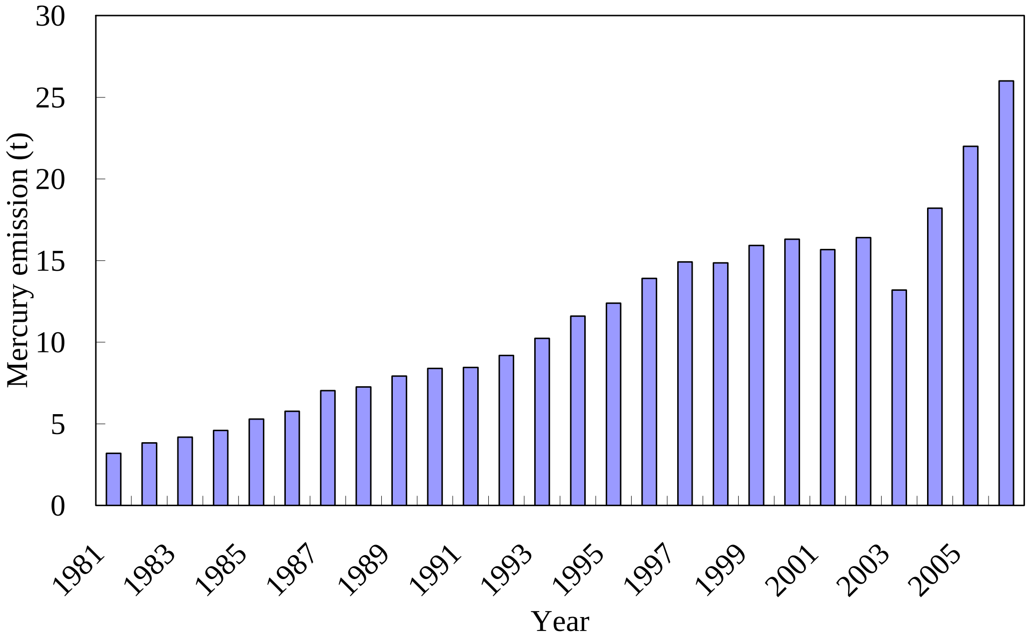


Figure 2. Mercury emission from coal combustion in Guizhou from 1986 to 2006 (Data from Tang et al., 2007)

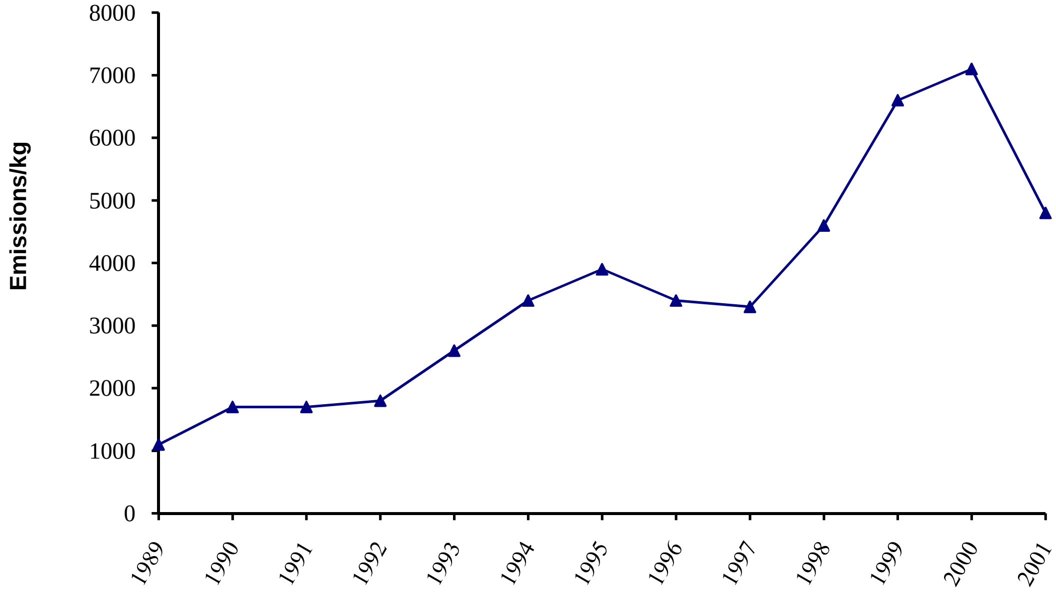


Figure 3. Mercury emission from the primitive Zn smelting of 1989-2001 in Hezhang County (Data from Feng et al., 2002)

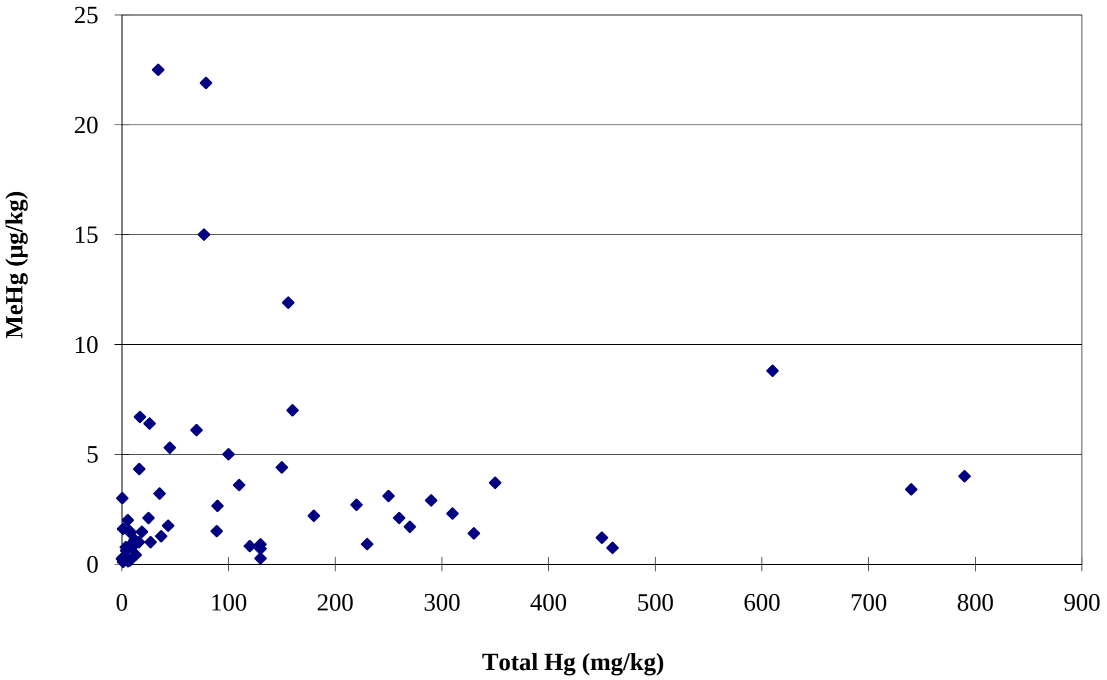


Figure 4. The relationship between total Hg and MeHg in surface soils from Guizhou Hg mines (Data from Horvat et al., 2003; Qiu et al., 2005, 2006b).

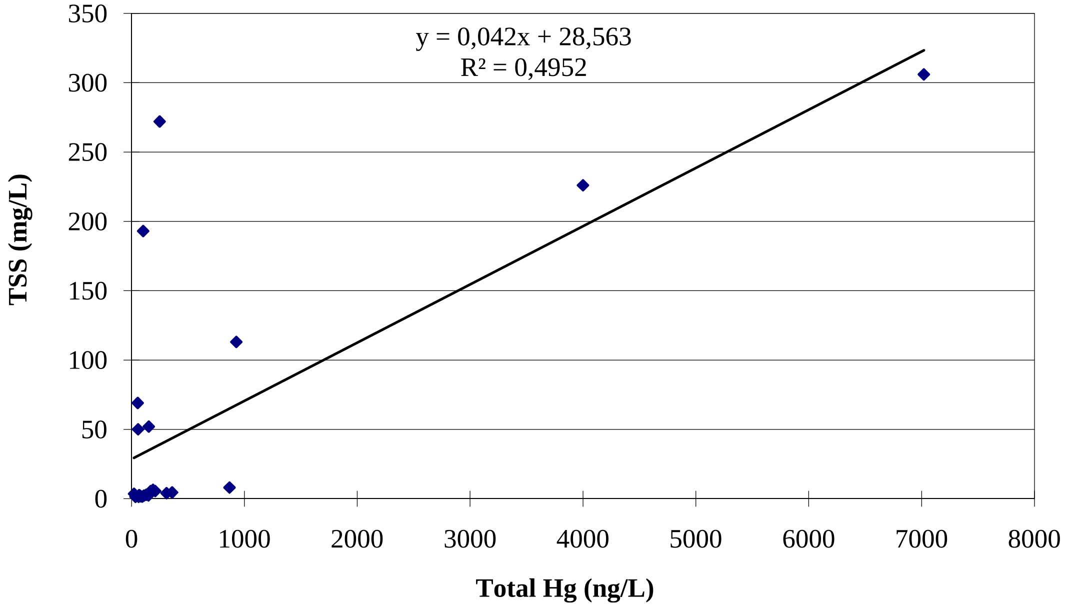


Figure 5. The relationship between total Hg and suspended substances in surface waters from Guizhou Hg mines (Data from Qiu et al., 2006a,b)

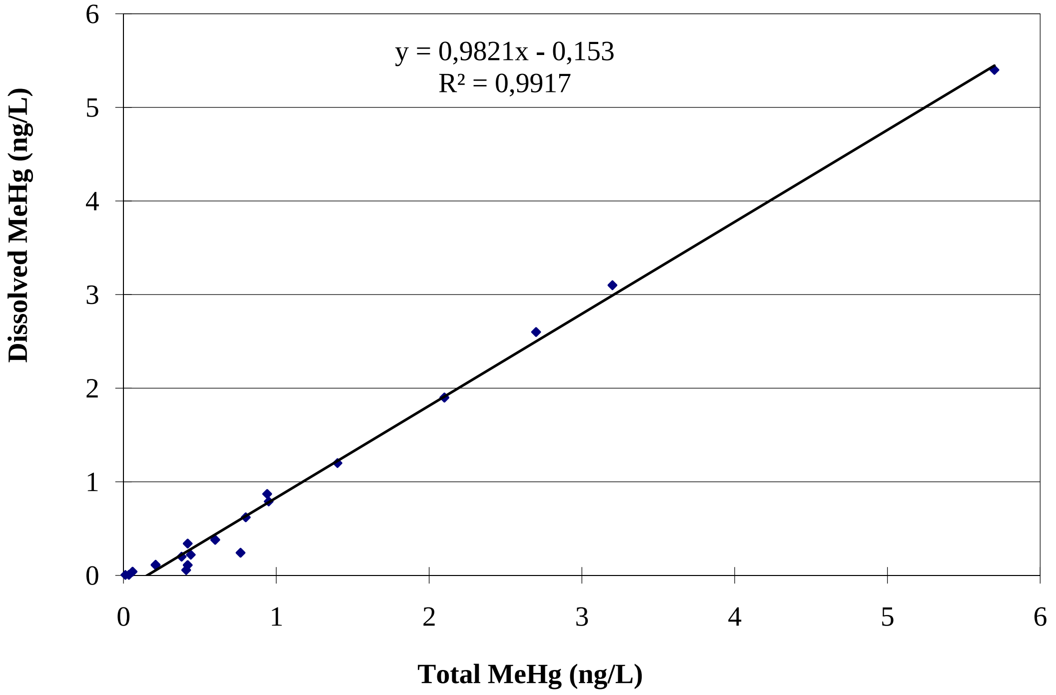


Figure 6. The relationship between total MeHg and dissolved MeHg in surface waters from Guizhou Hg mines (Data from Qiu et al., 2006a).

Risk Assessment and Risk Management of Harmful Substances for the soil-human health pathway in the Framework of the German Federal Soil Protection Ordinance — Mercury as an Example

Andreas Zeddel

Landesamt für Natur und Umwelt des Landes SH, Germany

Introduction

The German Federal soil protection ordinance comprises Trigger Values for the exposure-pathways soil-to-human, soil-to-groundwater and soil-to-edible plant to identify “harmful changes in soil functions”. Trigger Values are applied to risk assessment in the exploratory investigation phase in order to diagnose the needs for further investigations. Because of the hazard-based nature of these values – especially for the soil-to-human-pathway – they can release remediation measures in certain cases. The derivation of these values is well documented and the chosen exposure scenarios are as realistic as possible concerning the ‘worst case’. Using mercury as an example the derivation of trigger values for the soil-to-human pathway as well as the underlying conventions will be presented.

Principles of risk assessment

According to Article 1 of the German Federal Soil Protection Act (BBodSchG, see (1)), the purpose of the Act is to protect or restore the functions of the soil on a permanent sustainable basis. These actions shall include prevention of harmful soil changes (to the soil), rehabilitation of the soil, of contaminated sites and of waters contaminated by such sites.

Harmful soil changes (to the soil) within the meaning of this Act are harmful impacts on soil functions that are able to bring about hazards, considerable disadvantages or considerable nuisances for individuals or the general public. To identify these hazards for soil functions, the German Federal soil protection ordinance (BBodSchV, see (2)) comprises Trigger Values or Action Values for the exposure-pathways soil-to-human, soil-to-groundwater and soil-to-edible plant.

Trigger values were used especially for assessment of suspect (contaminated) sites in the exploratory investigation phase. If these values are exceeded, more investigations (detailed investigation phase) with respect to the individual case in question are required, taking the relevant soil use into account, to determine whether a harmful soil change or site contamination exists.

If Action Values for impacts or pollution are exceeded (in the exploratory or detailed investigation phase), it normally gives signal to the presence of a harmful soil change or site contamination, taking the relevant soil use into account - normally measures are required.

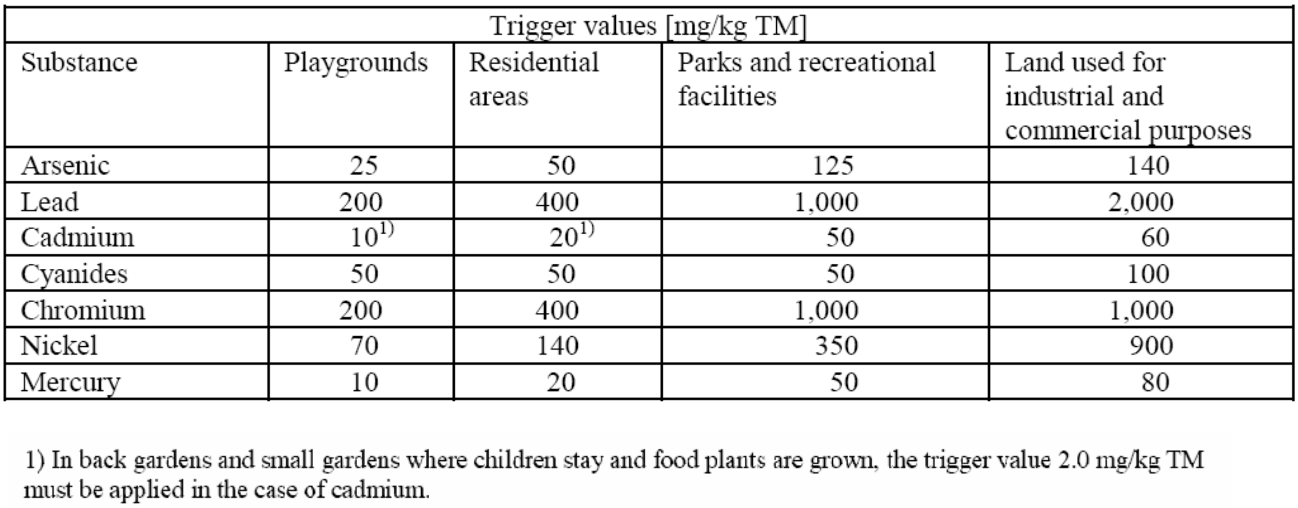
It has to be mentioned, that Trigger Values as well as Action Values are of ‘hazard-based nature’. That means, that all circumstances account for a sufficient possibility of a damage – not only a slight possibility. In the exploratory investigation phase these circumstances are not well known, therefore realistically worst-case assumptions were taken.

It is the aim of an exploratory investigation – done by the competent authority – to identify possible hazards and to order detailed investigations (or other measures) by the party who caused a (possible) harmful soil change. Therefore decision making has to be provable to a court in case of a clash between the competent authority and the polluter.

If the detailed investigation confirms all assumed circumstances in the individual case, contaminant concentrations in soil above the Trigger Values can release remediation measures.

Soil-human health pathway - using Mercury as an Example

Trigger levels in the case of soil-to-human-pathway are related to the use of the respective site. The decision whether the soil contamination implies a hazard (or does not) has to take into account, how the site is actually used and what future use can reasonably be expected. The Trigger Values of Arsenic and heavy metals for four usages are shown in figure 1:

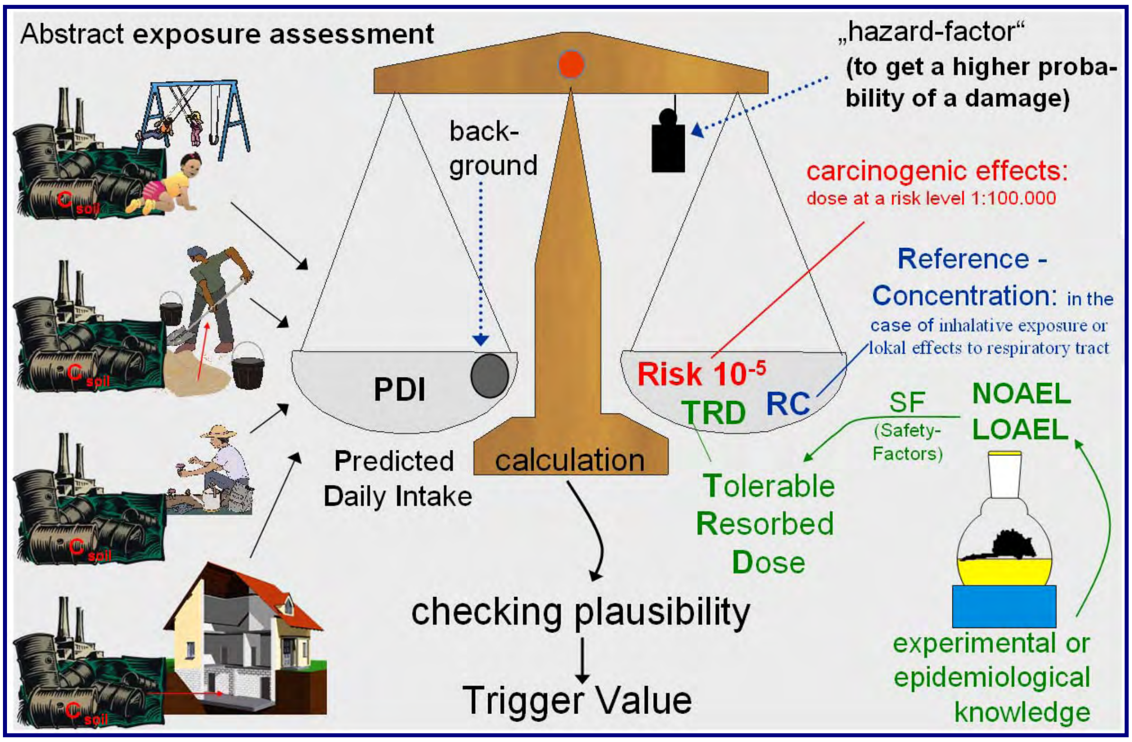


Trigger values [mg/kg TM]				
Substance	Playgrounds	Residential areas	Parks and recreational facilities	Land used for industrial and commercial purposes
Arsenic	25	50	125	140
Lead	200	400	1,000	2,000
Cadmium	10[1)]	20[1)]	50	60
Cyanides	50	50	50	100
Chromium	200	400	1,000	1,000
Nickel	70	140	350	900
Mercury	10	20	50	80

1) In back gardens and small gardens where children stay and food plants are grown, the trigger value 2.0 mg/kg TM must be applied in the case of cadmium.

The derivation of these values was describes in detail in 1999: “Promulgation of Methods and Standards for Derivation of Trigger Values and Action Values according to the Federal Ordinance on Soil Protection and Contaminated Sites” (BAnz. 18 June 1999).

The principles and the proceeding are shown in figure 2 with the ‘calculating-scales’:



The proceeding and the concretisation for mercury presented here were published in 1999 [1].

Assessment standards for human toxicology

The starting point in derivation of trigger-values for the soil-to-human pathway is the tolerable resorbed doses (TRD) achieved from experimental or epidemiological data.

From short time and chronic exposure LOAEL (lowest observed adverse effect level) or NOAEL (no observed adverse effect level) are derivated for inhalativ, oral and dermal intake.

Wherever possible, derivation is based on reliable human data that have been reported in detail. Where such data are not available, data from animal experiments are used and extrapolated, using certain factors (SF), to sensitive persons (groups of persons, figure 3).

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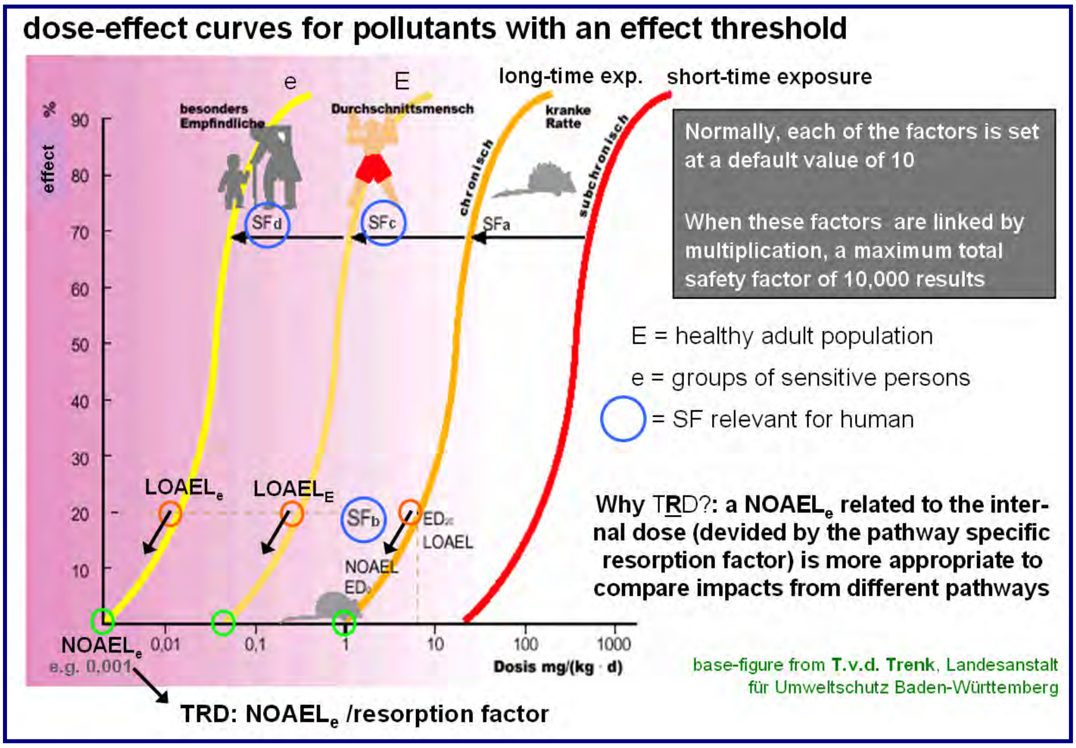
1) G. Bachmann et al., 1999: „Berechnung von Prüfwerten zur Bewertung von Altlasten“, special edition of the compendium „Bodenschutz“, Erich Schmidt Verlag, Berlin; see: http://esv.info/id/350305825/katalog.html



dose-effect curves for pollutants with an effect threshold

Normally, each of the factors is set at a default value of 10

When these factors are linked by multiplication, a maximum total safety factor of 10,000 results

E = healthy adult population

e = groups of sensitive persons

○ = SF relevant for human

Why TRD?: a NOAEL$_e$ related to the internal dose (devided by the pathway specific resorption factor) is more appropriate to compare impacts from different pathways

base-figure from **T.v.d. Trenk**, Landesanstalt für Umweltschutz Baden-Württemberg

In general, safety factors should be replaced with better assessments, whenever the relevant information for this is available – this was done in the case of mercury as seen later.

Mercury as an Example:

The crazy ‚Mad Hatter' of Lewis Carroll's „Alice in Wonderland" (1865) is becoming widely associated with the effects of Mercury on behaviour as well as physiology. Mercury was used to process the felt hats used in England around Lewis' time. Erratic, flamboyant behaviour was one of the most evident alterations caused by mercury. Others included excessive drooling, mood swings, various debilities. The phrase 'mad as a hatter' had been in common use already in 1837! Hatters had used mercury nitrate ($Hg(NO_3)_2$) for washing animal furs (3).

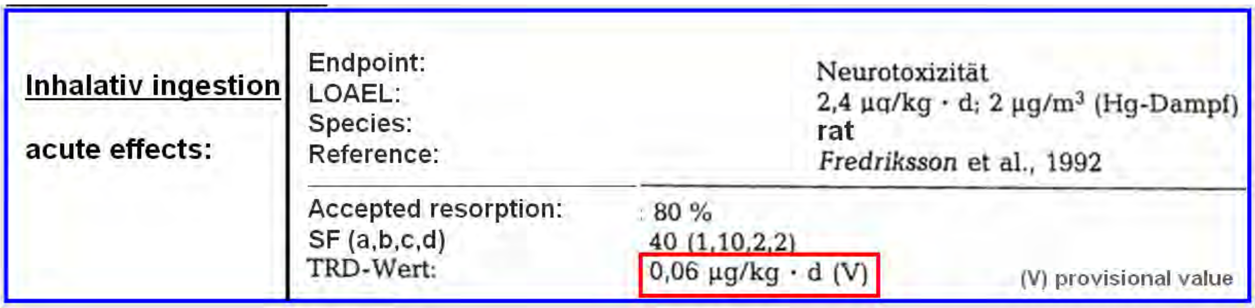
Picture and left text was taken from (3)

Due to different toxicities, inorganic (especially $HgCl_2$) and organic (especially Methyl-Hg) mercury-species are discriminated.

The severity of mercury's toxic effects depends on the form and concentration of mercury and the route of exposure. Exposure to elemental mercury can result in effects on the nervous system, including tremor, memory loss and headaches. Other symptoms include bronchitis, weight loss, fatigue, gastro-intestinal problems, gingivitis, excitability, thyroid enlargement, unstable pulse, and toxicity to the kidneys.

Exposure to inorganic mercury can affect the kidneys, causing immune-mediated kidney toxicity. Effects may also include tremors, loss of coordination, slower physical and mental responses, gastric pain, vomiting, bloody diarrhea and gingivitis (4).

The following calculations for the TRD-value for inorganic mercury – distinguished in inhalativ and oral intake as well as acute and chronic effects – were done:

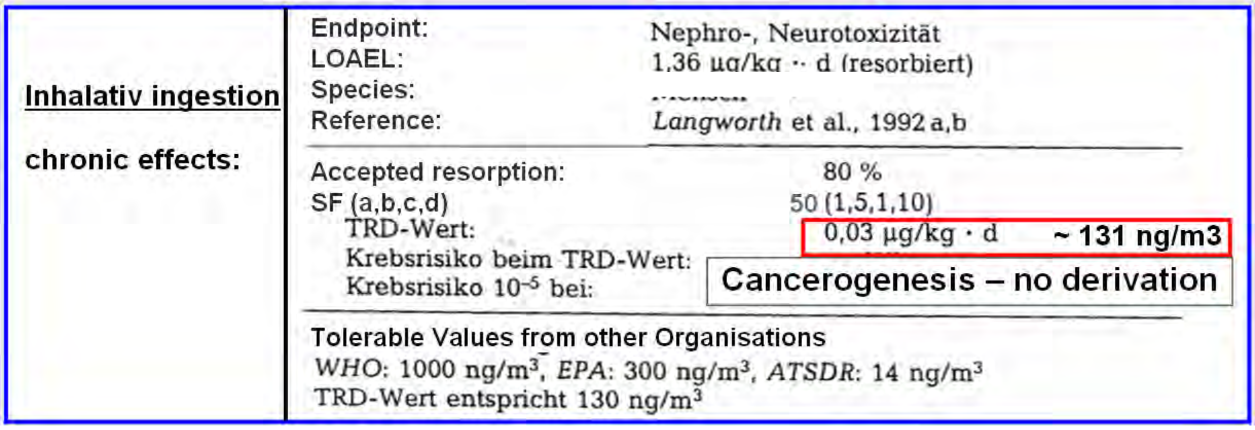


Inhalativ ingestion

acute effects:

Endpoint:	Neurotoxizität
LOAEL:	2,4 µg/kg · d; 2 µg/m³ (Hg-Dampf)
Species:	rat
Reference:	*Fredriksson* et al., 1992
Accepted resorption:	80 %
SF (a,b,c,d)	40 (1,10,2,2)
TRD-Wert:	0,06 µg/kg · d (V)

(V) provisional value



Inhalativ ingestion

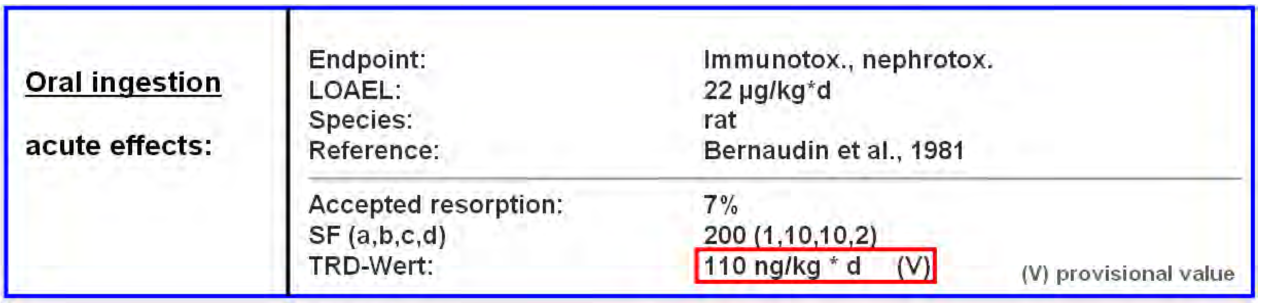
chronic effects:

Endpoint:	Nephro-, Neurotoxizität
LOAEL:	1,36 µg/kg ·· d (resorbiert)
Species:	[illegible]
Reference:	*Langworth* et al., 1992 a,b
Accepted resorption:	80 %
SF (a,b,c,d)	50 (1,5,1,10)
TRD-Wert:	0,03 µg/kg · d ~ 131 ng/m3
Krebsrisiko beim TRD-Wert:	Cancerogenesis – no derivation
Krebsrisiko 10^{-5} bei:	

Tolerable Values from other Organisations

WHO: 1000 ng/m³, *EPA*: 300 ng/m³, *ATSDR*: 14 ng/m³

TRD-Wert entspricht 130 ng/m³

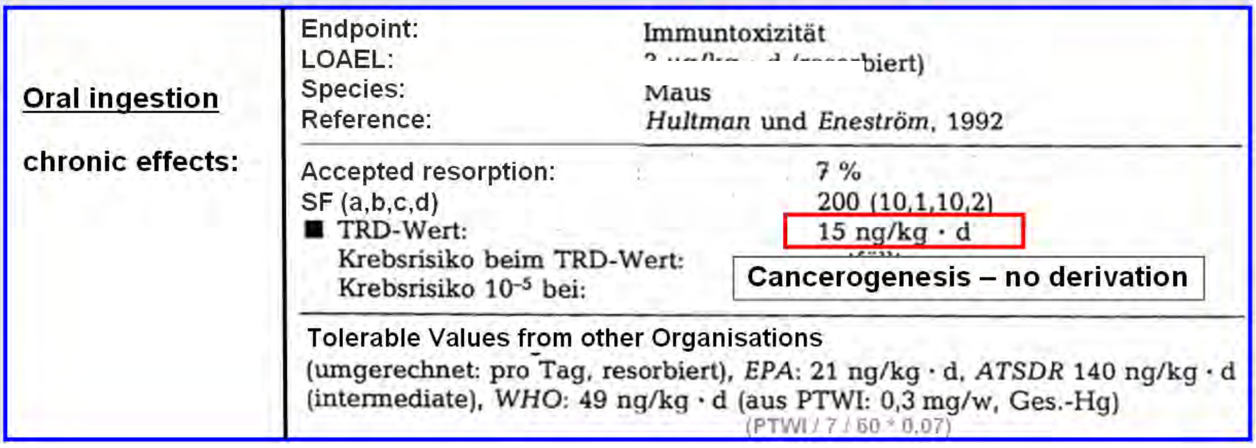


Oral ingestion

acute effects:

Endpoint:	Immunotox., nephrotox.
LOAEL:	22 µg/kg*d
Species:	rat
Reference:	Bernaudin et al., 1981
Accepted resorption:	7%
SF (a,b,c,d)	200 (1,10,10,2)
TRD-Wert:	110 ng/kg * d (V)

(V) provisional value



Oral ingestion

chronic effects:

Endpoint:	Immuntoxizität
LOAEL:	[illegible]biert)
Species:	Maus
Reference:	*Hultman* und *Eneström*, 1992
Accepted resorption:	7 %
SF (a,b,c,d)	200 (10,1,10,2)
■ TRD-Wert:	15 ng/kg · d
Krebsrisiko beim TRD-Wert:	Cancerogenesis – no derivation
Krebsrisiko 10^{-5} bei:	

Tolerable Values from other Organisations

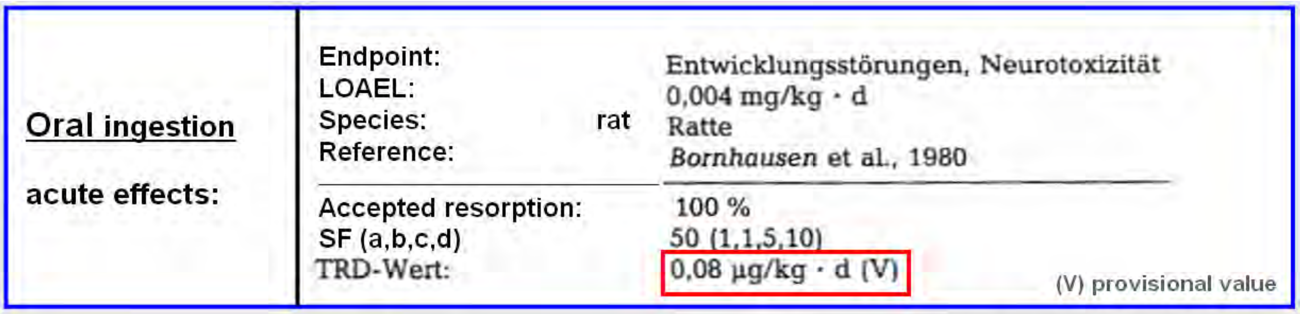
(umgerechnet: pro Tag, resorbiert), *EPA*: 21 ng/kg · d, *ATSDR* 140 ng/kg · d (intermediate), *WHO*: 49 ng/kg · d (aus PTWI: 0,3 mg/w, Ges.-Hg)

(PTWI / 7 / 60 * 0,07)

Regarding **Methyl Mercury** only oral ingestion is practical relevant.

The Symptoms of methyl mercury toxicity, also known as **Minamata disease**,
- the poisoning caused an outbreak of nervous disorders and deaths from the 1950’s to the 1970’s
- range from tingling of the skin, numbness, lack of muscle coordination, tremor, tunnel vision, loss of hearing, slurred speech, skin rashes, abnormal behaviour, intellectual impairment, to cerebral palsy, coma and death, depending on the level of exposure.

Teratogenic effects are the most sensitive effects on humans: A disastrous epidemic of methyl mercury poisoning occurred in rural Iraq early in 1972, due to the ingestion of home-made bread prepared from wheat treated with a methyl mercury fungicide. About 6000 cases of mercury poisoning were diagnosed. Over 500 cases were fatal. A dose-response relationship was determined, indicating that exposures in the range of 10 to 20 µg/g in the maternal hair might adversely affect the foetus (5 % risk). The corresponding body-dose per day was 0,7-1,4 µg/(kg *d) (60 kg weight; µg/(kg *d) was also written as µg/kg *d):



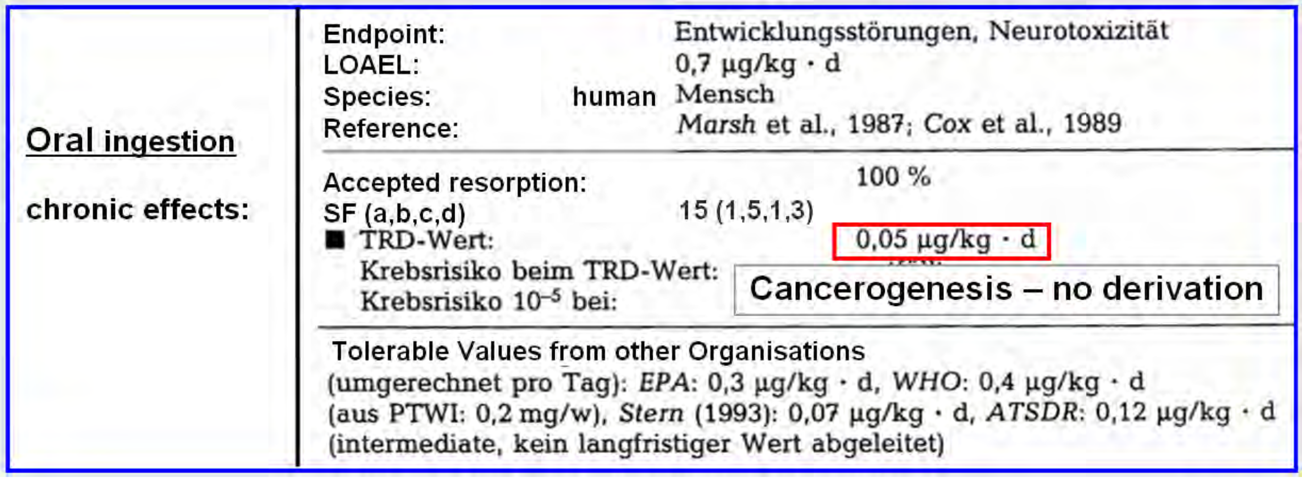
Oral ingestion

acute effects:

Endpoint: Entwicklungsstörungen, Neurotoxizität
LOAEL: 0,004 mg/kg · d
Species: rat Ratte
Reference: *Bornhausen* et al., 1980

Accepted resorption: 100 %
SF (a,b,c,d) 50 (1,1,5,10)
TRD-Wert: 0,08 µg/kg · d (V)

(V) provisional value



Oral ingestion

chronic effects:

Endpoint: Entwicklungsstörungen, Neurotoxizität
LOAEL: 0,7 µg/kg · d
Species: human Mensch
Reference: *Marsh* et al., 1987; *Cox* et al., 1989

Accepted resorption: 100 %
SF (a,b,c,d) 15 (1,5,1,3)
■ TRD-Wert: 0,05 µg/kg · d
Krebsrisiko beim TRD-Wert:
Krebsrisiko 10^{-5} bei:
Cancerogenesis – no derivation

Tolerable Values from other Organisations
(umgerechnet pro Tag): *EPA*: 0,3 µg/kg · d, *WHO*: 0,4 µg/kg · d (aus PTWI: 0,2 mg/w), *Stern* (1993): 0,07 µg/kg · d, *ATSDR*: 0,12 µg/kg · d (intermediate, kein langfristiger Wert abgeleitet)

In comparision: the WHO has derivated a TRD of 0,4 µg/kg*d in 1972; WHO (JECFA) 2004 lowered this value to 0,2 µg/kg*d (from PTWI 0,096 mg/w). The values from other organisations are in the range of the hazards-oriented dose (‘GD’) – see the following chapter!

Hazard factor

The hazards concept within the meaning of the Federal Soil Protection Act is only correlated with the sufficient probability of an adverse effect and not with the certain occurrence of the hazard. The hazards-oriented dose (‘GD’) lies between the NOAEL_e and the LOAEL_E (see figure 3). For sensitive individuals, the hazards orientation would be set between "unlikely" (NOAEL_e) and "very likely" (LOAEL_E), and sometimes at a level of "sufficiently likely". To determine **the hazards-oriented dose**, an interpolation must be carried out that begins with the NOAEL_e or TRD value and leads to a result that is considerably smaller than the LOAEL_E and that, if possible, **corresponds to the presumed LOAEL_e**.

A meaningful and plausible result for a hazards-oriented dose is obtained by multiplying the TRD value with the appropriate geometric mean of the human-relevant safety factors (SF) that have been used to extrapolate the TRD value.

Mercury as an Example:

In this manner the TRD-value - oral - for organic mercury of **50 ng/(kg*d)** was derived from a LOAEL of 700 ng/(kg*d). A safety-factor for the extrapolation of a NOAEL from the LOAEL (SF_b=5) and a safety-factor for especially sensitive persons (SF_d=3) are chosen in this case. The hazard-factor was achieved by building a geometrical mean of these safety-factors: SQR(5*3)=3,9. The resulting hazard-based body dose is therefore **195 ng/(kg*d)**.

Comparing all calculations and taking into account the different resorption-factors of each mercury species it can be seen, that the chronic oral intake of methyl mercury was the most sensitive effect caused by all mercury species.

Hg species	**effect**	**TRD [ng/(kg*d)]**	**SF (SF a,b,c,d)**	**Hazard factor**	**GD [ng/(kg*d)]**	**Resorption [%]**	**hazards-oriented-received dose [ng/(kg*d)]**
Inorganic Inhalative	**acut**	**60**	**40 (1,10,2,2)**	**6.3**	**1460**	**80 %**	**1825**
	chronic	**30**	**50 (1,5,1,10)**	**7.1**	**210**	**80 %**	**260**
Inorganic oral	**acut**	**110**	**200 (1,10,10,2)**	**14.1**	**1550**	**7 %**	**22140**
	chronic	**15**	**200 (10,1,10,2)**	**4.5**	**70**	**7 %**	**1000**
Organic oral	**acut**	**80**	**50 (1,1,5,10)**	**7.1**	**570**	**100 %**	**570**
	chronic	**50**	**15 (1,5,1,3)**	**3.9**	**200**	**100 %**	**200**

Exposure assessment

Conventions about the exposure of men, especially children, to contaminated soil are the second stand for calculation trigger-values. E.g. a soil incorporation rate of 33 mg soil/ kg*d for children on playgrounds was derived from the following assumptions:

Daily Intake Rates:

- children's playgrounds: 10 kg body weight
  0.5 g/d soil ingestion
  0.625 m^3/h respiration
  frequency: 240 d/year (2 h/d)
  ➔ daily ingestion rate : 33 mg/ kg BW * d
  ➔ daily inhalation rate: 0.082 mg/ kg BW * d
- residential areas: (factor 1/2)
  ➔ daily ingestion rate : 16.5 mg/ kg * d
  ➔ daily inhalation rate: 0.041 mg/ kg BW * d
- parks and recreation: (factor 1/5)
  ➔ daily ingestion rate : 6.6 mg/ kg * d
  ➔ daily inhalation rate: 0.016 mg/ kg BW * d
- industrial areas: working time: 8 h/d, 5 d/w, 45 w/y, 40a
  reduction through wetness, factor: 1/3

More information about exposure factors can be found in (3).

It is to clarify, if these assumptions are appropriate to China.

Background exposure to mercury

To receive a trigger-value, information about the background exposure by food, drinking water and air is necessary. If no other information is available, a conventionary contingent of 80 % of the TRD was chosen, that is 'filled' by this background.

The background exposure on mercury in Germany by oral ingestion was assessed to 30-300 ng/(kg*d). As a worst case assumption the total mercury intake was assumed to be methyl mercury. Data from 47 children in Germany - Duisburg about dietary Hg-intake (1994) have a range from 3.9 - 141.5 ng/(kg*d); 90 % of the collective is below 27.5 ng/(kg*d) (="90. Percil"). The TRD of 50 ng/(kg*d) is filled up to 60-600 % by food; therefore no better assumption about background exposure is possible and a contingent of 80 % of the TRD by the (especially food) background was chosen in the case of mercury too.

Trigger Values for inhalative and oral intake

From these data a primary trigger-value for (organic, oral) mercury was calculated – e.g. for children oral uptake on playgrounds:

$$\text{Test threshold [mg/kg]} = \frac{\textit{hazards oriented body dose}}{\textit{soil ingestion rate}}$$

$$= \frac{\textit{received dose} \bullet (\textit{hazard factor } F_{(Gef)} - \textit{std. value background})}{\textit{soil ingestion rate}}$$

$$= \frac{\textit{received dose}\left[\frac{ng}{kg \bullet d}\right] \bullet (F_{(Gef)} - 0.8)}{33 \frac{mg}{kg \bullet d}}$$

With precise data:

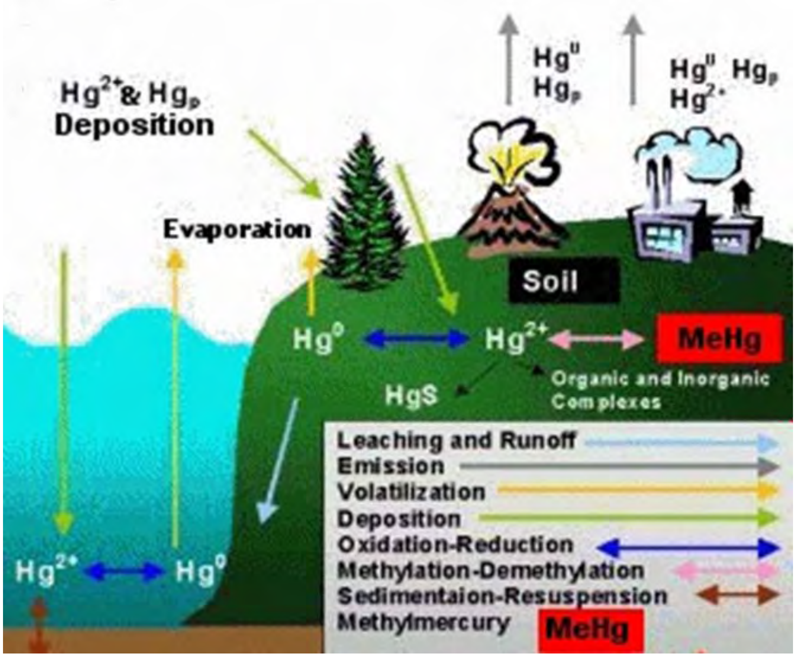
$$\text{TV Hg-inorganic:} = \frac{15 * (4,5 - 0,8)}{0,07 * 33} = 24 \text{ mg/kg}$$

received dose = TRD_{oral} / $Resorption_{oral}$

$$\boxed{\text{TV Hg-organic:} = \frac{50 * (3,9 - 0,8)}{1 * 33} = \underline{4,7 \text{ mg/kg}}}$$

Plausibility checks

Mercury species can be transformed in various media – see figure on the right from source (4). In (some) soil methylation of inorganic mercury is possible!



Keeping in mind the ratio of inorganic and organic mercury in 'worst case' of approx. 1 : 1, **the Hg Trigger Value was fixed with 10 mg/kg for playgrounds.**

Trigger Values for all other usages with ingestion are derivated in the same manner (s. figure 1).

Next plausibility check is comparing the derivated values with the soil background in Germany. Data from the Federal States of Germany (LABO 1995) shows that the 90. percentils of the Federal States are in a range of 0,08 - 1,58 mg/kg. These data indicate, that there is no conflict with the lowest derivated Trigger Value of 10 mg/kg for playgrounds.

Biomonitoring informations were checked for disagreement with the assessment standards for human toxicology. The corresponding Hg soil concentrations in the regarded area are about 10-50 mg/kg and shows:

- All investigations of urine are without attracting attention
- 90 % of all blood investigations are without attracting attention
- Maximum content of mercury in blood : 24,8 µg/l (~ ca. 20 µg/d)
- Correlation between the content of mercury in blood and soil was not investigated.
- For the real exposure apparently the pathway ‘in-door contamination’-human health plays the dominant part! But no quantification of this pathway was possible, due to the very individual contamination (and cleaning) procedures in-door.

<u>Trigger Value for land used for industrial and commercial facilities</u>

The exposure scenario for this usage assumes that only an inhalativ intake of soil dust by workers is relevant. Since the basic toxicological data are oriented to permanent exposure (24 hours/day, 365 days/year), while exposure in industrial and commercial facilities takes place only during working hours, a weighting factor is introduced. This factor expresses the relationship between hours per year and hours of presence per year in contaminated industrial and commercial facilities. The following assumptions were made:

- Working time: 8 hours/day on 5 days/week and 45 weeks/year,
- Soil moisture and other factors reduce the exposure to dust to 1/3 of the year.

The exposure duration (D) is therefore calculated with 600 h/a and a weighting factor Z is then obtained as follows: Z = 365 d/a x 24 h/d : 600 h/a = 14.6. The concentration factor (A) for pollutants in the soil's fine-grain fraction is set at 5 for anorganic substances.

Mercury as an Example: The Calculation for inorganic mercury in detail:

$$\text{Test threshold [mg/kg]} = \frac{TRD - anal.\,conc. \bullet \left(F_{(Gef)} - background\right) \bullet weighting\ factor\ Z}{dust\ concentration \bullet concentration\ factor\ A}$$

$$= \frac{TRD - anal.\,conc. \left[\frac{ng}{m^3}\right] \bullet \left(F_{(Gef)} - 0.8\right) \bullet 14.6}{0.325 \frac{mg}{m^3} \bullet A}$$

$$\text{TV Hg}_{\text{inorganic}}: \quad = \quad \frac{131 * (7{,}1 - 0{,}8) * 14{,}6}{0{,}0325 * 5} \quad = \ 7429 \text{ mg/kg}$$

The calculated Trigger Value exceeds the Trigger Values of 10 – 20 – 50 mg/kg for playgrounds, residential areas and parks by far!

A difference is assumed to be justified if it is assured that compliance with Trigger Values for industrial and commercial facilities will not result in secondary pollution on surrounding areas (diffuse run-off or blowing of soil material or by mudslides).

A Trigger Value of 80 mg/kg was chosen to get a justified difference in this case.

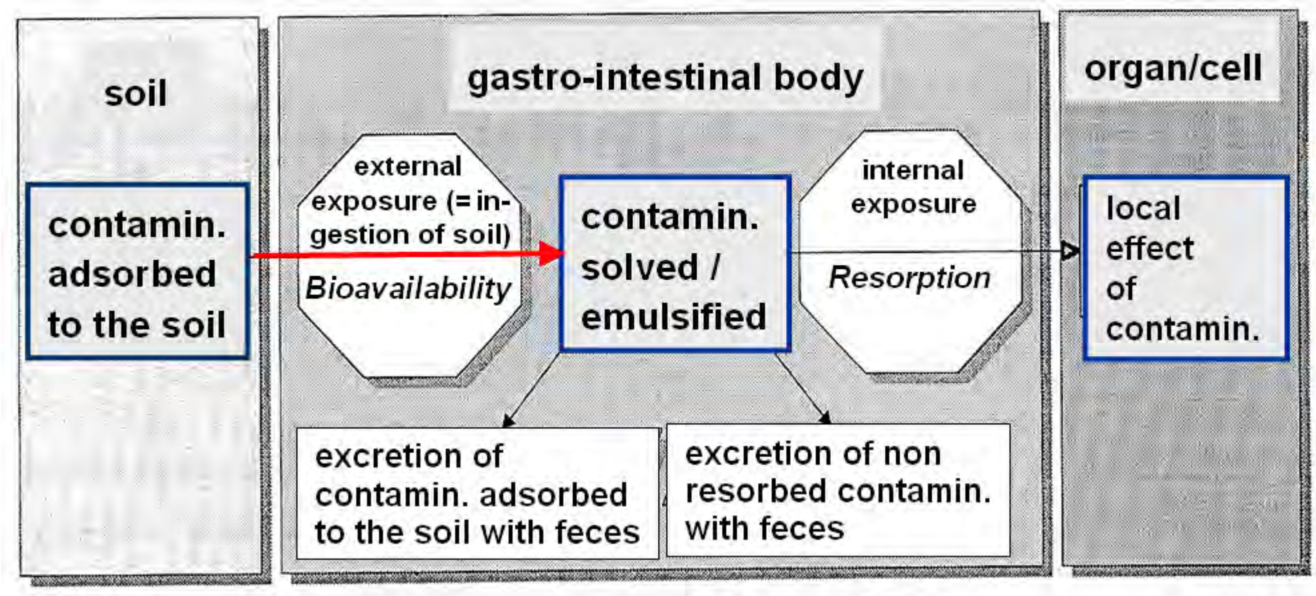
Exceeding trigger values; options for detailed investigations

According the BBodSchG exceeding Trigger Values shall mean that investigation with respect to the individual case in question is required.

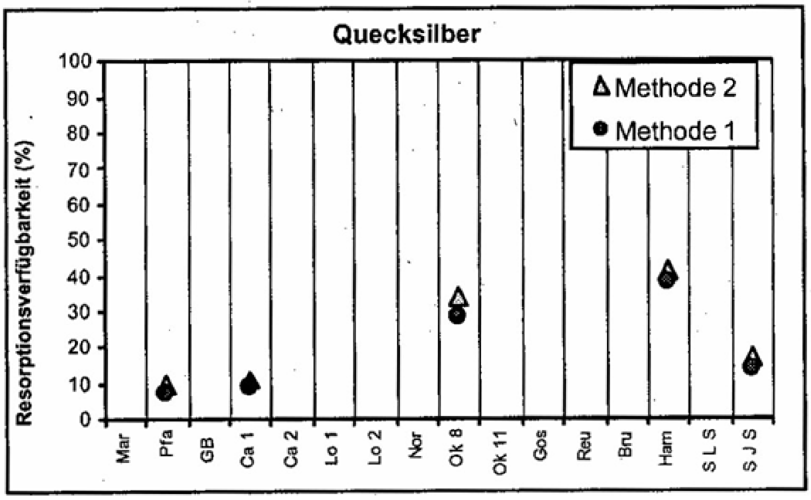
In case of land used for industrial and commercial facilities the mentioned risk for surrounding areas is to be verified by the real usages; otherwise the calculated value is suitable.

Next the assumed ratio of inorganic and organic mercury in soil has to be elicited.

To derive Action from Trigger Values inter alia the bioavailability of contaminants in soil must be considered – see the red arrow in the following figure – depending on the contaminant behaviour (species, sorption status ect.) in the individual case. This is a main reason why no Action Values are presented in the BBodSchV for the pathway soil – human health!



Testing the bioavailability of contaminants by extracting with synthetic saliva, synthetic gastric juice and synthetic intestine juice (including solubilisation by milk-powder) is based in Germany on some standardized methods.



For example results for several mercury contaminated sites are shown right hand for two methods. In the case of site 'Pfa' 10 % of mercury is bioavailable: assuming that the site is a residential area, the Trigger Value of **20 mg/kg** can be dilated up to **200 mg/kg** before measures for soil remediation should be taken.

If there is no organic mercury in soil analytically demonstrable, only in the case of inorganic mercury concentrations about **500 mg/kg,** risk for children by oral intake is probable. This example demonstrates, that the Trigger Values according the BBodSchV are not fixed thresholds, but a tool for decision making with regard to all circumstances and exposure possibilities – they are a tool for risk management.

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(1) http://www.bmu.de/files/pdfs/allgemein/application/pdf/soilprotectionact.pdf

(2) http://www.bmu.de/files/pdfs/allgemein/application/pdf/bbodschv_uk.pdf

(3) http://www.corrosion-doctors.org/Elements-Toxic/Mercury-mad-hatter.htm

(4) http://www.ec.gc.ca/MERCURY/EH/EN/eh-hc.cfm#T

Remediation Technologies

Christian Weingran

HIM GmbH – Department Remediation of Contaminated Sites, Germany

1 Introduction

A big number of contaminated sites is the result of past industrial practice associated with several industrial branches, like coal and metal mining, petroleum and chemical industries, metal-plating, manufactured gas plants and coal gasification. The (underground) storage, the industrial sewage systems and the industrial and municipal landfills are important sources of soil and groundwater contamination. But also facilities like dry-cleaners and filling stations play an important role. Not to forget military sources (airports, storage facilities).

The input of contaminants had been taken place at points or on larger areas, the contaminants could have been liquids or solids, the contamination process could have happened as an accidental spill or a leakage over a long period. Different contamination pattern are the result of different types of input.

The physical state of contaminants is one of the factors determining the possibilities of clean-up. Contaminants may be present:

- as pure particulate,
- adsorbed onto soil particles,
- in organic soil particles, such as plant material and humic substances,
- as a solid (or pure liquid) phase in the pores of soil particles,
- as dissolved components in an aqueous phase in the pores of soil particles,
- and partly adsorbed onto the pore walls in such particles.

The contaminants fall into the main categories volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), metals and inorganics.

The migration conditions will be governed by the specific physico - chemical characteristics of the contaminants, such as solubility, specific gravity, adsorption coefficient, and biodegradability. The implementation of appropriate remediation strategies requires a good understanding of the processes governing the exchange of contaminants with the soil aqueous, gaseous and solid phases.

Besides the physico-chemical properties of the contaminants the direction and the speed of migration depend directly on local natural underground parameters, eg. pH/oxidation/reduction potential, contents of silt and clay and humic substances and on the key aquifer characteristics.

2 Remedial design

Suspect sites are first subject to a preliminary investigation. The history of the site is studied in order to yield indications about the nature of the contaminants. Soil and groundwater are sampled. Information on geologic profiles and site conditions are collected.

Site-specific field measurement and modeling techniques should allow a reliable field scale quantification of the contaminant source strength (type, level and location) as well as the characterization of the contaminant plume. The most common approach to source characterization is based on soil and groundwater samples which are obtained from boreholes, ditches, piles etc.

A risk assessment is usually used to decide whether there is or there is not a need to eliminate or reduce the (environmental and/or human health) risks posed by a contamination. Concentration is not the only fact, the conditions of exposure of contaminants need assessment. The acceptable risk is a political decision that has to be supposed / supported by scientists (e.g. toxicologists). The risk varies according to specific characteristics of contaminants and their toxic, carcinogenic, mutagenic potential. Concentrations of contaminants are compared with quality criteria. If contamination exceeds these values, a further and more extensive investigation must be carried out. If the risks need to be reduced e.g. to protect the valuable resource groundwater, a remediation strategy must be developed to address them.

The planning process is the beginning of really spending money. A careful consideration of all aspects during the planning phase helps to save money during the later construction and remediation phase. With small amounts of money substantial changes of the strategy and remediation pattern are still possible. Spend money now – save later.

Before talking about technology many questions have to be answered:

- What is the current status and future use of the site?

- Are there urgent social, economical or environmental needs?
- How much time is available to complete the remediation?
- Who is to pay? How much money is available? Is there money in the short or in the long time? When? Are there any conditions?

Then the information about the contaminants and the contaminated media have to be checked:

- What type of contaminant? What concentration? Single contaminant or mixture?
- Point source or area? / deep level or close to surface / Source or plume?
- Is the contamination in contact with groundwater or with human beings?
- Which media is contaminated? What is known about its properties?
- What is known about the geological and hydro-geological conditions?

If there is a lack of information it is of high importance to get this information as soon as possible and as complete as possible before starting to think about a strategy. Developing a strategy on a wrong database might cost a lot of money and might not be successful.

3 Approaches to remediation

There are two basic approaches to remediation:

- Elimination of the risks by removing or destroying contaminants
- Control or management of risks, reduction to an acceptable level by reducing contaminant concentrations or by containing the contaminants, such as installing barriers between the contaminants and potential receptors.

In the past the cleanup was very often based on approaches aiming at maximum risk control or even risk elimination (excavation/containment/groundwater extraction). From a technical point of view these approaches are still the fastest way to solve the problem. If there is an urgent need to reuse the sites or to solve a problem this is an advantage. The high costs associated with these methods are a big disadvantage and were prohibitive in many projects. As a consequence concepts which focus on the control of the groundwater plume or the containment of the source rather than the elimination of the source have received increasing attention during recent years.

A lot of active and passive in-situ technologies have been developed, that address the contamination of soil and groundwater and avoid the (effects and cost of) excavation and the above ground environmental impacts. In-situ methods that are less costly but require more time are available. But they have less predictable results and may require long time monitoring and aftercare.

Passive technologies make sense for the treatment of the plume to achieve a long term protection and in addition short term active technologies removing parts of the source are used to reduce concentration in the plume. Appropriate source control actions should be considered the highest priority. Improperly addressed contaminant sources complicate the long term cleanup effort.

The application of in-situ approaches to subsurface remediation increase the emphasis on adequate site characterization and thorough understanding of the subsurface system targeted for remediation.

4 Technology selection

To assess the applicability and potential performance of remediation methods, information is required on the contaminants present (e.g. types, concentrations, speciation, and distribution) and the physical, chemical, and biological properties of the material to be treated. In most cases this involves collecting supplementary data beyond that necessary for the risk assessment and initial remedy selection. In general, the suitability of a remediation method depends on many factors including

- contaminated media,
- contaminants,
- remediation objectives,
- current status of the site,
- location of the site,
- time available to complete the treatment, and
- money available to pay for the treatment.

The selection of remedial options should consider the primary (target levels) and secondary effects (environmental impacts) as well as the achievability and sustainability.

Technologies are categorized as ex-situ (after contaminated soil or groundwater has been removed for the treatment) or in-situ (without removing the contaminated media). Ex-situ treatment may be performed onsite using for example mobile or transportable treatment systems or off-site fixed treatment facilities.

The processes are frequently combined in treatment trains. A treatment train is a sequential combination of technologies or unit processes which treat recalcitrant matrices more effectively than any single technology could. E.g. soil washing becomes the prelude to chemical or biological treatment.

5 Technologies for Soil and Ground Water Remediation

5.1 Containment

A method that is currently in wide use is to contain the contamination where it occurs. In its ultimate form this requires the complete encapsulation of the contamination by the provision of surface cover and in-ground vertical and horizontal barriers. Primary functions are the control of leachate production, of soil fluid movement and the limitation of surface water ingress.

Containment can be used to prevent further migration of the contaminants, but does not provide a means for correcting the problem in the long term. The effectiveness of containment technologies decreases with depth and geologic complexity, such as fractured aquifers.

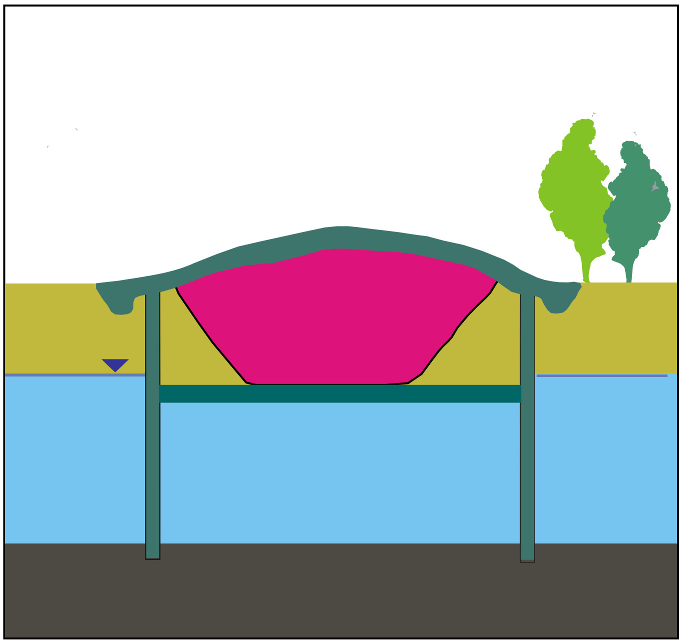


Fig. 1: Containment

Vertical Containment Barriers (VCBs) are used to isolate the contaminated material from contact with groundwater and to control the migration of contaminated groundwater and soil gas. They are frequently used in conjunction with hydraulic measures to control the groundwater plume or with an active or passive system to control gas emissions. They must be underlain by an impermeable layer of fine grain deposits or bedrock.

When used as the primary remediation method, VCBs must be designed to last for decades. Barriers will perform satisfactorily only for a limited time. Because experience is limited, predicting performance is difficult.

5.2 Excavation (and disposal or ex-situ treatment)

Excavation to remove source materials at hot spots represents one of the most common alternatives for remediation. The excavated soil is treated in on site or off site soil treatment facilities. Excavation for ex-situ treatment can be very costly, with costs increasing and efficiency decreasing with depth. This strategy is used in the case of urgent social, economical or environmental needs, e.g. the remediation of the contact zone of an inhabited site. Even when selecting passive in-situ strategies excavation as measure to reduce the release of contaminants of the source is an appropriate technology.

5.3 In-situ Technologies for Soil

In-situ treatment methods avoid the above-ground environmental impacts and costs associated with excavation. Some methods are particularly attractive for application on operating sites and other sites where buildings and structures need to be preserved. In-situ technologies for treating soil can be classified like their ex-situ counterparts on the basis of the underlying treatment principle, such as physical separation, thermal treatment and biological degradation. In-situ treatment methods may be combined with P&T methods to treat contaminated groundwater. Heat may be introduced to support bioremediation or vapor extraction.

Accurate identification of all contaminants present is essential because of the danger that a treatment adopted to remedy some contaminants could lead to adverse or counterproductive reactions with other contaminants. This may result in increased toxicity or mobility. An understanding of the physical characteristics of the site is essential for all in-situ techniques, especially those requiring infiltration of treatment agents.

- The effectiveness of in-situ treatment methods is determined by a variety of factors, including:
- Nature, extent, and distribution of contaminants.
- Contact achieved between contaminants and treatment agents, often the extent to which the contaminants can be solubilized.

- Control over processing conditions in the ground which are not visible, especially when working at considerable depth.
- Ability to effectively remove treatment products and excess agents from the ground;
- Time available for treatment in terms of access to the site and natural factors, such as groundwater flow rates.

Minimal information is available on the long-term effectiveness of in-situ treatment methods that do not remove or destroy contaminants. In-situ treatment may have significant implications on the engineering properties of the ground and hence on any subsequent construction work (e.g. infiltration may affect the stability of neighboring buildings).

5.3.1 In-situ Stabilization/Solidification

is a process of alteration of inorganic contaminants to an immobile state by injection or infiltration of stabilizing agents into a zone of contaminated soil. Contaminants are physically bound or enclosed within a stabilized mass, or their mobility is reduced through chemical reaction. Excellent understanding of the hydro geologic regime is essential. It is best applied to moderate to high permeability soils.

5.3.2 In-situ Soil Flushing

Injection or infiltration of a solution into a zone of contaminated soil to mobilize or solubilize contaminants, followed by down gradient extraction of groundwater (flushing solution mixed with the contaminants) and above ground treatment and/or re-injection.

Solutions may consist of surfactants, co-solvents, acids, bases, solvents, or plain water. Surfactants enhance mobility of hydrophobic organic compounds by lowering interfacial tension between water and contaminants; co-solvents increase the solubility.

Any variety of configurations of injection wells, directional wells, trenches, infiltration galleries and extraction wells or collection trenches may be used to contact the flushing solution with the contaminated zone. Contaminants treated are VOCs, SVOCs, petroleum hydrocarbons, PCBs and pesticides. The method may enhance existing pump and treat systems but can increase plume size and concentrations. To recover surfactants and to remove contaminants from extracted groundwater with surfactants is difficult.

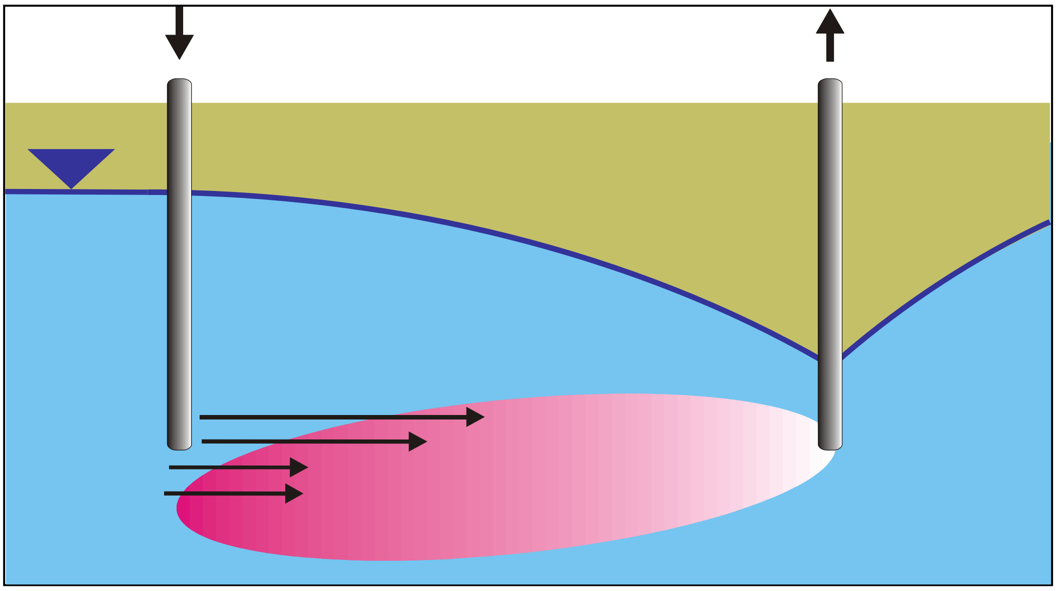


Fig. 2: Surfactant Flushing

5.3.3 In-situ Oxidation

In-situ chemical oxidation is based on the delivery of chemical oxidants to contaminated media. Strong oxidants like hydrogen peroxide, potassium permanganate (KMnO4) or Fentons Reagent (whereby hydrogen peroxide is applied with an iron catalyst creating a hydroxyl free radical) are used.

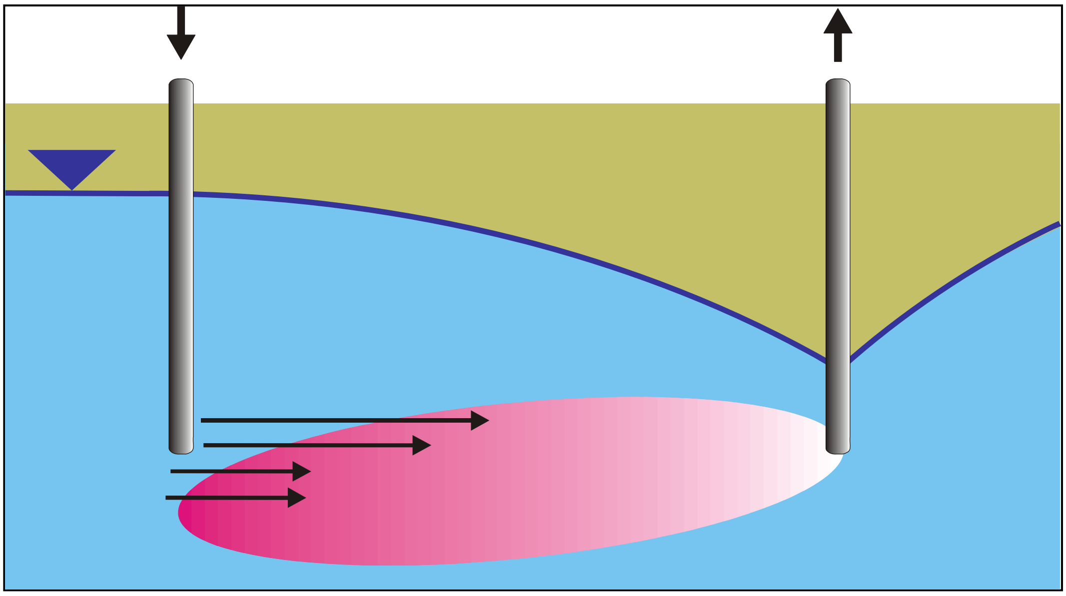


Fig. 3: In-situ Chemical Oxidation

Oxidants are injected or re-circulated through a well or injector head directly into the subsurface, mixed with a catalyst. Best for VOCs, SVOCs and petroleum hydrocarbons. It may require large quantities of oxidizing agent. Incomplete oxidization or formation of intermediate contaminants is possible, other carbon sources compete for oxidant. Successful implementation of this technology requires an effective means for disperging the oxidant to the subsurface contaminated regions.

5.3.4 Electrokinetics

Electrokinetics is a process that separates and extracts heavy metals and organic contaminants from saturated or unsaturated soils, sludges and sediments. A low intensity direct current is applied across electrode pairs that have been implanted in the ground on each side of the contaminated soil. The electrical current causes electroosmosis and ion migration, which move the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards respective electrodes depending on their charge. The contaminants may then be extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant. Also reagents may be introduced at the electrodes to enhance contaminant removal rates.

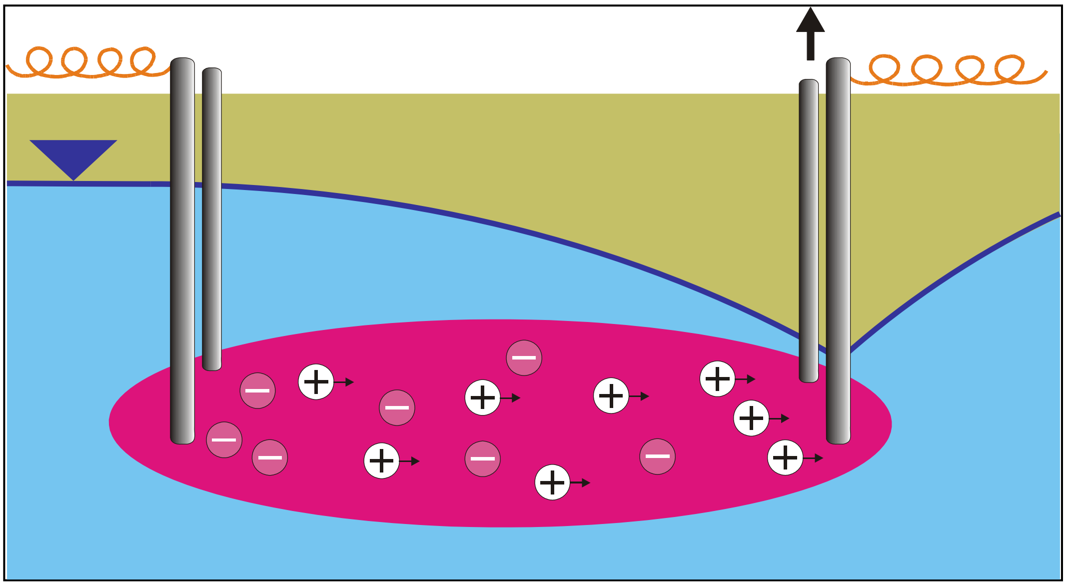


Fig. 4: Electrokinetics

5.3.5 Soil Vapor Extraction

Soil vapor extraction (SVE) is a process that physically separates contaminants from soil. SVE systems are designed to remove VOCs from soil beneath the ground surface in the unsaturated zone. By applying a vacuum through a system of vertical or horizontal underground wells, contaminants are pulled to the surface as vapor or gas. Vapors extracted are typically treated using carbon adsorption (CA), incineration, catalytic oxidation, or condensation. CA is most commonly used and is adaptable to a wide range of VOC.

SVE is as popular as P&T but it has very often the same poor results. Soil vapor extraction often fails and leaves contaminants sorbed to solids in the vadose or in the saturated zone. SVE is very effective for the removing the labile fractions of contaminants located in the vapor and free liquid phases or adsorbed to the external surfaces of the soil matrix. But it will not be effective for removing contamination trapped in the interior of the soil matrix. The quantity trapped in the interior of the soil matrix may exceed surface contamination by 1-2 orders of magnitude. SVE cannot be relied upon to return long-contaminated soils to their pristine conditions.

Several technologies were developed to enhance the effectiveness of soil vapor extraction:

Thermal Enhancement

Use of steam, heated water, hot air or radio frequency (RF) or electrical resistance/ alternating current (AC) heating to alter temperature-dependent properties of contaminants in-situ to facilitate their mobilization, solubalization, and removal. VOC and SVOC may be vaporized; they then rise to the vadose zone where they are removed by vacuum extraction and treated. Steam is best applied to moderate to high permeability geologic materials. RF and AC heating may be applied to low permeability, clay rich geologic materials as the clay will preferentially capture the RF or AC energy.

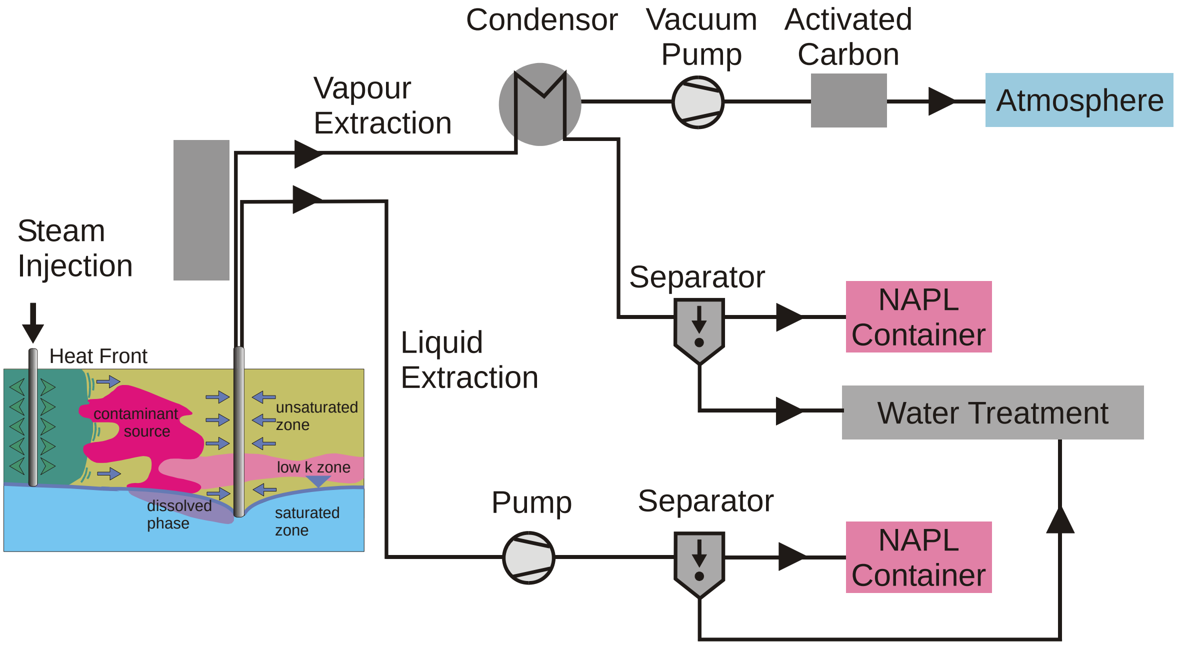


Fig. 5: In-situ Thermal Treatment of Soil

Thermal enhancement leads to higher recovery rates, remediation of difficult soils low permeability zones (clay, silt) and to shorter remediation times. But it could increase the size of the plume and temporarily destroy biomass.

Hydraulic and Pneumatic Fracturing

are techniques adapted from petroleum industry to create enhanced fracture networks to increase soil permeability to liquids and vapors and accelerate contaminant removal. The fractures serve as avenues for bioremediation, steam or hot air injection or contaminant recovery and can also improve pumping efficiency and the delivery for other in-situ processes. Mostly applicable for unconsolidated sediments and bedrock.

Air Sparging (AS)

expands the remediation capabilities of SVE to the saturated zone. AS involves injecting air or oxygen under pressure into the saturated zone to volatilize contaminants in groundwater. The injected air removes adsorbed VOCs in soil and dissolved contaminants in groundwater as the air rises through the formation. Volatilized vapors migrate into the vadose zone where they are extracted by vacuum, generally by a soil vapor extraction system.

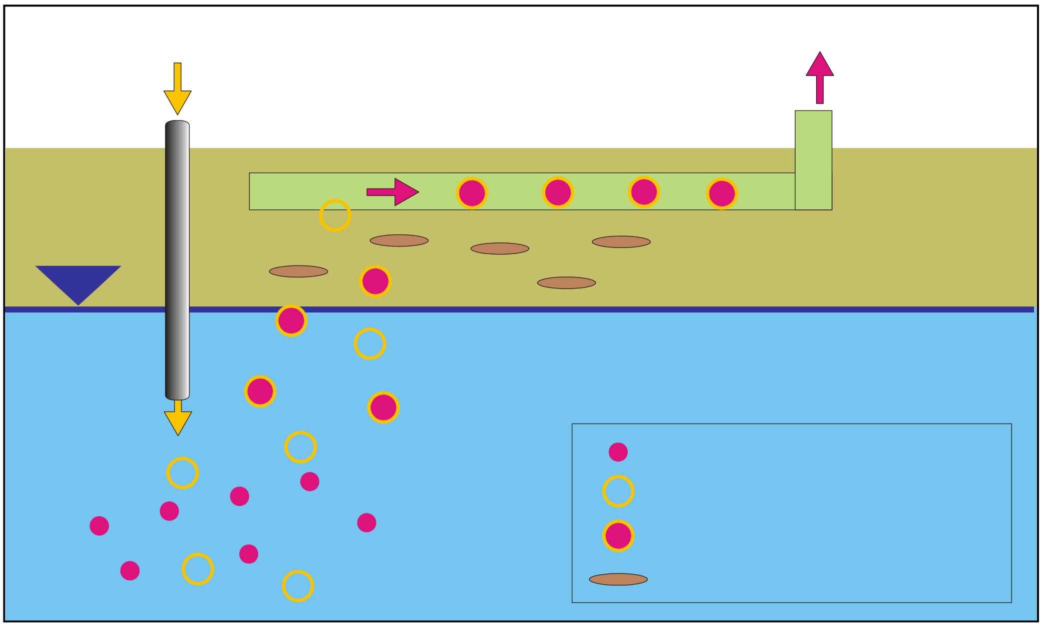


Fig. 6: Air Sparging System

Most applicable for volatile organic contaminants relatively moderate to high permeability geologic materials. AS can also be used to promote biodegradation in saturated and unsaturated soils by increasing subsurface concentration of oxygen.

5.4 Ex-situ Technologies for Soil

5.4.1 Biological degradation

Bioremediation techniques are destruction or transformation techniques directed toward stimulating the microorganisms to grow and use the contaminants as a food and energy source by creating a favorable environment for the microorganisms. Generally, this means providing some combination of oxygen, nutrients, and moisture, and controlling the temperature and pH.

Although not all organic compounds are amenable to biodegradation, bioremediation techniques have been successfully used to remediate soils, sludges, and ground water contaminated by petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals.

The rate at which microorganisms degrade contaminants is influenced by the specific contaminants present; oxygen supply; moisture; nutrient supply; pH; temperature; the availability of the contaminant to the microorganism (clay soils can adsorb contaminants making them unavailable to the microorganisms); the concentration of the contaminants (high concentrations may be toxic to the microorganism); the presence of substances toxic to the microorganism, e.g., mercury; or inhibitors to the metabolism of the contaminant.

Available ex-situ biological treatment technologies include biopiles, composting, landfarming, and slurry phase biological treatment.

5.4.2 Thermal Treatment

Thermal treatments offer quick cleanup times but are typically the most costly treatment group. Cost is driven by energy and equipment costs and is both capital and O&M-intensive. Thermal processes use heat to increase the volatility (separation); burn, decompose; or melt (immobilization) the contaminants. Separation technologies include thermal desorption and hot gas decontamination. Destruction technologies include incineration, open burn/open detonation, and pyrolysis. Vitrification immobilizes inorganics and destroys some organics.

Separation technologies will have an off-gas stream requiring treatment. Destruction techniques typically have a solid residue (ash) and possibly a liquid residue (from the air pollution control equipment) that will require treatment or disposal.

5.4.3 Soil Washing

Ex-situ soil washing processes are mostly based on mineral processing techniques. Soil washing is a water-based process for scrubbing soils ex-situ to remove contaminants. The process removes contaminants from soils by dissolving or suspending them in the wash solution or by concentrating them into a smaller volume of soil that can be further treated through particle size separation, gravity separation, and attrition scrubbing.

The concept is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. Complex mixture of contaminants in the soil and heterogeneous contaminant compositions make it difficult to find a solution that will consistently and reliably remove all of the different types of contaminants.

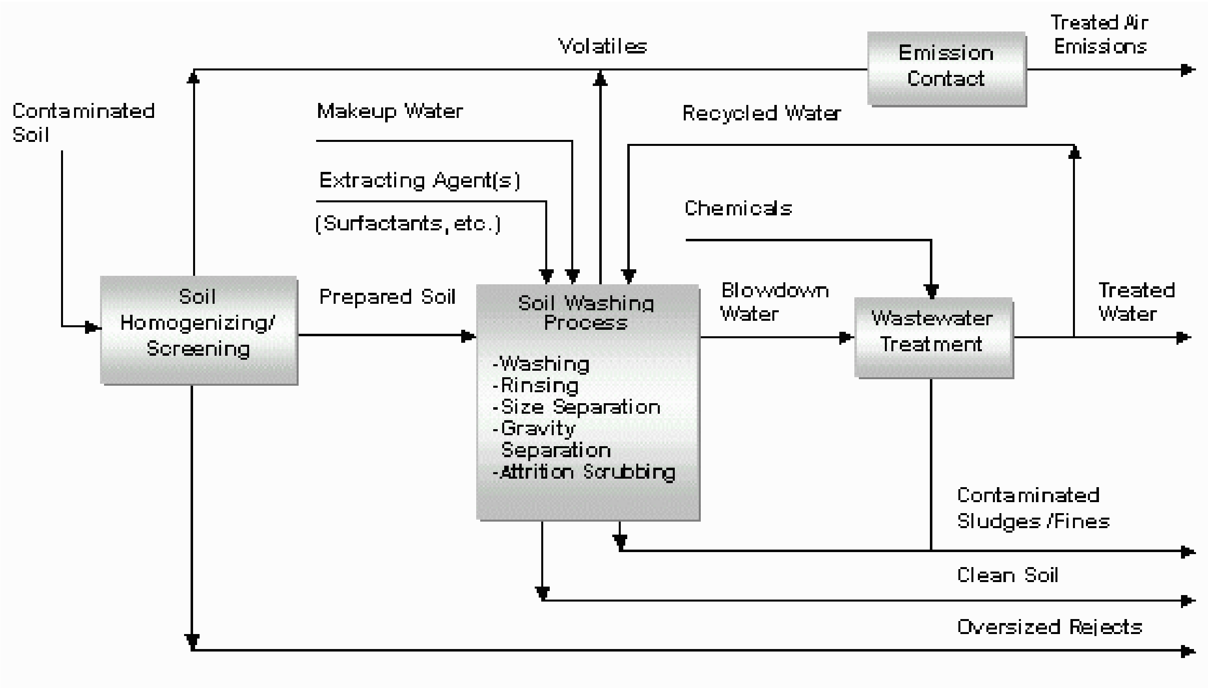


Fig. 7: Soil Washing

Soil washing systems offer the greatest promise for application to soils contaminated with a wide variety of heavy metal, and organic contaminants. The clean, larger fraction can be returned to the site for continued use.

5.5 In-situ Methods for Groundwater

In-situ treatment of groundwater requires water to pass through a treatment zone where injection of agents in solution or in gaseous form cause degradation or promote natural degradation of contaminants or a solid substrate exists that supports physical separation of the contaminants by adsorption, chemical or biological degradation, or reduction in toxicity.

The two processes may be used in combination. In-situ treatment of groundwater may be combined with in-situ treatment of the unsaturated zone. In-situ groundwater treatment also may be combined with P&T operations. The flow of groundwater through or to the treatment zone may be the result of natural gradients; induced by pumping from vertical or horizontal wells, or by infiltration of water; or achieved through injection of heated water or steam.

In-situ groundwater remediation requires a thorough understanding of the hydrogeology of the site and its environs, and in many cases requires the prior removal or containment of the source of the contamination and removal of free product. Modeling groundwater and contaminant movement is often required to design the treatment system. Thus, neither the water flow nor the distribution of contaminants can be assumed to be homogeneous.

As for all in-situ methods, ensuring contact between contaminants and the treatment agent is major practical difficulty. Contaminants may be adsorbed onto mineral surfaces and held in capillary pores. Effective long-term treatment requires that these contaminants be released to the groundwater. A variety of means may be used to promote the movement of contaminants through the subsurface.

Care is required in the selection and design of an in-situ groundwater treatment system to ensure that any chemical introduced into the ground during treatment does not itself become a pollutant, that mobilization of contaminants other than those that are primary object of the treatment or are naturally present is prevented; and treatment end products are not more harmful than the original compounds.

5.5.1 Permeable Reactive Barriers (PRB)

A PRB, (or passive barrier, passive treatment wall, treatment wall, trench), consists of an in-ground trench that is backfilled with a reactive medium to provide passive treatment of contaminated groundwater passing through the trench. The treatment wall is placed at strategic location to intercept the contaminant plume.

The selection of the reactive medium is based on the targeted contaminants and the hydrogeologic setting of the site. Zero-valent iron is the most common medium used in PRBs to date. Examples of other reactive media include microorganisms, zeolite, activated carbon, peat, phosphate, bentonite, limestone, and amorphous ferric oxide.

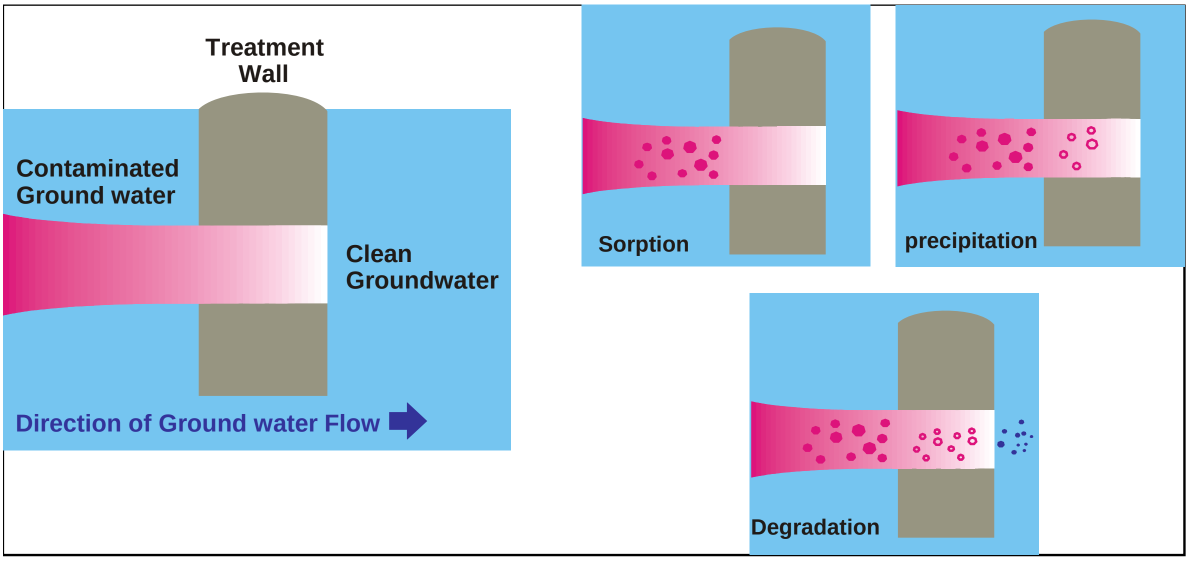


Fig. 8: Permeable Reactive Barriers / Treatment Walls

Different fillings do their job through different chemical processes: sorption, precipitation, degradation:

- **Sorption barriers** contain fillings that remove contaminants from groundwater by adsorbing contaminants to the barrier surface.
- **Precipitation Barriers** contain fillings that react with contaminants in groundwater as they seep through the wall.
- **Degradation barriers** cause reactions that degrade the contaminants in the groundwater (oxidation, reduction). For example, fillings of iron granules degrade certain volatile compounds. Walls may also be filled with a mixture of nutrients and oxygen sources which stimulate the activities of microorganisms.

Hydrogeologic setting is critical to application; geologic materials must be relatively conductive and a relatively shallow aquitard must be present to provide a basement to the system.

Reactive walls downgradient of contaminated areas are currently being discussed as an alternative method to traditional groundwater remediation technologies. PRBs may be used to treat contaminated groundwater at the boundary of a site, or to restore the groundwater throughout a site.

The volume of groundwater treated by a PRB is typically much lower than it would be for a P&T system at the same site because PRBs treat only the groundwater that passes through the barrier, while P&T systems actively extract groundwater from an aquifer, usually at multiple locations throughout the plume.

The most important advantages of this technology for passive in-situ-treatment of contaminated groundwater are the comparatively low costs (but for a long time) associated with operation and maintenance (O&M). There is not so much experience with the reactivity lifetime/ the system long term performance and the replacement of treatment units.

PRB systems may be configured as funnel and gate designs. In such configurations groundwater flow is routed by two or more walls through a permeable reactive zone.

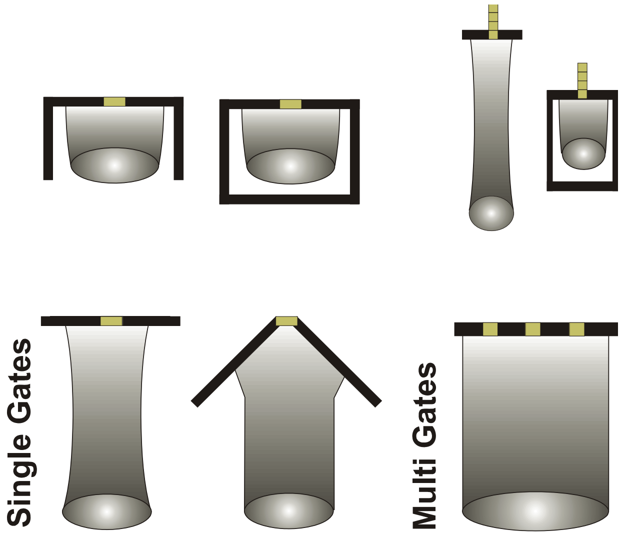


Fig. 9: Funnel & Gate Buildings (single gate [left], multi gate [right]

5.5.2 Bioremediation

Bioremediation is a managed or spontaneous process in which microbiological processes are used to degrade or transform contaminants to a less toxic or nontoxic form, thereby mitigating or eliminating contamination. Microorganisms (yeast, fungi, or bacteria) depend on nutrients and carbon to provide the energy needed for their growth and survival. Degradation of natural substances in soils and sediments provides the necessary food for the development of microbial populations.

In the presence of sufficient oxygen (aerobic conditions) and nutrients, microorganisms will ultimately convert many organic contaminants to carbon dioxide, water and microbial cell mass. In the absence of oxygen (anaerobic conditions), the electron acceptor is a compound other than molecular oxygen, such as sulfate, nitrate, or carbon dioxide, and the contaminants will be ultimately metabolized to methane, limited amounts of carbon dioxide, and a trace amount of hydrogen gas. Oxygen provides maximum energy. Thus, aerobic bioremediation generally proceeds more quickly and provides a more complete degradation of the organic compounds

Many of the more persistent contaminants are resistant to microbial remediation, because their toxicity to the organisms, preferential feeding of microorganisms on other substrates, unfavorable environmental conditions lack of capability to use the compounds as a source of carbon and energy. PCBs and PAHs can be transformed or partially metabolized as a second substrate. Though they might not be suitable for growth substrate, they may be degraded by co-metabolism, where microorganisms growing on one compound produce an enzyme which transforms another compound on which they can not grow.

Most bioremediation technologies have focused on the addition of oxygen to facilitate the biodegradation. Alternate electron acceptors can be used for bioremediation in the saturated zone. Nitrate, sulfate and salts of iron (III) can substitute oxygen. Various types of anaerobic bacteria exist in nature that can use the anaerobic electron acceptors.

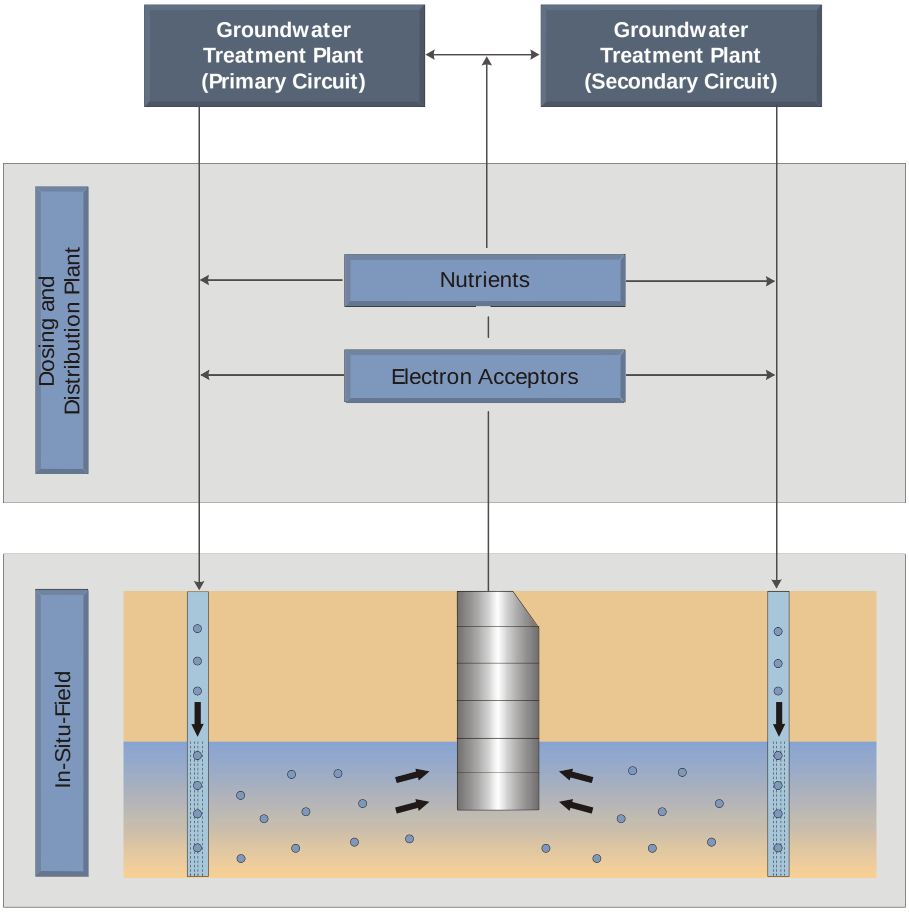


Fig. 10: In-situ Bioremediation

Enhanced bioremediation technologies increase biodegradation rates by supplying nutrients and electron acceptors, or control other factors that can be rate-limiting. Alteration of the environmental conditions can often stimulate development of appropriate microbial populations that can degrade the organic compounds. Such changes may include adjusting the concentration of the compound, pH, oxygen concentration, or temperature, or adding nutrients or microbes that have been acclimated to the compound.

Enhanced in-situ remediation involves the percolation or injection of groundwater or uncontaminated water mixed with nutrients and saturated dissolved oxygen, using injection and extraction wells.

Bioventing systems treat soil in-situ by injecting atmospheric air into unsaturated soil. The air provides a continuous oxygen source, which enhances the growth of microorganisms naturally present in the soil and accelerates the natural processes.

Biosparging systems inject a gas under pressure into the saturated zone to transfer volatile compounds to the unsaturated zone for biodegradation.

The effectiveness in controllable environments (e.g. bioreactors) has been demonstrated, in uncontrolled environments such as the subsurface it is much more difficult to achieve, demonstrate and assess.

5.5.3 Natural Attenuation

For a long time the self cleaning capacity of the soil and groundwater was not recognized. Now we start to understand that nature is a cleaner. Natural Attenuation (NA) makes use of natural processes to contain the spread of contamination and reduce the concentration and amount of pollutants at contaminated sites. It includes a variety of physical, chemical, and biological processes. They act without human intervention to reduce the mass toxicity, mobility, volume, or concentration of contaminants in soil or groundwater.

NA is an in-situ treatment method used as one part of a site cleanup that also includes other strategies. The processes contributing to NA are acting at varying rates and degrees of effectiveness, depending on the types of contaminants present, and the physical, chemical and biological characteristics of the soil and groundwater.

In certain-situations, natural attenuation is an effective option and the most appropriate way to remediate some contamination problems.

NA is sometimes mislabeled as a “no action” approach. However, NA is really a proactive approach that focuses on the confirmation and monitoring of natural remediation (Monitored Natural Attenuation, MNA). Hydrocarbons are good candidates for NA.

Responsibly proposed natural attenuation at a groundwater remediation site requires demonstration that the processes mentioned will occur at a sufficient rate to remediate the plume prior to impact at a receptor. It is necessary to understand and to control the process. Based on this understanding a prediction of the results of the process and a monitoring plan to control this process can be made.

Therefore a site assessment must identify soil characteristics such as soil type, hydraulic conductivity and organic content, groundwater characteristics such as direction, gradient and velocity of flow, temperature, pH and dissolved oxygen content inside and outside the plume, the horizontal and vertical extent of contamination in soil and groundwater, historical behavior of the plume, and the ability for attenuation of the plume under site conditions and a detailed review of receptors and migration pathways in the area surrounding the site.

The rates of natural processes are typically slow. Long-term monitoring is necessary to demonstrate that contaminant concentrations are continually decreasing at a rate sufficient to ensure they will not become a health threat. The NA sites need to be well-characterized.

5.6 Ex-situ Technologies for Groundwater

Treatment methods developed for drinking water, sewage treatment, and industrial effluent can be adapted, provided that the physical, chemical, and biological properties of the liquid to be treated and the design and operational requirements of the treatment system have been considered. Contaminated waters or soil may contain complex mixtures of contaminants at wide-ranging or very high concentrations. In addition, these concentrations may fluctuate over time, and the volumes of liquid to be treated and time scales may vary considerably. Often remediation projects are short term projects. These complex conditions have implications for cost, which will be higher for the remediation technology.

5.6.1 Pump - and - treat (P&T)

Cleanup of groundwater by P&T methods is probably the longest established and most commonly used in-situ remediation technology. P&T involves extracting contaminated groundwater through recovery wells or trenches and treating the extracted groundwater and reintroducing to the aquifer. P&T is complex because whilst pumping may effectively remove NAPL pools on or below groundwater, the pumping process itself

- may enhance diffusion gradients and
- contaminant mass transfer of soil-sorbed compounds and/or
- residually saturated NAPLs within the vadose zone,
- promoting the growth of existing NAPL pools or
- creating new pools.

Groundwater extraction often causes an initial decrease in contaminant concentrations in the extracted water, followed by a leveling of concentrations, and sometimes a gradual decline that is generally expected to continue over decades. The failure of P&T has been attributed to the failure of the flowing water to remove the residual saturated (i.e. immobile) phase of the contaminant from the soil.

Pollutants	**Activated carbon adsorption**	**Stripping**	**Biological degradation**	**Precipitation/ Flocculation**	**Ion exchange**
AHC	+	+	+	-	-
BTEX	+	+	+	-	-
hvCHCs	+	+	±	-	-
Vinyl chloride	-	+	±	-	-
Phenols	+	-	+	-	-
PAHs	+	±	±	-	-
HCs	+	±	±	-	-
Ammonium	-	-	+	-	-
Cyanides	-	-	-	-	+
Heavy metals	-	-	-	+	+

+ Suitable ± partly suitable - unsuitable

Fig. 11: Ex-situ Treatment Technologies for contaminated groundwater, leachates and surface water

5.6.2 Air stripping

Stripping with air or steam is used to remove dissolved volatile organic compounds from water. Air stripping involves transferring a dissolved substance from the liquid to the gas phase whereas steam stripping is essentially a distillation process in which the volatile contaminants are removed. The driving force of the removal is the concentration difference between the liquid an the air phases.

Air stripping can be accomplished using aeration tanks, cascade aerators, spray basis, or packed towers. The stripped water is collected at the bottom of the tower and the emissions may be treated by activated carbon. Factors that control stripping efficiency include tower height and diameter, the air-to-water ratio and the temperature. Packed towers include an aeration system, devices to insure that the mass transfer occurs optimally, and packing material (polypropylene).

5.6.3 Activated Carbon Adsorption

Adsorption is a physical mechanism based on the properties of some porous materials to fix molecules on their surface. Specific surface governs this mechanism. Adsorption on activated carbon is a widely used method for removing organic pollutants dissolved in water. Adsorption capacity values vary depending on the compounds to be removed.

5.6.4 Resin Adsorption

Resin adsorption is a physical-chemical process in which dissolved substances are removed from solution by synthetic or natural materials. The resins may be ionic or nonionic; the nonionic materials form stronger bonds which are harder to reverse. Therefore, weak ionic or nonionic resins are more widely used. Synthetic resin adsorbs dissolved substances by trapping and holding the solutes in its molecular structure. In comparison to activated carbon, resin adsorption is more selective for some compounds. Capital costs are low, operating cost are high.

5.6.5 Ion Exchange

Ion exchange is an adsorption process which has been demonstrated for removal of most inorganic dissolved salts, some organic dissolved substances and some low molecular weight lipophilic compounds.

5.6.6 Filtration

Filtration is an effective method that separates low levels of solids from an aqueous phase by passing through a semi-permeable medium. For contaminated groundwater granular media (sand) filters are used to filter suspended solids by gravity or auxiliary pressure. The filter bed is regenerated by back washing and removing solids by flocculation or sedimentation.

5.6.7 Reverse Osmosis

Reverse Osmosis (RO) is a filtration process by which inorganic salts and some organic substances are removed from solution by passing the contaminated groundwater through a semi-permeable membrane under pressure. The contaminants are concentrated on one site of the membrane while water passes through. Most commonly used membranes include cellulose acetate, polyamides, and polysulfones. The removing efficiency of organic compounds usually decreases with an increase in polarity and hydrogen bounding with the filter.

5.6.8 Chemical or UV Oxidation

UV/oxidation processes combine the use of ultraviolet light (UV) and chemical oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2) to destroy organic contaminants in groundwater. In most UV/oxidation processes, high intensity UV radiation is combined with H_2O_2 to oxidize organic contaminants to Carbon dioxide and water.

A wide variety of organic contaminants are susceptible to destruction by UV/oxidation. UV has most often been used for contaminant concentrations in groundwater below 500 mg/l. A key advantage of the technology is that it is a destruction process, as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase.

The process is only efficient at rather low wavelengths (<200 nm). The stream treated must provide for good transmission of UV light, should be relatively free of heavy metal ions and have low alkalinity and carbonates. The cost may be higher than competing technologies because of energy requirements.

5.6.9 Ion exchange

This process is employed for removing dissolved anions in contaminated groundwater. Removal method can be percolation through specific resins or clays.

6 Conclusion

The selection of the appropriate technology is critically **dependent upon the goals** which are set for site remediation (which can be defined on various levels, e.g. reduction of potential or reduction of actual risk) and the remediation strategy: e.g. a risk reduction/management strategy may suggest the use of pump and treat systems, physical and/or hydraulic containment systems.

The **remediation strategy** developed for a particular site may combine both approaches and several different methods. Different mobility of the components of a mixture of contaminants will require different methods, strategies and priorities of remediation.

Integrated strategies consisting e.g. of P&T for hydraulic control and dissolved plume mass removal combined with source targeted technologies have been determined to be a most effective long term solution in many cases and may lead to cost-effective remediation measures specifically suitable to large industrial areas, where the source zones are often poorly defined or hardly accessible.

Selection and integration of technologies should use the most effective contaminant transport mechanisms to arrive at the most effective treatment scheme. To assess the applicability and potential performance of technologies, information is required on the contaminants present and the physical, chemical, and biological properties of the material to be treated.

Remediation of Contaminated Sites – Strategies

Martin Bittens

Helmholtz Centre for Environmental Research – UFZ, Germany

Introduction

In Germany and other European Countries, a large number of regions exist where industrial, military and mining activities during the past century have led to vast contaminations in soil, groundwater and surface waters.

Main features of these sites are:

- The occurrence of multiple sources with usually unknown extent
- A multitude of large contaminant plumes in groundwater
- The presence of multi-compound mixtures
- The extreme investigation and remedial costs for site revitalization

Large-scale contaminated sites may severely affect human health, the environment and the economy. Currently some 20,000 of these so called megasites exist in Europe (including CEE States) with estimated costs for required revitalization measures that exceed the amount of 100 Billion Euros. These figures clearly demonstrate that revitalization of megasites demands innovative site investigation and remediation strategies to make it economically feasible.

Strategic Background

Streamlining site investigations and cleanup decision a dynamic framework is needed that allows project managers to achieve clearly defined project objectives. According the TRIAD approach which is being recommended by the U.S Environmental Protection Agency following elements should be integrated in such an approach (EPA, 2005):

a. A systematic planning, to assure that the level detail in project planning matches the required use of collected data
b. A dynamic work plan that relies on real-time data to reach decision points
c. On-site analytical tools that make dynamic work plans possible

The TRIAD approach links decisions, data and technologies (Figure 1).

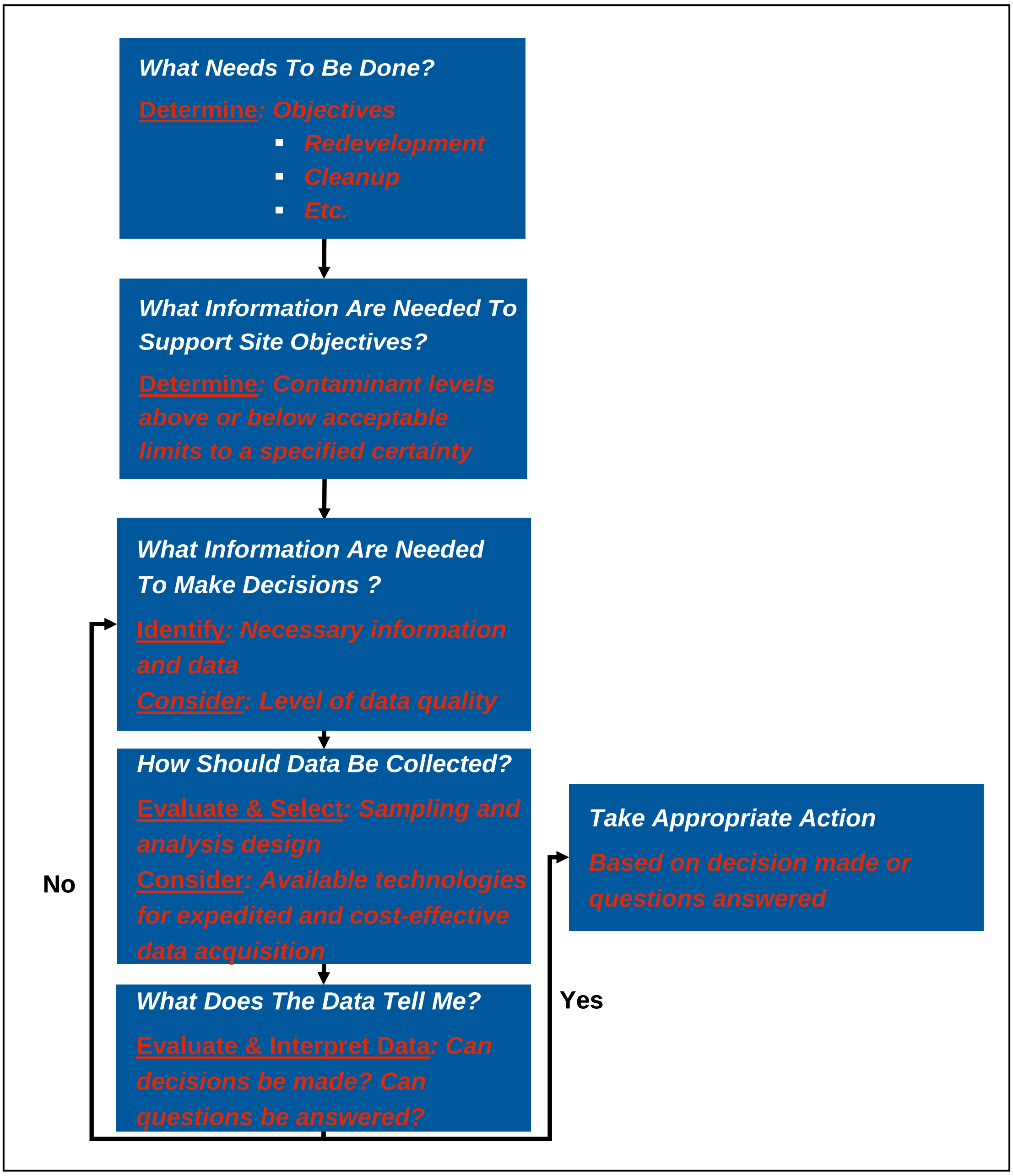


Figure 1:Linking Decisions, Data and Technologies

Site Investigation

In preparation of effective site investigation measures a series of factors need to be considered:

- What technologies are available (expedited and high resolution investigations, data collection)?
- What are potential exposure pathways?
- Hot spot detection

- Background level of contaminants of concern (COC)?
- Are the infrastructure systems contaminated?
- Assess the risk the site may pose to human health and the environment
- Design a conceptual site model (CSM)
- Calculate cleanup levels
- Examine unacceptable environmental conditions (cost for site improvement, operation, and maintenance)

Some of the factors are of particular relevance in developing an appropriate remediation strategy for large scale contaminated sites and will be discussed in detail in the followings chapters.

CSM

The Conceptual site Model (CSM) is one of the primary planning tools that can be used to support the decision making process managing contaminated land and groundwater on a large scale. The CSM organizes available information about a site in a clear and transparent structure and facilitate the identification of data and information gaps. Once the CSM is established, additionally needed data can be gathered and integrated in the CSM, followed by a revision of the CSM and a refinement of decision goals, if required. Thus, the CSM matures and enables an improved understanding of the site characteristics, such as contamination status, receptor profiles, etc., and the re-adjustment of decision criteria.

Characterization of the Conceptual Site Model approach

Following information needs to be integrated in a CSM:

- Site contamination concerns by graphical or written representations (or "conceptualizations"),
- How contaminations got at the site?
- Whether or not contaminations are migrating or degrading?
- How variable concentrations are across the site?
- What receptors might be exposed?
- What risk-reduction strategies are most feasible?

Once the CSM is established, it can be used as a basis to:

- Support the development of a framework for conducting and scoping a site investigation of the site or cleanup action that takes into account the future land use
- Elaborate a detailed description of the site and its setting that is used to form hypotheses about the release and ultimate fate of contamination at the site
- Identify sources of contamination at the site, potential chemicals of concern, and the media (soil, groundwater, surface water, and structures) affected
- Quantify how contaminants may be migrating from the sources, and the media and pathways through which migration and exposure of potential human or environmental receptors could occur (including possible air releases)
- Evaluate of potential or preferred cleanup options
- Develop site-specific sampling designs and procedures for sample collection and analysis
- Estimate site conditions that may lead to unacceptable risks and warrant further study

By integrating permanently data and information to a CSM in a step-wise fashion, it achieves an increasing level of complexity. During the life cycle of a CSM following maturity levels will be achieved:

(a)Maturity Level I:

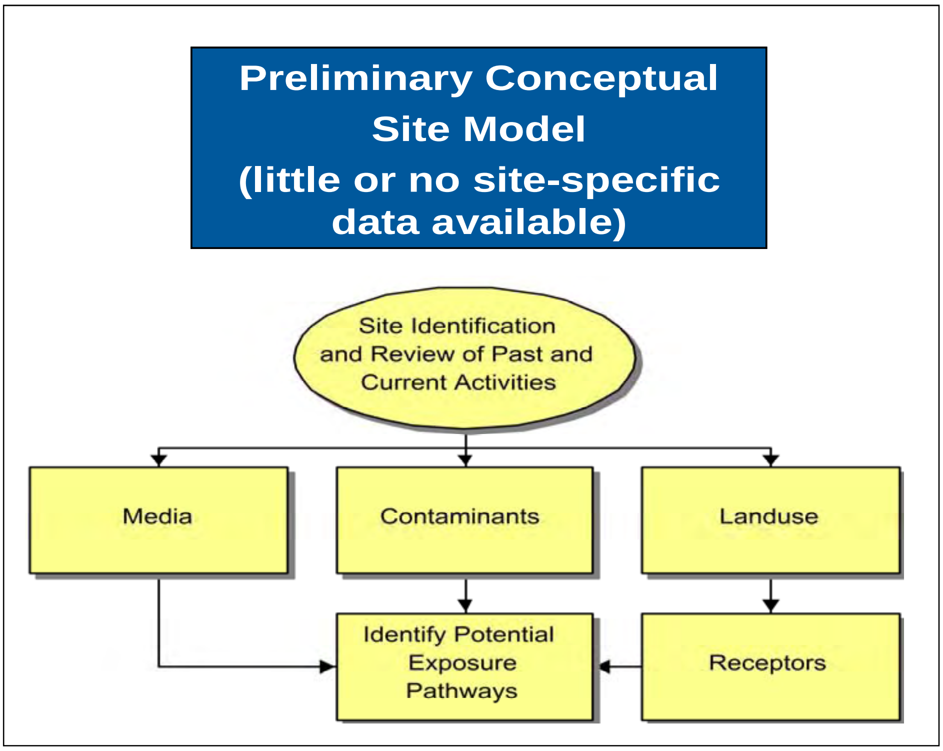


Figure 2:CSM – Maturity Level I

Maturity Level I – Key Decisions

1. Is there a potential threat to human health and the environment?

2. Which chemicals from what media pose a potential risk under the land use scenario?

(b)Maturity Levels II, III

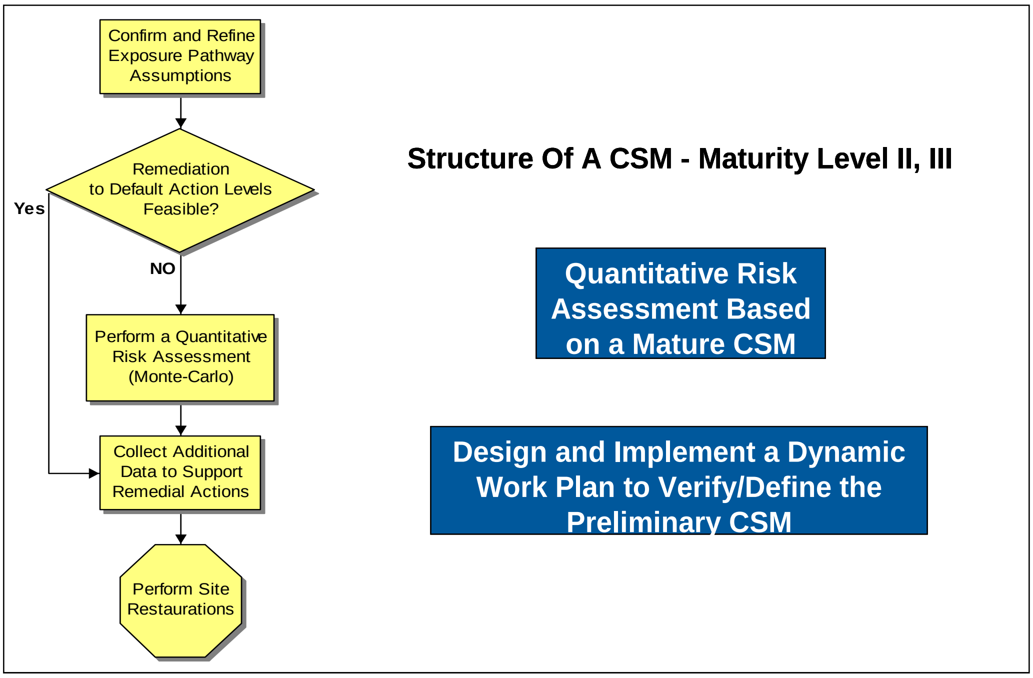


Figure 3:CSM – Maturity Levels II and III

Maturity Level II, III – Key Decisions

1. Does a risk exist above tolerable levels based on default criteria?

2. What action level would be acceptable based on default risk criteria?

3. Based on realistic exposure and response scenarios, what site cleanup goals or action levels are required?

At maturity level III a CSM should give reliable answers to following questions:

- What is the proposed reuse or current use of the site?
- Is the proposed reuse of the site politically, economically, and socially viable?
- What media are impacted and by what type of contamination?
- Are there any potentially complete receptors pathways networks present at the site?
- What exposure point concentration might represent a potential risk?
- Do the exposure assumptions used in the risk assessment match the reuse scenario?

- What method reporting limits are needed to assure the delineation of potential hot spots?
- What are some of the available remedies for the site?
- What are the potential human exposure pathways?

It should be noted that a CSM:

- May not be limited to soil and groundwater contamination,
- Need to consider all potential exposures and receptors, e.g. human health, ecological receptors.

CSM Data Acquisition and Data Sources

In order to build-up a complete, full-matured CSM data and information are required from different areas or disciplines:

- Archeological/Historical Use,
- Sources: archives, historical databases,
- Physiography: region with similar geologic structures and climate,
- Sources: geological state offices, planning divisions of communities and cities,
- Climatic data: hydrologic budget, fauna, flora, and land use, precipitation rates, air temperature, and prevailing wind speed and direction,
- Sources: worldwide weather stations (www.worldclimate.com/worldclimate, meteorological offices),
- Geology: types of geologic materials, structural geologic features, depositional environments, and geomorphology,
- Sources: geological state offices,
- Hydrogeology,
- Aquifer characteristics:
    a. Type (examples: unconfined, confined, or semi-confined),
    b. Characteristics (examples: hydraulic conductivity, transmissivity, storitivity)
    c. Geology (materials and structure),
- Hydrologic budget:
    a. Recharge rates (examples: precipitation, artificial recharge),

    b. Discharge rates (examples: evaporation, transpiration, groundwater pumping),

- Groundwater flow:
  a. Hydraulic gradient (examples: groundwater elevations, flow direction),
  b. Flow velocity (travel time),
  c. Boundary conditions (examples: Dirichlet, Neumann),

  Sources: water agencies, geological state offices, research institutes.

CSM Models and Tools

- Spatial Analysis Decision Assistance (SADA): A software program that integrates visualization, geospatial analysis, statistical analysis, human health and ecological risk assessment, cost-effective analysis, sampling design, and decision analysis (www.tiem.utk.edu/~sada/)
- U.S. EPA Field Environmental Decision Support (FIELDS): An ArcView® extension that combines geographic information systems (GIS), global positioning systems (GPS), database analysis, and imaging technologies to identify, assess, communicate, and help solve environmental problems; includes modules for human health and ecological risk assessment, sampling design, remediation design (www.epa.gov/region5fields/)
- U.S. DOE Pacific Northwest National Laboratory Visual Sampling Plan (VSP): VSP provides statistical solutions for sampling design to decide where samples should be collected and how many are needed (http://dqo.pnl.gov/vsp)
- Center for Subsurface Modeling support (CSMoS): CSMoS provides public domain groundwater and vadose zone modeling software (www.epa.gov/ahaazvuc/csmos.html)
- Center for Exposure Assessment Modeling (CEAM): CEAM provides proven predictive exposure assessment techniques for aquatic, terrestrial, and multimedia pathway for organic chemicals and metals (www.epa.gov/ceampubl/)
- Army Risk Assessment Modeling System (ARAMS): ARAMS is a computer-based, modeling- and database-driven analysis system for estimating human and ecological health impacts and risks associated with MRCs and other potential contaminants of concern. ARAMS is based on a widely accepted risk paradigm that integrates exposure and effects assessments to characterize risk (http://www.wes.army.mil/el/arams/arams.html)
- OnSite OnLine Tools for Site Assessment (OnSite): The OnSite set of online tools for site assessment contains calculators for formulas, models, unit conversion factors and scientific demonstrations to assess the impacts from ground water contaminants (http://www.epa.gov/athens/onsite/)

CSM Examples

(a) Graphical Solution – Exposure Pathways

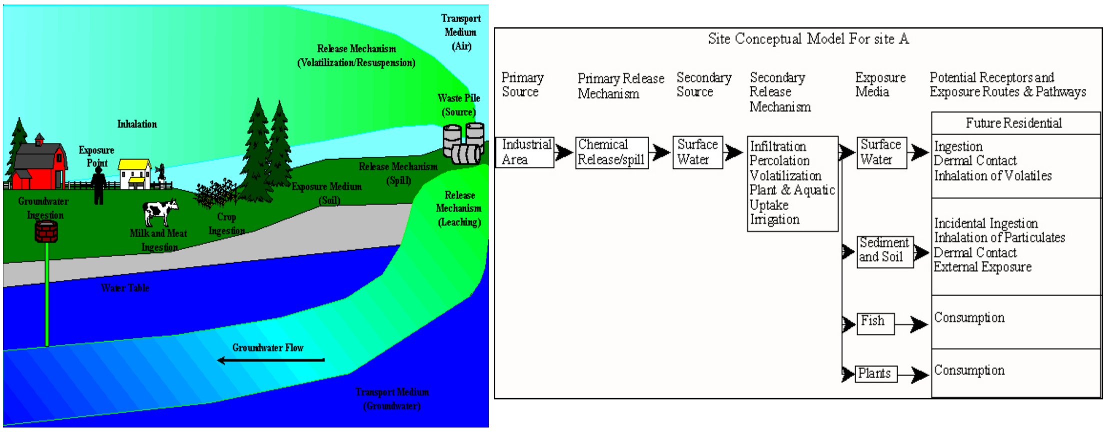
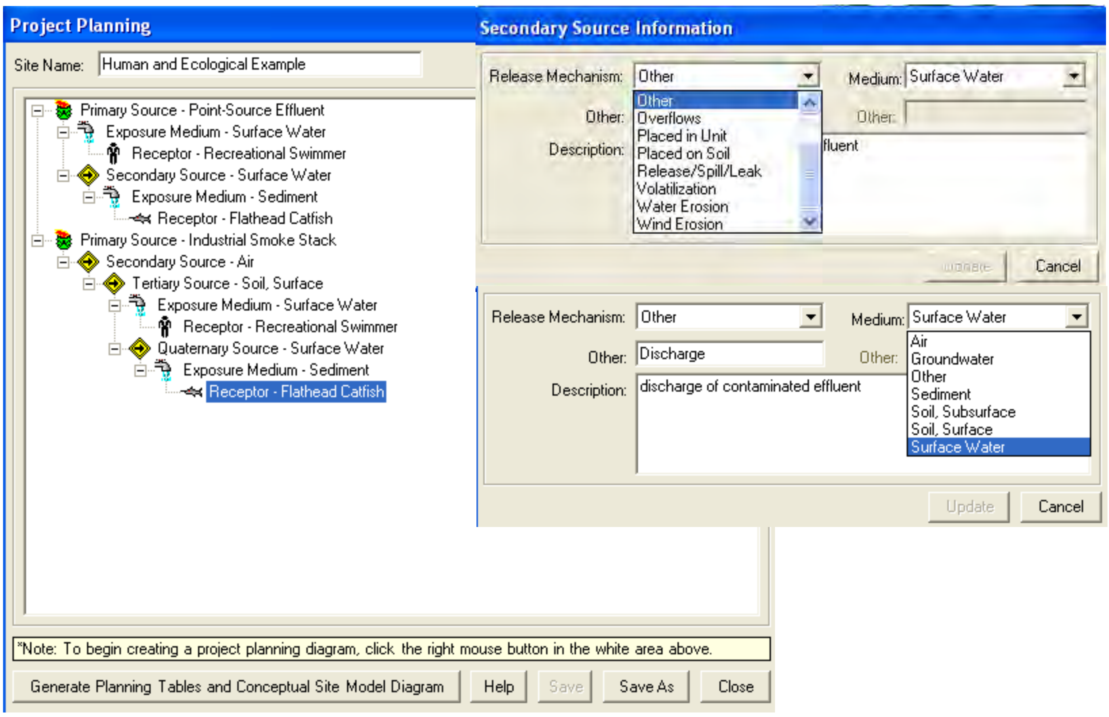


Figure 4: Classic Graphical Conceptual Model/Stem-and-Leaf Conceptual Model

(b) Computer Based Solution (1) – Exposure Pathways



Site Name: Human and Ecological Example

- Primary Source - Point-Source Effluent
  - Exposure Medium - Surface Water
    - Receptor - Recreational Swimmer
  - Secondary Source - Surface Water
    - Exposure Medium - Sediment
      - Receptor - Flathead Catfish
- Primary Source - Industrial Smoke Stack
  - Secondary Source - Air
    - Tertiary Source - Soil, Surface
      - Exposure Medium - Surface Water
        - Receptor - Recreational Swimmer
      - Quaternary Source - Surface Water
        - Exposure Medium - Sediment
          - Receptor - Flathead Catfish

Release Mechanism: Other
Other
Overflows
Placed in Unit
Placed on Soil
Release/Spill/Leak
Volatilization
Water Erosion
Wind Erosion
Other:
Description: fluent
Medium: Surface Water
Other:

Release Mechanism: Other
Other: Discharge
Description: discharge of contaminated effluent
Medium: Surface Water
Air
Groundwater
Other
Sediment
Soil, Subsurface
Soil, Surface
Surface Water
Other:

*Note: To begin creating a project planning diagram, click the right mouse button in the white area above.

Figure 5:Computer Based CSM (ARAMS/FRAMES)

(c) Computer Based Solution (2) - Modeling

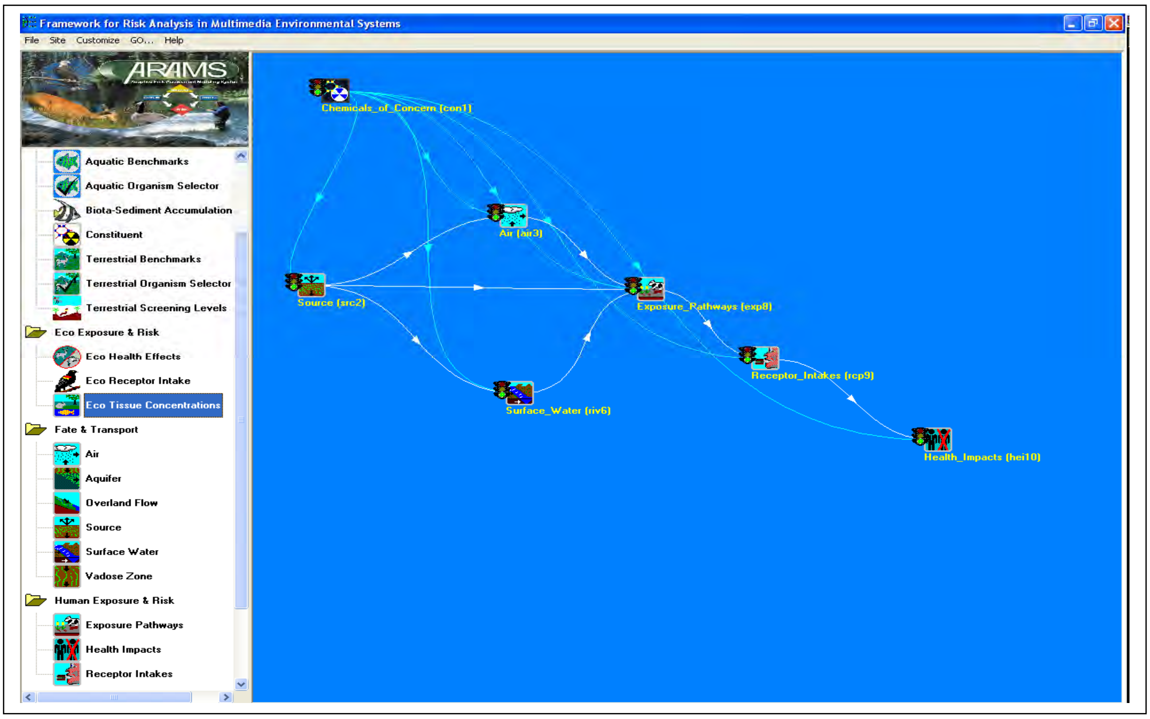


Figure 6: Computer Based CSM (ARAMS/FRAMES) – Multimedia Fate, Transport and Risk Modeling

(d) Computer Based Solution (3) – Risk Calculation

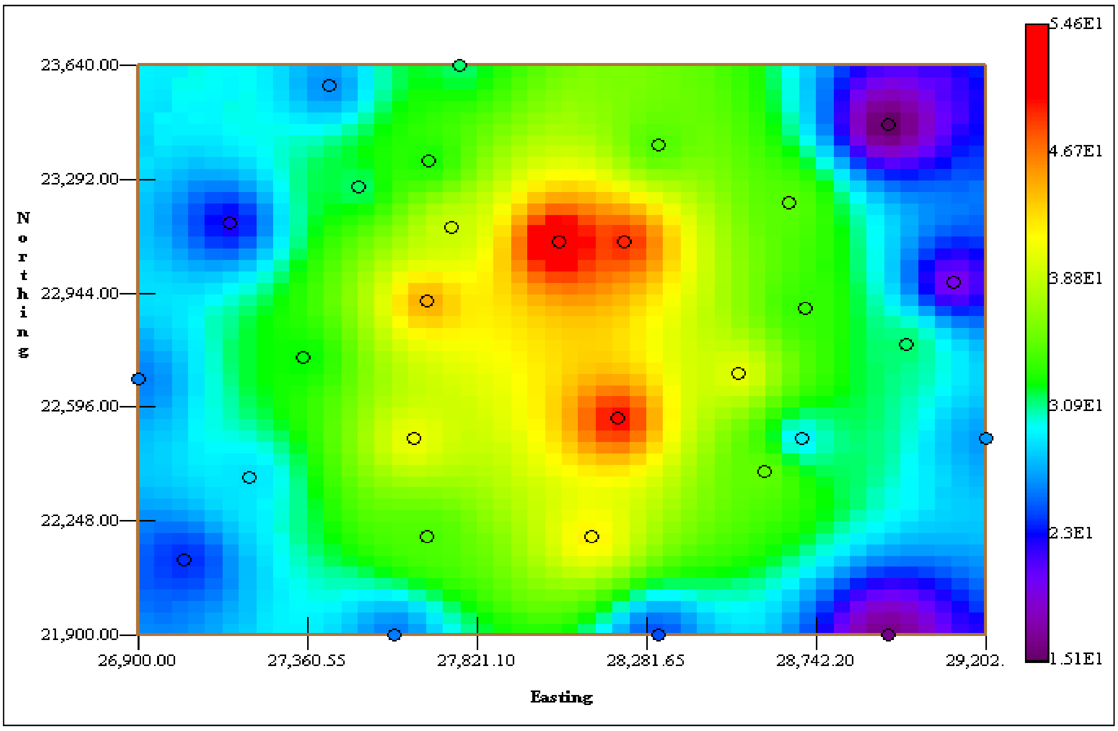


Figure 7: Computer Based CSM (SADA) – Risk Map/Spatial Distribution

(e) Computer Based Solution (3) – Uncertainty

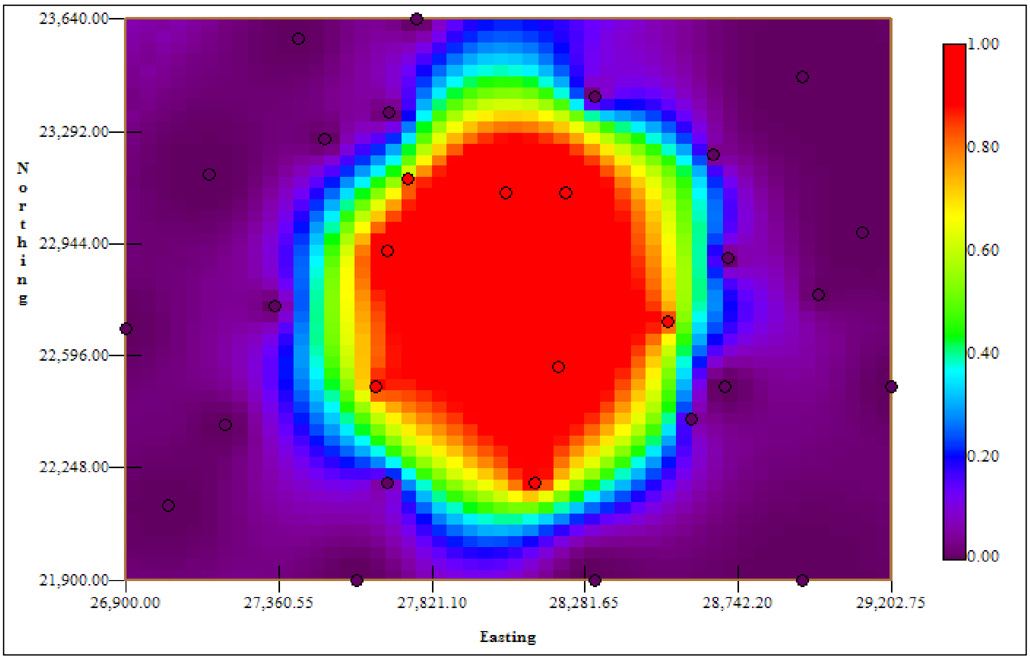


Figure 8: **Computer Based CSM (SADA) – Risk Probability Map**

(f) Computer Based Solution (4) – Areas of Concern

Using Preliminary Remediation Goals (PRG), Areas of Concern (AOC) can be identified. PRG are obtained by back calculation from acceptable or tolerable risks. They represent chemical-specific concentration goals for individual chemicals in specific medium and land use combinations.

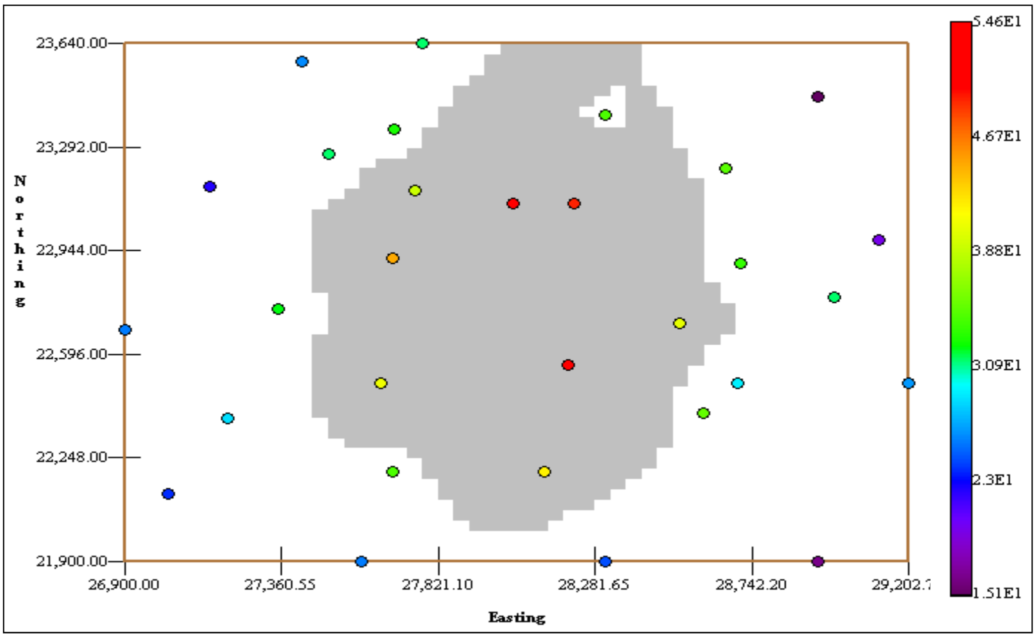


Figure 9: **Computer Based CSM (SADA) – Risk Based Area of Concern**

Hot Spot Detection

The detection of hot spots is essentially for the design of source removal measures. Particularly on contaminated sites of large extent, the hot spot search would cause enormous costs if it is performed on basis of soil and/or groundwater samples taken from a regularly grid mesh. A more cost effective approach is the application of geostatistical methods which allow the hot spot identification under definite boundary conditions. Originally encoded as Ellipgrid PC by Oak Ridge National Laboratory a 2d initial Ellipgrid model can be applied to calculate (SADA 2008):

- the probability of hitting or, conversely, missing an elliptical hot spot of a defined size
- the maximum size of a hot spot that would, with a defined probability, be hit by a sample grid definition
- a grid of samples based on finding a hot spot of a defined size with a distinct probability

If any two of the three parameters are known, SADA calculates the third one:

Probability	**Size & Shape**	**??**
Probability	**??**	**Grid Specs**
??	**Size & Shape**	**Grid Specs**

Figure 10: SADA Algorithm for 2D Hot Spot Search

The concept of hot spot searches in two dimensions can easily be extended into the third dimension through the use of simulation. A grid is specified in three dimensions, and the location of ellipsoids is simulated across the site. The likelihood of hitting such a hot spot is simply the ratio of simulated hits to total simulations (SADA, 2008):

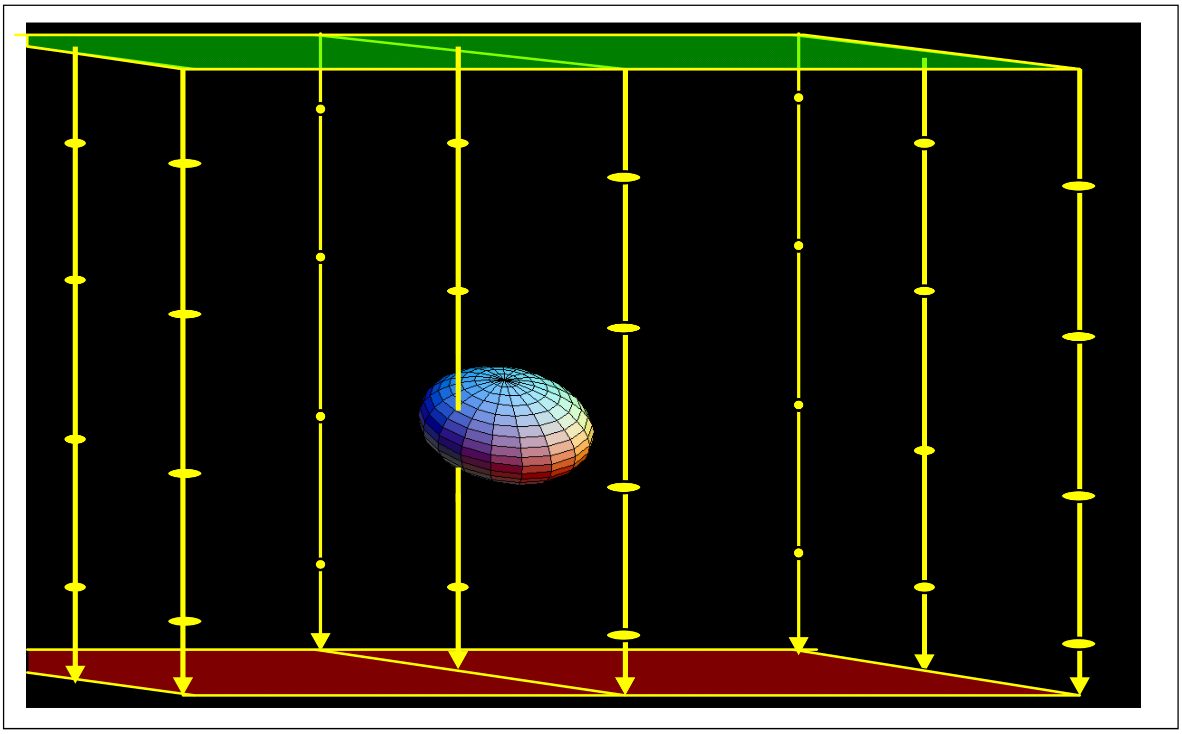


Figure 11: **SADA 3D Hot Spot Search**

Literature

EPA, 2005 Road Map to Understand Innovative Technology Options for Brownfields Investigation and Cleanup, Fourth Edition. U.S. Environmental Protection Agency. EPA-542-B-05-001.SADA ,2008

Spatial Analysis and Decision Assistance (SADA) Version 5. Environmental Assessment Methods in SADA: Initial Sample Designs. Presented by Robert Stewart, April 2008. University of Tennessee, Knoxvill.

Bayerisches Landesamt für Umwelt

Remediation of the chemical production facility of Marktredwitz

Gernot Huber

Bavarian Environment Agency, Germany

Introduction

The “Chemische Fabrik Marktredwitz” (CFM) site occupies 0.5 square kilometres and was previously operated as a chemical production facility. It is located in the centre of Marktredwitz, Bavaria, Germany close to the border of the Czech Republic (fig. 1).

Founded in 1788, CFM was one of the oldest chemical manufacturing facilities in the world. Mercury was processed at the CFM site for the production of pesticides, herbicides, and other mercury-containing products. The facility was closed down in 1985.

CFM caused serious environmental pollution during the centuries of operation. The main contaminant was mercury, which was not only accumulated on the premises, but was transported – by exhaust air, effluents and waste – into the city of Marktredwitz and downstream the rivers Röslau and Kösseine with their flood plains (fig. 2).

This is an overview of the measures performed during remediation of the CFM, i.e. one of the most important Hg- contaminated sites in Germany, and of projects accompanying the remediation as well as follow-up projects in the vicinity of the site. Decontamination and restoration of the contaminated site and its surroundings was done between 1986 and 2000; follow-up measures last until today.

Basic studies on the case-specific risk assessment for Marktredwitz

A research project on risk assessment for the mercury-contaminated site in Marktredwitz (LGA/GKSS, 1992) was realised prior to the remediation of the CFM.

Analytical methods for the determination of mercury, especially the differentiation of inorganic and organic forms of Hg, have been tested, and the Hg content of soil, water and air was measured in Marktredwitz and its surroundings. Transport pathways for mercury by air and water have been specified.

Some results are summarized as follows: mercury was detected primarily bound to fine fraction of the soil up to 90 mg/kg, methyl-, ethyl- and phenyl-mercury up to 131 µg/kg, 11 µg/kg and 0.6 µg/kg (especially in the upper soil layers). Average daily discharge of mercury (primarily bound to high molecular colloids) on the soil–water pathway has been determined up to 0.11 µg/m²d, on the soil-air pathway (with a share of organic species of 9 - 15%) up to 51 µg/m² d. In the grass of the Kösseine meadows maximum mercury content of 6.9 mg/kg was documented.

Remediation of the CFM premises

The premises of the CFM were located in the centre of Marktredwitz adjoining the river Kösseine. Infiltration of liquid waste, deposition and incineration of refuse and production residuals as well as accidents caused a severe Hg - contamination of the site. A detailed investigation revealed elevated mercury content in the buildings (up to 3 300 mg/kg in brick-structures), in the soil (up to 5 000 mg/kg) and in soil- and groundwater (up to 200 mg/l in infiltrating wastewater). The vertical expansion of the Hg-contamination was about 4 m, locally up to more than 7 m, into the sub-soil. Due to these facts, a complete decontamination of the premises was done between 1986 and 1996 (Kolb, 1999).

Deconstruction of the buildings and soil excavation

The remediation was done step by step:

- Disposal of production residuals from highly contaminated production lines and storage areas (e.g. sub-surface dumps), deconstruction of contaminated production lines (e.g. distillation and incineration), deconstruction of supply and return systems and of the dilapidated sewer system.
- Deconstruction of building parts with highest contamination (i.e. plastering) and demolition of the buildings under protective enclosure.
- Excavation of soil – partially containing liquid mercury – down to 7 m below ground level. Most relevant contaminations were found in areas with broken down sewers or fissured foundations. The remediation target of 10 mg/kg at the base of the excavation was reached in most areas.

Groundwater drainage and groundwater remediation

During demolition and excavation a groundwater drainage and clean-up system was operated (fig. 3). For the protection of the nearby river Kösseine a vertical groundwater barrier (200 m length / 20 m depth) was installed. The backwater was extracted from remediation wells within the premises; decontamination of the Hg-polluted groundwater was done by a 3-step water treatment facility. The remediation target for groundwater was 1 µg/l Hg.

Cleaning-up and disposal of contaminated materials

In the process of remediation 100 000 metric tons of contaminated residues from deconstruction / demolition and excavation were dealt with. The disposal route for the material was predisposed by the level of contamination. Material with lower concentration of mercury (35 000 metric tons; < 50 mg/kg Hg) was deposited in a mono-landfill, which had been built for this remediation project. Medium charged material (55 000 metric tons; 50 – 5000 mg/kg Hg) was treated in an off-site soil treatment facility, also specially constructed for the remediation of the CFM, and afterwards deposited on the mono-landfill. Material with a very high content of mercury (5 000 metric tons), e.g. production residuals and plaster from brick buildings, were deposited in a sub-surface landfill (Neufa-Herode, 800 m below surface level).

Mono-landfill

The mono-landfill with a fill volume of 145 000 m³ was set up close to the soil treatment facility near Marktredwitz. The 4-ply mineral base sealing is 1 m thick, the 3-ply mineral surface sealing is 0.75 m thick (kf < 5 x 10-10 m/s).

Soil treatment facility

The soil treatment system (modular system, process units preassembled in about 60 containers) consisted of two main processes: soil washing and vacuum distillation (fig. 4). The principle of this combined treatment process is to concentrate the mercury in the fine-grained portion of the soil by soil washing (blade washers and an attrition scrubber dislodge the mercury and other contaminants from the soil particles, the mobilized contaminants are separated by means of classification, sorting, rinsing, and dewatering) and to clean the resulting highly contaminated, fine particle fraction using vacuum distillation (the mercury and other compounds are volatilized from the solids due to a thermal evaporation process at low pressure conditions of 50-150 hPa and an average temperature of 350 to 400°C) as a downstream treatment. An additional treatment system incorporated water treatment and process air treatment. Residual Hg-concentrations after treatment have been documented to be well below 50 mg/kg, even if peaks of very high input concentrations amount to more than 5 000 mg/kg mercury (Gröschel W., Defregger F.,1988).

Total cost

The total cost for the decontamination of the CFM premises was about 90 million € (in 1996).

Revitalisation of the CFM premises

The premises in the centre of Marktredwitz were completely decontaminated and could thus been made available for different types of uses. Today an office and shopping centre – now an important part of the townscape - is located on the site. Figure 5 shows the deconstruction and excavation areas after finishing the remediation measures and after constructing the shopping mall on the site.

Measures in the vicinity of the CFM: the city of Marktredwitz

Due to exhaust air (among others distillation of mercury, incineration of Hg- containing waste) and the deposition and relocation of refuse and production residuals in the surroundings of the production facility, parts of the centre of Marktredwitz were contaminated, too. A total content of mercury in the soil up to 180 mg/kg was determined (higher values were measured locally on wastelands, on landfills and on the banks of the river Kösseine).

In order to classify the contamination near the CFM and to evaluate the environmental health risk from possible exposure to Hg-contamination for the inhabitants of Marktredwitz, two comprehensive research projects (gsf, 1995 und 1998) were carried out. Risk assessment was based on information from 1 300 sampling sites with 8 000 data concerning concentration of mercury mainly in soil, water, air, plants and vegetables.

Risk assessment was done by a quantitative exposition estimate based on modelled transfer rates and doses for the mass transport soil to human, plant to human and air to human. A human bio-monitoring (blood and urine) of inhabitants of the city of Marktredwitz was performed and an environmental health risk assessment for the population was established.

Threshold values for mercury in soil for different types of uses were derived. The most vulnerable uses were housing areas with gardens (subject of protection: infant). The trigger value for mercury was 33 mg/kg; the action value was 178 mg/kg.

The following conclusions and measures were deduced from the research projects:

- In housing areas with gardens (residential areas) measured Hg - content was normally below the action value. The exposition for this type of use was without health risk, in general.
- Regarding the precautionary principle, the decontamination of gardens in housing areas in Marktredwitz was already performed for soil concentrations above the trigger value. Soil samples were taken from the gardens, the Hg- content was determined and for cases with Hg- content above trigger value, the topsoil was excavated and the site was refilled with uncontaminated soil.
- All investigations of urine and 90 % of all blood investigations of the inhabitants did not attract attention. According to GSF (1995 und 1998), even elevated Hg- content in blood samples (up to 24 µg / l) did not pose any health risk.
- Personal correlation between content of mercury in blood and soil was not proven. For the exposure pathway in-house contamination constituted the main part.
- In addition to the decontamination of gardens in housing areas, playgrounds in the city of Marktredwitz were decontaminated. Behaviour recommendations for residents were given.

Measures in the vicinity of the CFM: River and flood plains of Kösseine and Röslau

The severe contamination of the rivers Kösseine and Röslau was caused by discharge of contaminated wastewater into the river for a long period of production and by infiltration of highly loaded liquid waste from broken sewers at the premises. The transport of mercury bound to suspended solids and sediments in the river system and thus to the adjacent flood plains was observed up to 15 km downstream the CFM, even into the neighbour country, the Czech Republic (fig. 6). An overview of some of the highest Hg-concentrations in the environment determined between 1970 until now is given in figure 6. Measures downstream the CFM are reviewed in the following paragraphs (Huber G., Stuhrmann M., 1999).

Removal of highly contaminated river sediments

The sediments of the river Kösseine and Röslau are loaded with mercury up to 700 mg/kg (fig. 7). River sections with most elevated Hg-content due to increased sedimentation, especially fourteen backwaters (river barrages), two bayous and a cooling water pond of a power plant, were decontaminated by sediment removal. The sediment clearance was done using three techniques – excavation/dredging and ground suction after lowering water level and ground suction without lowering water level. A total of 34 000 metric tons of highly contaminated sludge was extracted. Thus more than 900 kg Hg were recovered from the river system.

Risk assessment for groundwater and drinking water

Annual inundation caused sedimentation of highly contaminated material onto the meadows and generated a relevant pollution of the soils downstream the CFM. Comprehensive soil and groundwater investigations in the flood plains as well as transport modelling were performed to estimate potential input of mercury from contaminated soil into the groundwater and in order to asses the risk for groundwater and drinking water quality (Biersack M., Röder R., 1999). Further downstream of Marktredwitz an important amount of drinking water is extracted from the deeper basement of the Röslau valley.

The alluvial soil in the meadows / flood plains reached Hg-concentrations of about 170 mg/kg near surface; a distinct decrease in concentration with depth was seen (fig. 8). A relevant input of mercury into the groundwater could not be detected until now and is not to be expected due to a low mobilisation potential (leachate concentrations << 5 µg/l, also at low pH). An endangerment of the drinking water supply of the local population could be denied.

Agricultural use in the flood plains: grassland farming

The contaminated meadows are used for grassland and for the production of cattle foodstuff (forage). Grass from selected fields is periodically sampled and evaluated for the foodstuff use (< 0.1 mg/kg). In order to ensure the agricultural use of the meadows as far as possible advisory notes concerning the agricultural practice have been worked out. Grass with Hg-content above 0.1 mg/kg is composted or used in bio-gas production; alternatively, higher contaminated areas are set-aside.

Human uses in the flood plains: playground, allotment gardens, market gardening

Areas with potential vulnerable uses in the flood plains, i.e. playgrounds, fields with vegetables (market gardening, allotment gardens) were mapped, soil-sampled and evaluated. The results of the use-specific assessment of the contamination were discussed with persons concerned; recommendations for case-specific measures were given. A playground was excavated and a field for market gardening was set-aside.

Bio-monitoring 1970 – 2007

The effect of mercury input into the river system and the corresponding ecosystems (i.e. water, suspended matter, sediment and macrophytes, macro-invertebrates, fish) has been monitored for nearly 40 years (Wachs B., 1999). Thus the consequences of the close-down of the CFM and of the remediation measures could be evaluated. The Hg input had caused a serious contamination of the environment downstream the CFM, but a considerable reduction of environmental concentrations after the close-down and the remediation could be reached (fig. 9, 10 -12). Thus, clean-up measures were effective even for areas farther downstream the CFM. However, the contamination that developed during centuries could not be remediated completely. Mercury concentrations in the environment are still well above background level in some areas and this will be the situation for any length of time.

Germany-Czech Republic: Transboundary commission for water quality protection

The effect of the past pollution from the CFM was not only limited to the German national territory. In the river system mercury was transported across the national border to the Czech Republic and an export of mercury - but in considerable lowered amounts - is still going on (fig. 2). Measures are realised in close contact to the Czech neighbour country. The Czech-German (Bavarian) transboundary commission for water quality protection co-ordinates monitoring programs and discusses monitoring results as well as possible further measures to reduce the mercury transfer to the Czech surface water system.

Conclusions

Some results and conclusions of the remediation of the CFM can be summarized as follows:

- The remediation of one of the greatest Hg-contaminated sites of Germany required enormous time and effort (>> 10 years and > 100 Mio €).
- The brownfield restoration of the CFM was a great success: a complete decontamination of soil and groundwater at the site and a revitalisation of central parts of the city could be achieved.
- The comprehensive scientific research indicates: there is no fundamental threat to human health – personal safety of the inhabitants of Marktredwitz could be confirmed.
- A substantial reduction of Hg content in the river ecosystem over a wide area due to closing down and remediation of the CFM and its surroundings could be achieved – but: contamination will still exist in future, further efforts are necessary.
- Local input of pollutants caused wide area contamination – remediation of emission sources as soon as possible is necessary.

Acknowledgment

I am very grateful to Dr. Bettina Haas for support in proof-reading and translation of this publication and Oliver Beckert in compiling the figures.

Literature

Biersack M., Röder R.: Mobilität und Mobilisierbarkeit von CFM-spezifischen Stoffen in den Flussauen unterhalb von Marktredwitz. In: Stadt Marktredwitz: Bodenschutz und Altlastensanierung Marktredwitzer Bodenschutztage, 1, 58 - 62 (1999).

Gröschel W., Defregger F.: Cleaning of Mercury-Contaminated Soil Using a Combined Washing and Distillation Process. In: NATO/CCMS Pilot Study, Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater, PHASE II, FINAL REPORT, 1998.

GSF: Zusammenfassung zum Projektvorhaben „Standortgerechte Bewertung der Belastung im Umfeld der Chemischen Fabrik Marktredwitz“, 1995.

GSF: Zusammenfassung zum Projektvorhaben „Expositionsanalytische Untersuchung von gesundheitsrelevanten Kontaminationen im Umfeld der ehemaligen Chemischen Fabrik Marktredwitz und standortgerechte Ableitung von Handlungsempfehlungen“ 1998.

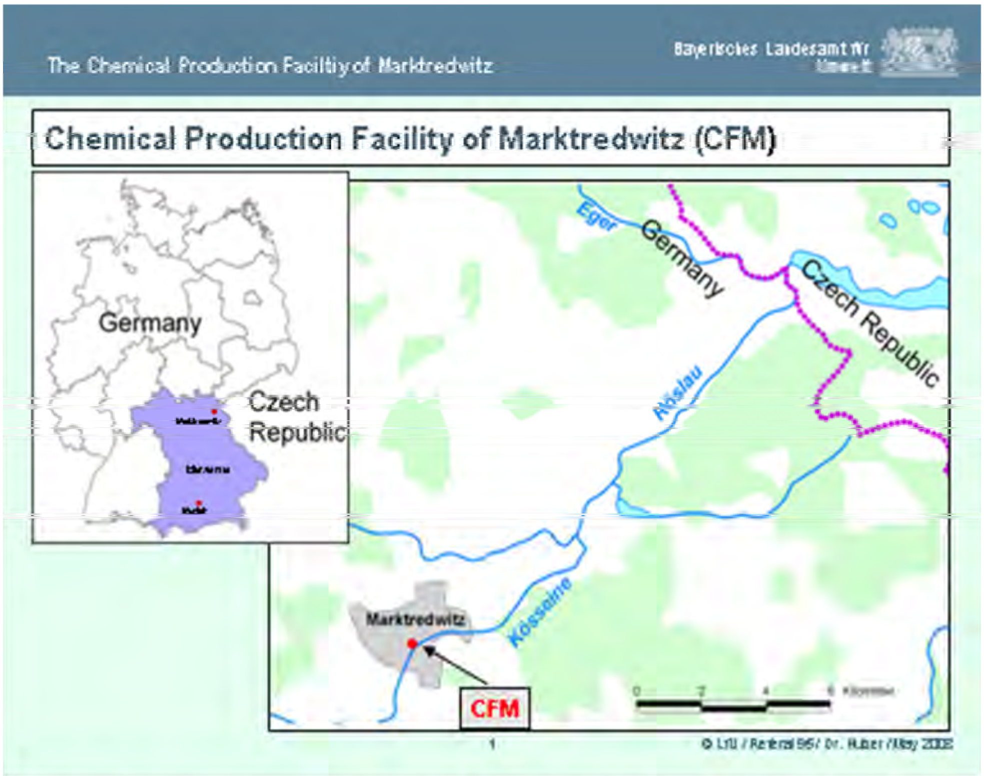
Huber,G., Stuhrmann M.: Übersichtsvortrag: Altlastensituation am Tagungsort. In: Stadt Marktredwitz: Bodenschutz und Altlastensanierung Marktredwitzer Bodenschutztage, 1, 43 - 47 (1999).

Kolb K.: Sanierung der Chemischen Fabrik Marktredwitz. In: Stadt Marktredwitz: Bodenschutz und Altlastensanierung Marktredwitzer Bodenschutztage, 1, 48 - 52 (1999).

LGA/GKSS: Schlussbericht zur „Untersuchung des Gefährdungspotentials von quecksilberkontaminierten Standorten in Bayern“, 1992.

Wachs B.: 30 Jahre Biomonitoring auf Quecksilber im Vorflutersystem des Raumes Marktredwitz. In: Stadt Marktredwitz: Bodenschutz und Altlastensanierung Marktredwitzer Bodenschutztage, 1, 53 - 57 (1999).

Figures:



The Chemical Production Faciltiy of Marktredwitz

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Chemical Production Facility of Marktredwitz (CFM)

1

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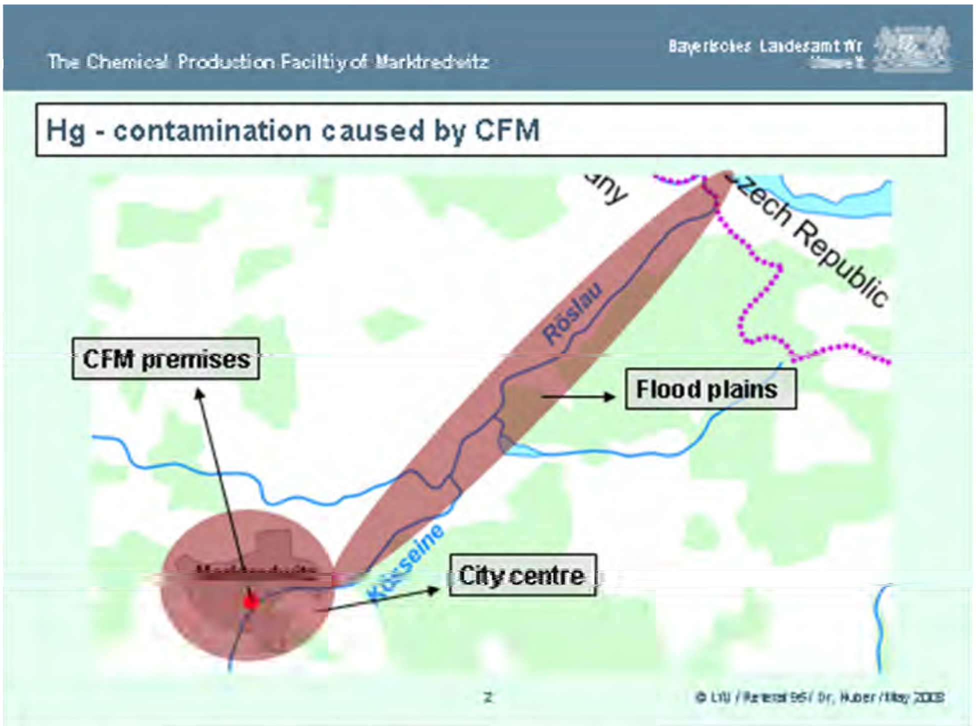
Figure 1: Location of the CFM in Marktredwitz (Bavaria, Germany) near the border to Czech Republic adjoining the river system Kösseine-Röslau.



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Hg - contamination caused by CFM

2

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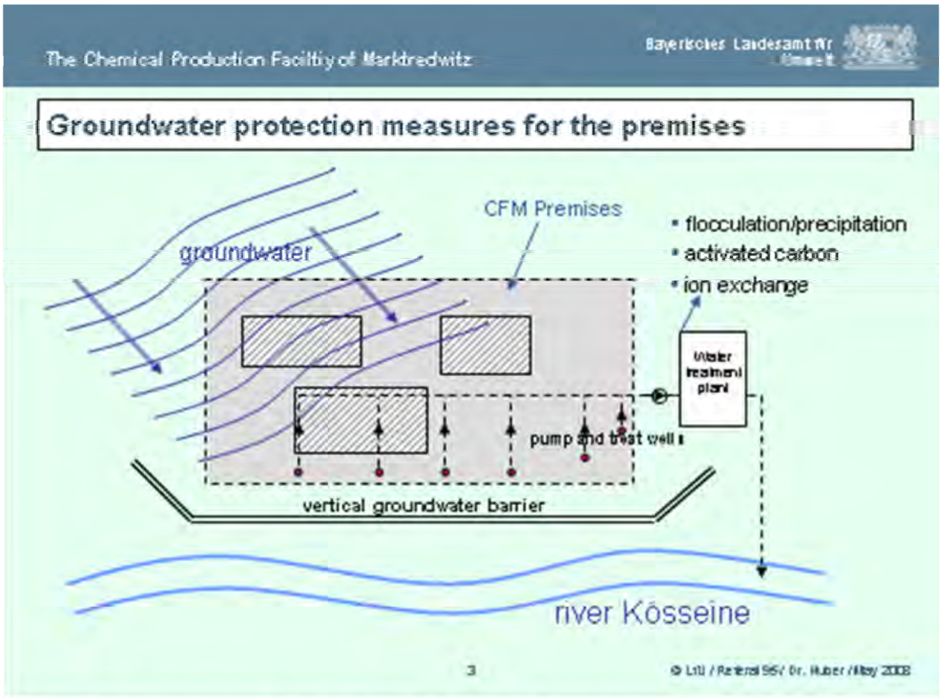
Figure 2: Areas contaminated due to Hg processing: CFM premises, areas of the city and flood plains downstream the CFM.



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Groundwater protection measures for the premises

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Figure 3: Protection of the river Kösseine by vertical groundwater barrier and groundwater remediation by pump and treat.

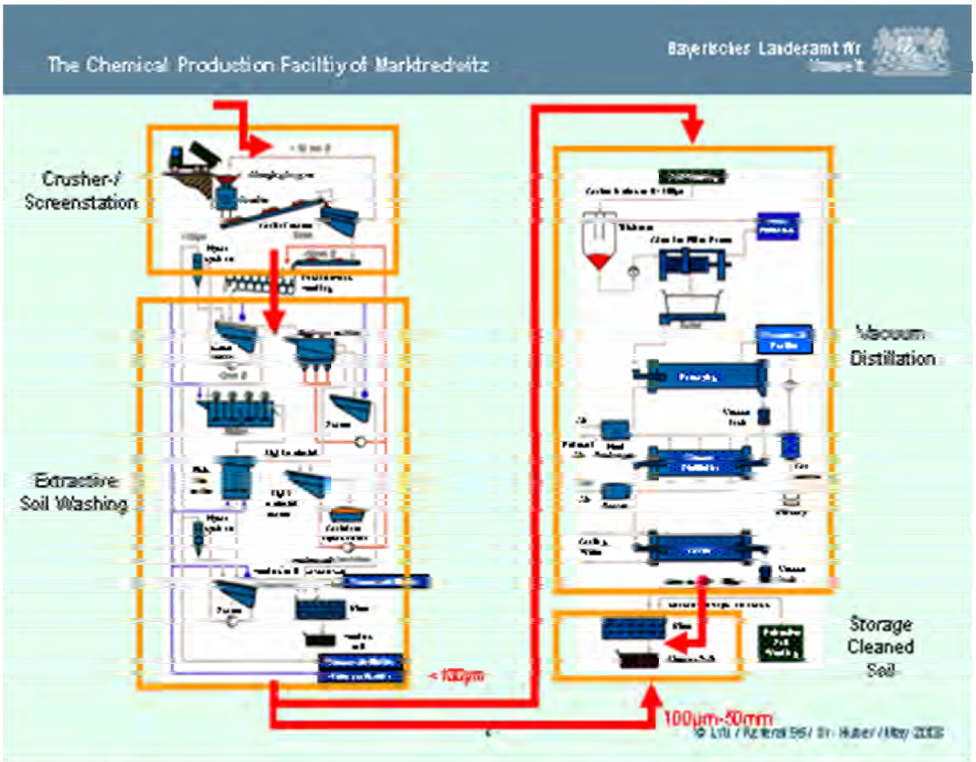

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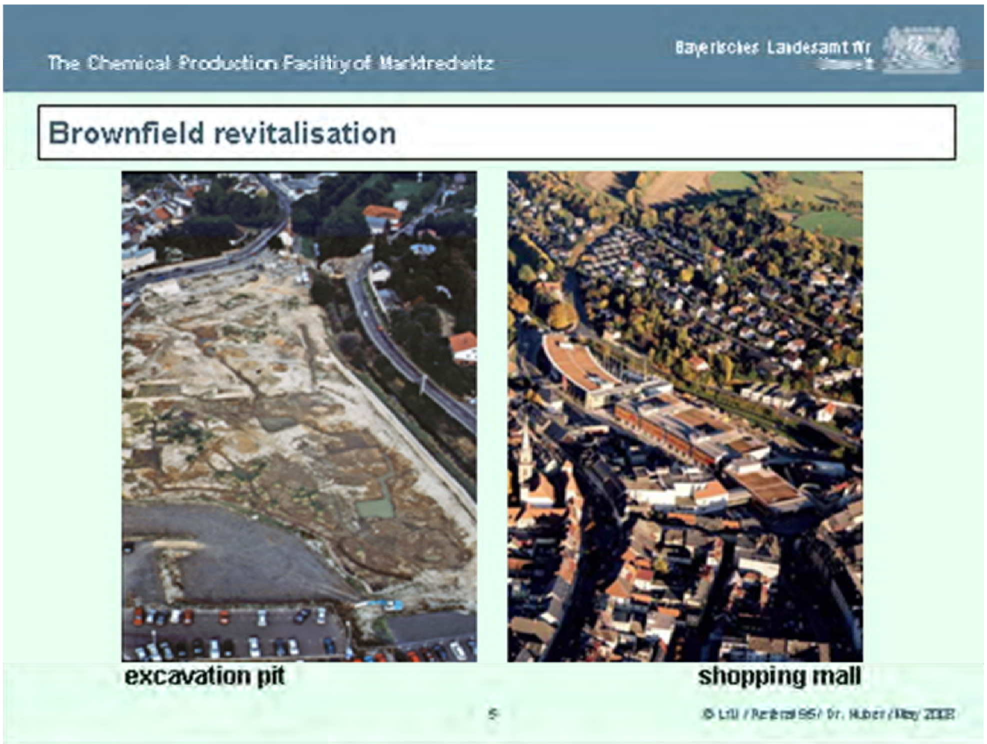
Figure 4: Soil treatment system for clean up of CFM materials with Hg < 5000 mg/kg by soil washing and vacuum distillation.



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Brownfield revitalisation

excavation pit

shopping mall

5

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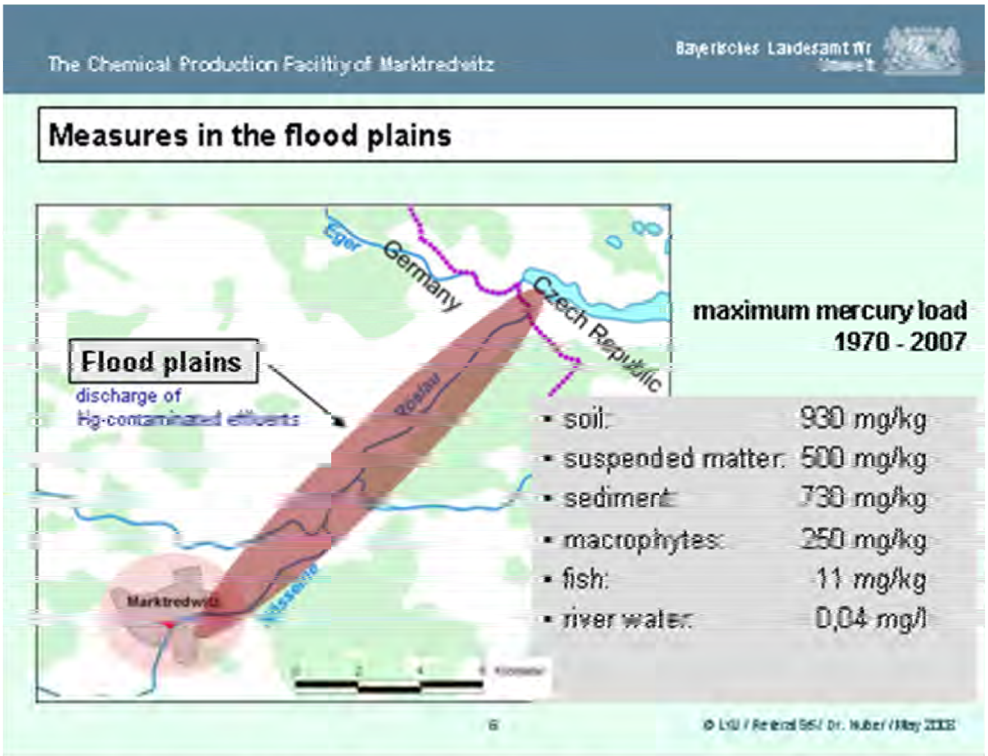
Figure 5: Former premise of the CFM after deconstruction and excavation (left) and construction of a shopping mall in the city centre.



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Measures in the flood plains

maximum mercury load 1970 - 2007

soil:	930 mg/kg
suspended matter:	500 mg/kg
sediment:	730 mg/kg
macrophytes:	250 mg/kg
fish:	11 mg/kg
river water:	0,04 mg/l

6

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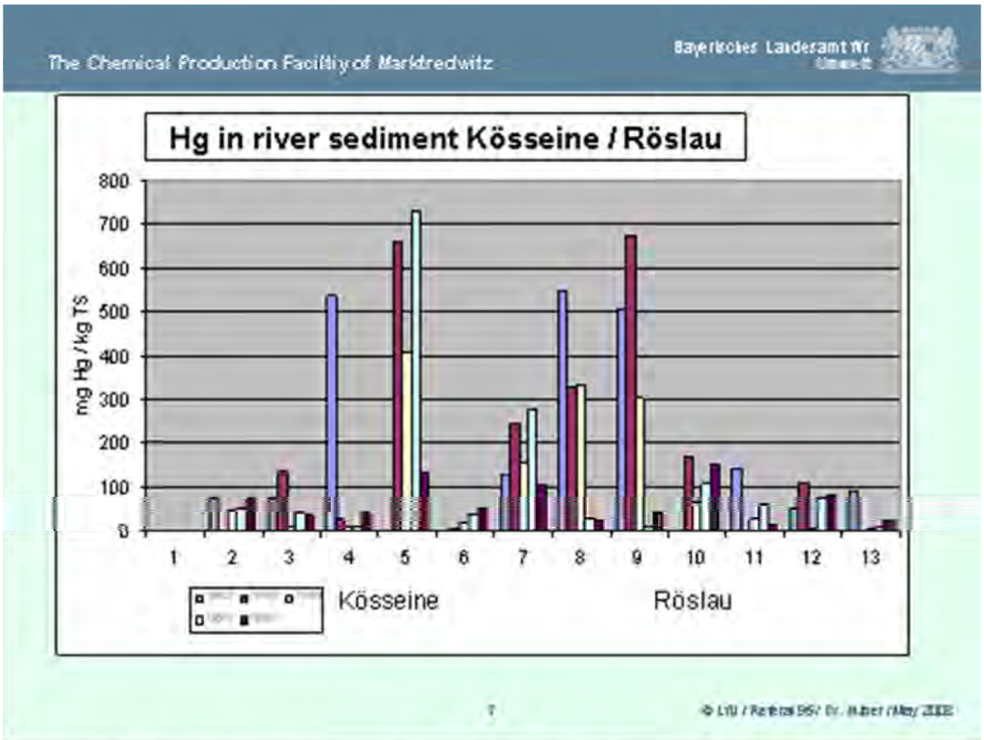
Figure 6: Some of the highest Hg concentrations measured in different compartments of the contaminated flood plains downstream the CFM.



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Hg in river sediment Kösseine / Röslau

7

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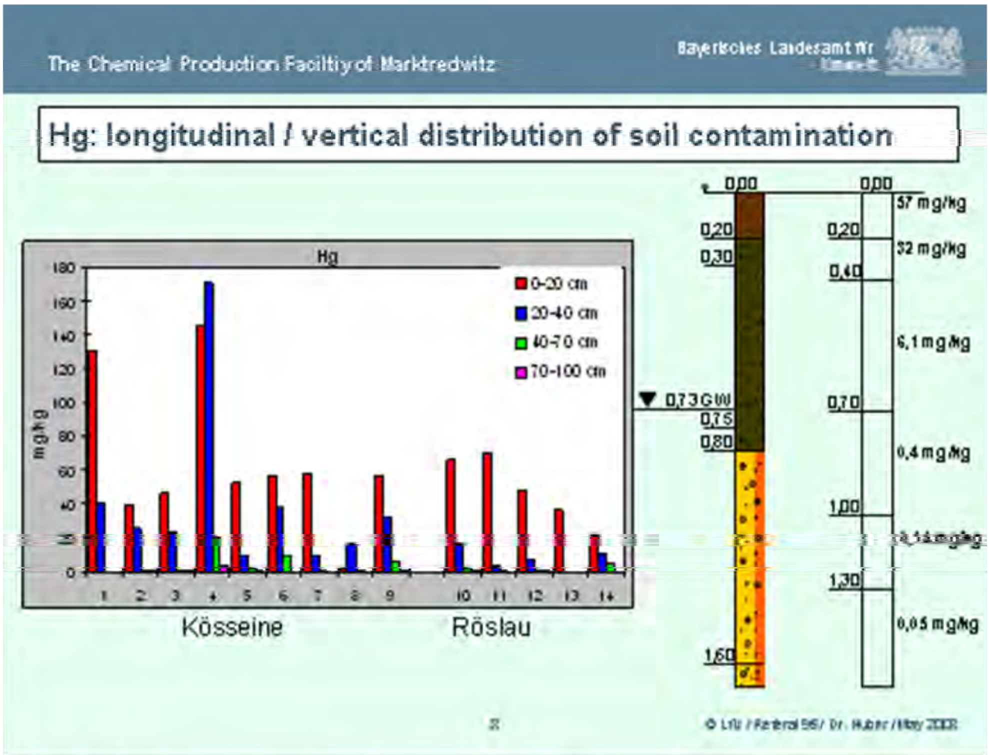
Figure 7: Hg concentrations in sediments at sampling points downstream theCFM.



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Hg: longitudinal / vertical distribution of soil contamination

8

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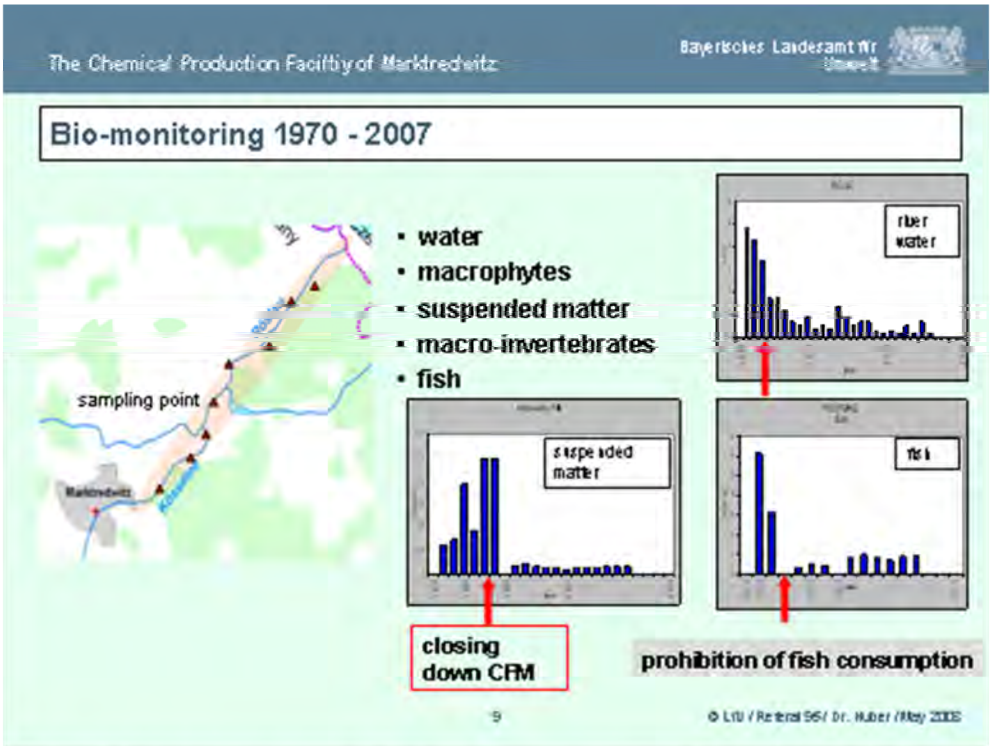
Figure 8: Hg concentration at soil sampling points in the flood plains downstream the CFM (left); typical vertical soil concentration at a distinct sampling point (right).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Bio-monitoring 1970 - 2007

- water
- macrophytes
- suspended matter
- macro-invertebrates
- fish

closing down CFM

prohibition of fish consumption

9

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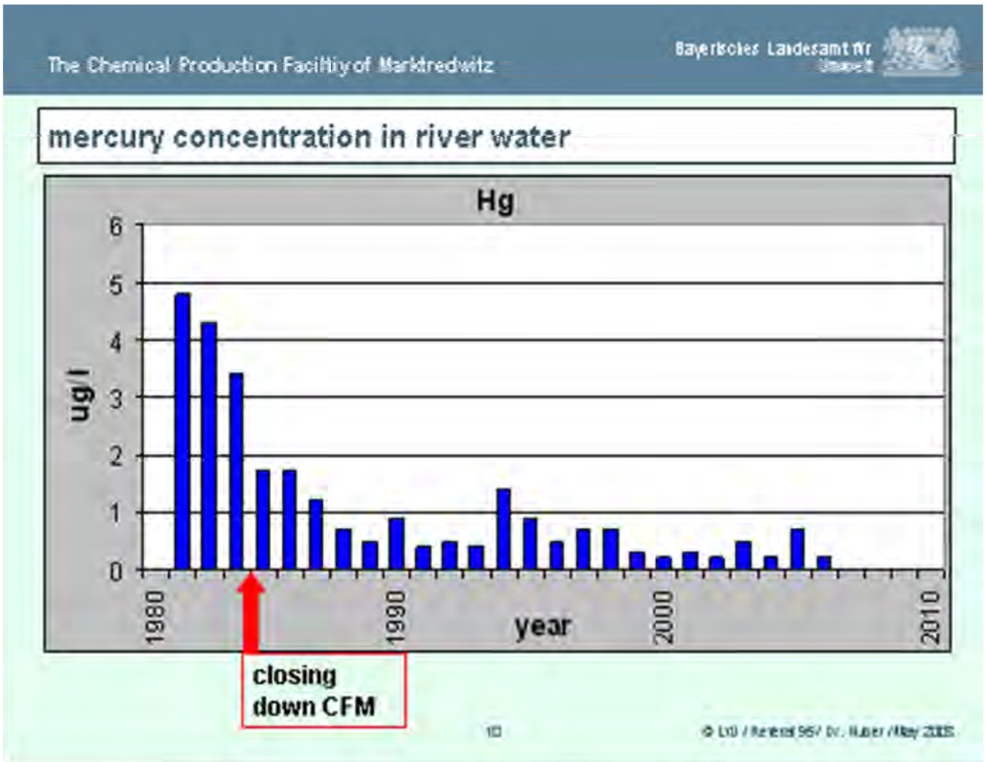
Figure 9: Bio-monitoring in the aquatic ecosystem before and after closing down and remediation of the CFM.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mercury concentration in river water

closing down CFM

10

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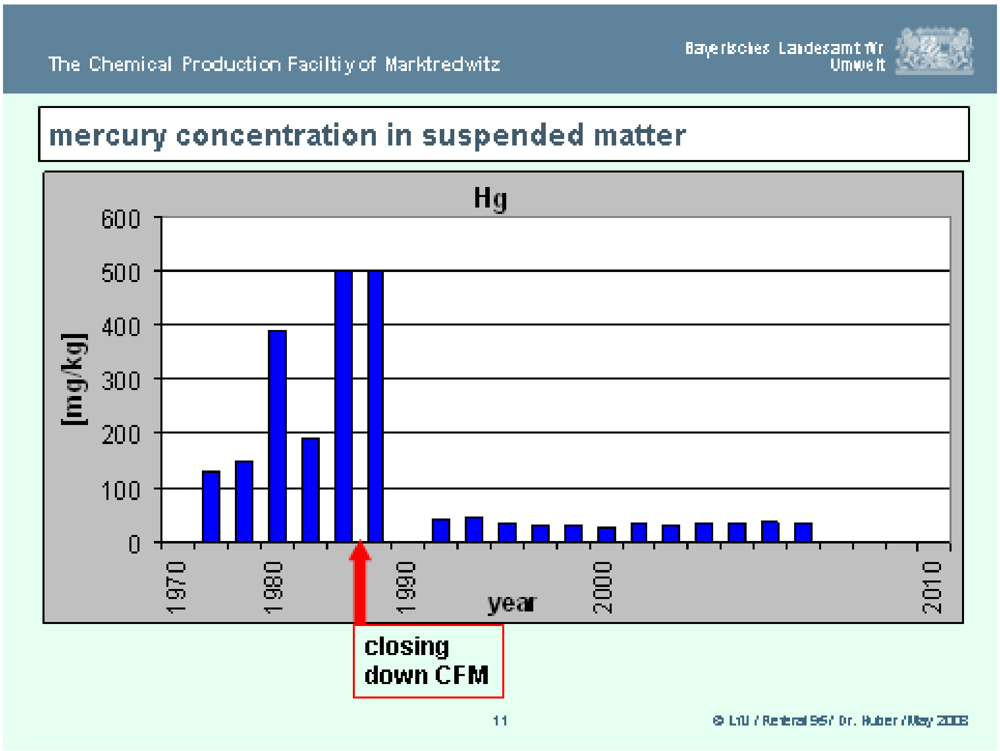
Figure 10: Results of monitoring in the aquatic ecosystem downstream the CFM: mercury in the river water



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mercury concentration in suspended matter

11

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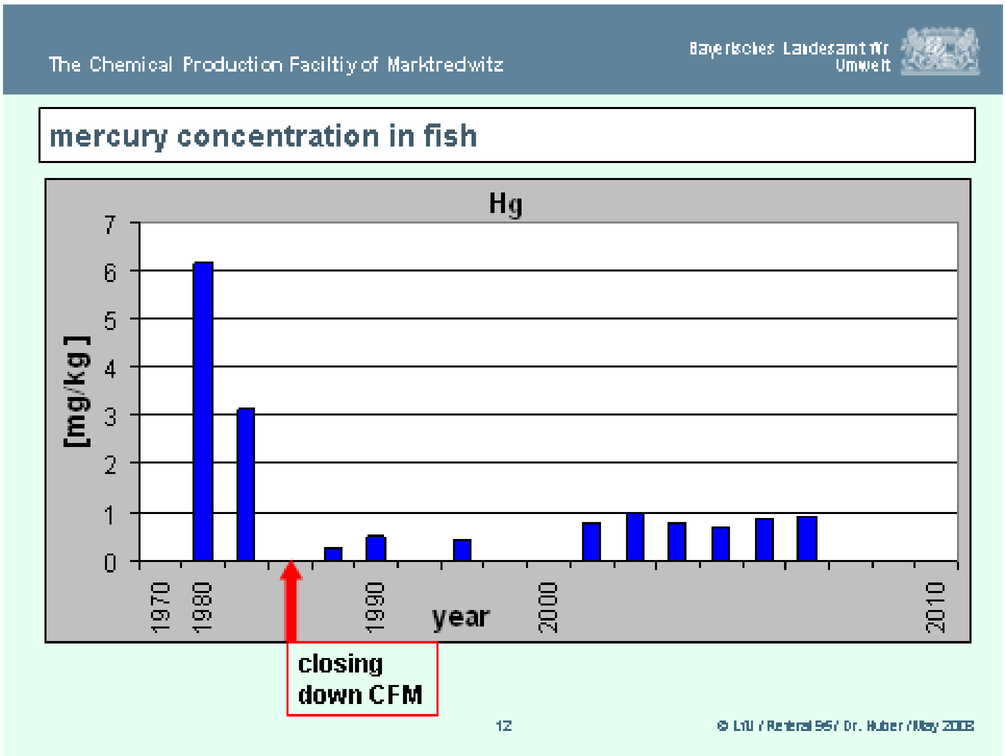
Figure 11: Results of monitoring in the aquatic ecosystem downstream the CFM: mercury in suspended matter.



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mercury concentration in fish

12

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Figure 12: Results of Bio-monitoring in the aquatic ecosystem downstream the CFM: mercury in fish.

The investigation of the mercury contamination in a Chinese plant: a case study

Jun Hu & Jianlong Wang

Laboratory of Environmental Technology, Institute of Nuclear and New Energy Technology,

Tsinghua University, Beijing, 100084, P.R.China

Introduction

Mercury persists in the environment and bioaccumulate in the food chain. It mainly affects the nervous system, of both humans and animals. Elemental mercury has been known for several hundreds years to cause tremors and sensory abnormalities in humans. Methyl mercury has adverse developmental effects on fetuses, infants and children. It also has adverse neurological effects on adults.

Solidification/stabilization technologies are used to immobilize liquid wastes converting them into solid forms. With growing awareness of its toxicity Performance requirements (e.g. leachability) for treated mercury wastes were more stringent.

According to the Identification standard for hazardous wastes of China (ISHWC)-Identification for extraction procedure toxicity (GB5085.3-1996). The allowable concentration of mercury in the leachate of the toxicity characteristic leaching procedure (TCLP) is less than 0.05 mg/L. Health standard for element mercury vapor in the air of workplace restricts worker exposure to mercury vapors to a low threshold limit value of 0.02 mg/m^3.

Methods

Processing materials

All mixed mercury waste including wall concrete and soil was obtained from a factory because of industrial applications. The waste was ground to a fine powder and the normal cement from our laboratory was provided.

Test methods

To assess the completeness of the initial reaction between the sulfur and mercury, after the first stage of processing, The TCLP (GB Method 5086) was conducted on a series of treated Hg wastes produced in this study. To reduce the volume of waste generated in this study, a modified version of the TCLP was conducted, using 20g of sample material while maintaining the same relative reagent quantities required for a standard TCLP test.

Long-term leaching behavior was evaluated with a leaching test in which solid samples were immersed in distilled water for 28 days. Contaminant concentrations in the leachate were then evaluated with the test that calculates cumulative mercury fractions released. Solutions from the TCLP and leach tests were measured using the mercury cold vapor method with an Atomic Absorption spectrometer.

Results and discussion

The investigation of mercury contamination and sampling sites

Mercury concentrations in soil at nine sampling sites

Mercury concentrations in soil are 1349.26, 25.52, 342.2, 360.79, 73.57, 175.86, 28.07 and 36.06 mg/kg at nine sampling sites, respectively (Fig.1-Fig.8), and the mercury concentration of the surface of polluted area is 4179.26 mg/kg.

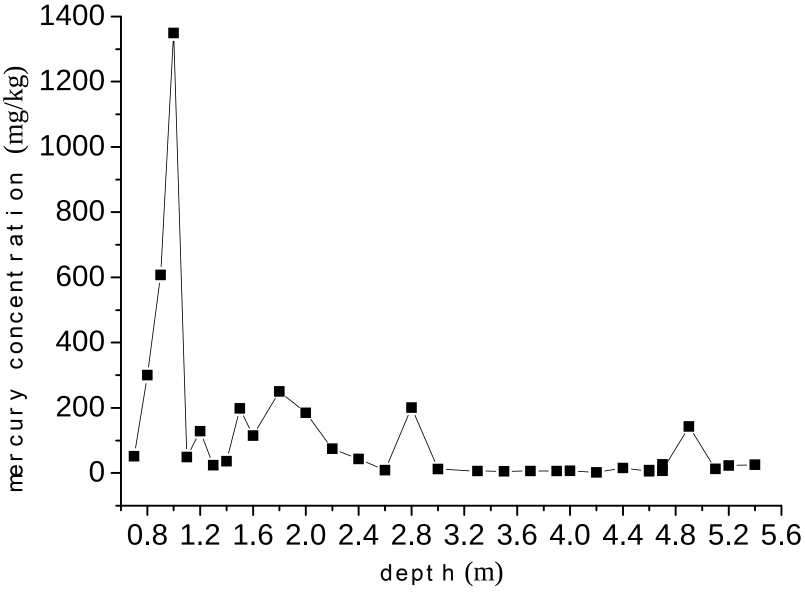

Fig.1 Variation of total Hg concentration (mg/kg) in soil depth (m) at the hall of the sampling sites.

These concentrations are much higher than the average Hg concentration in soil (0.038 mg/kg) (Wang et.al, 2005)

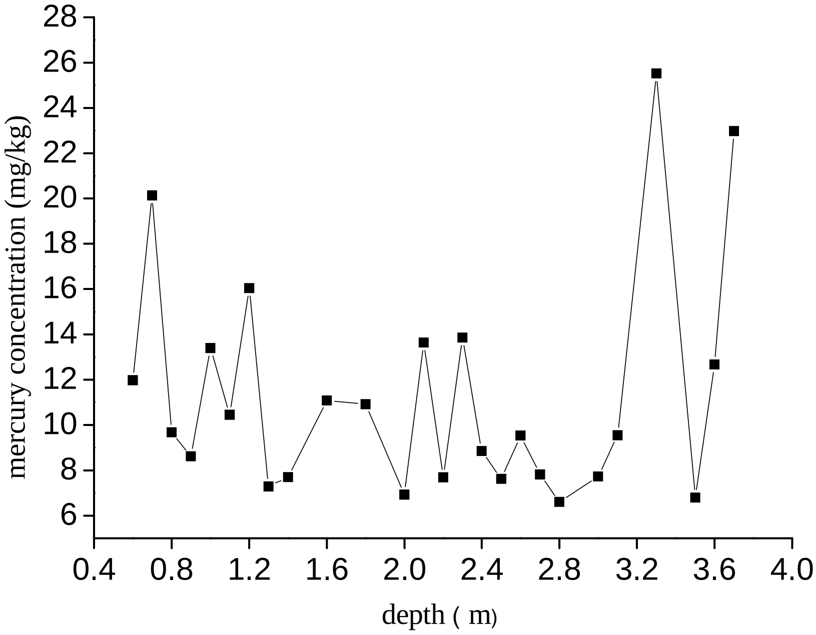

Fig.2 Variation of total Hg concentration (mg/kg) in soil depth (m) at the pump maintenance room of the sampling sites

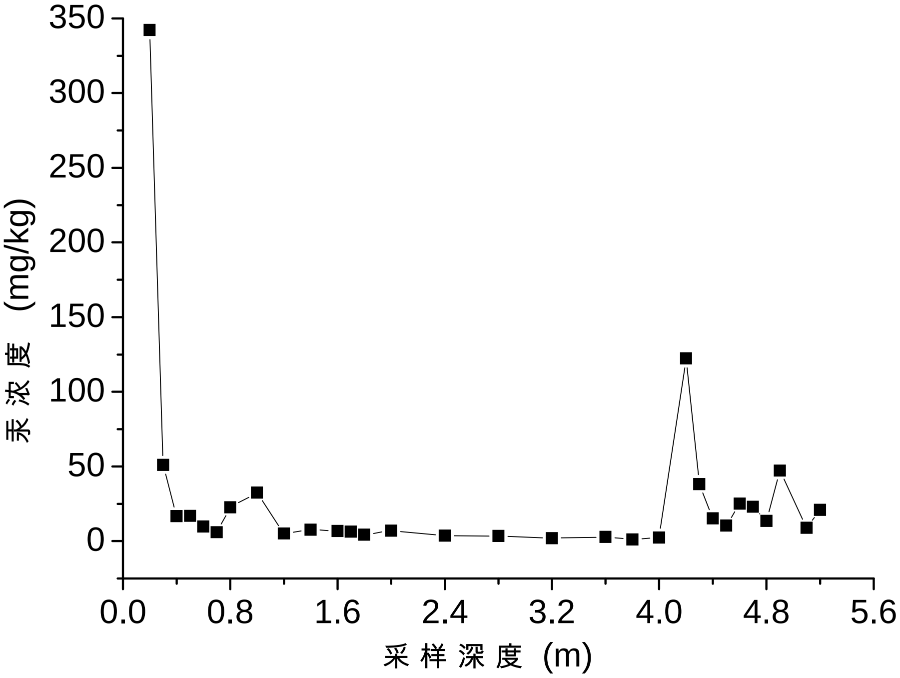

Fig.3 Variation of total Hg concentration (mg/kg) in soil depth (m) at the outdoor pit of pump maintenance room of the sampling sites

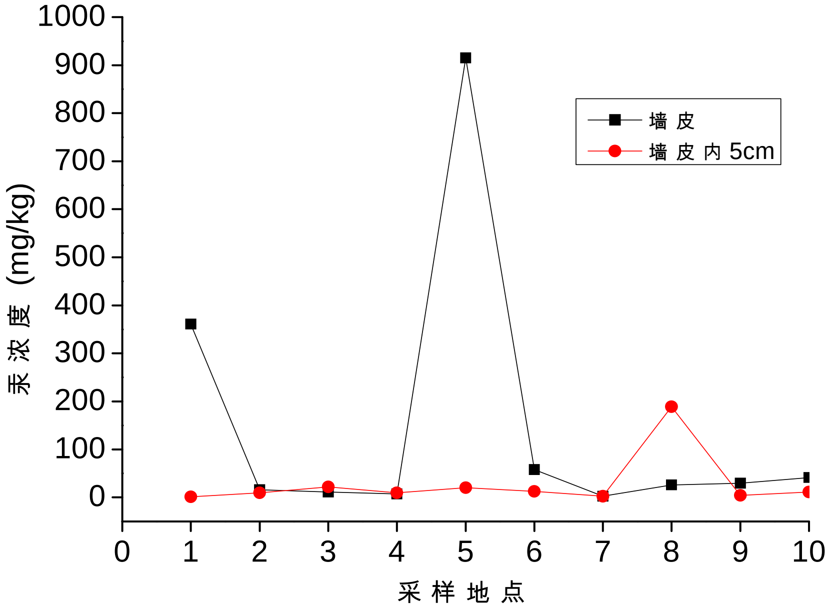

Fig.4 Variation of total Hg concentration (mg/kg) in 1 meter high (m) at the wall of the hall

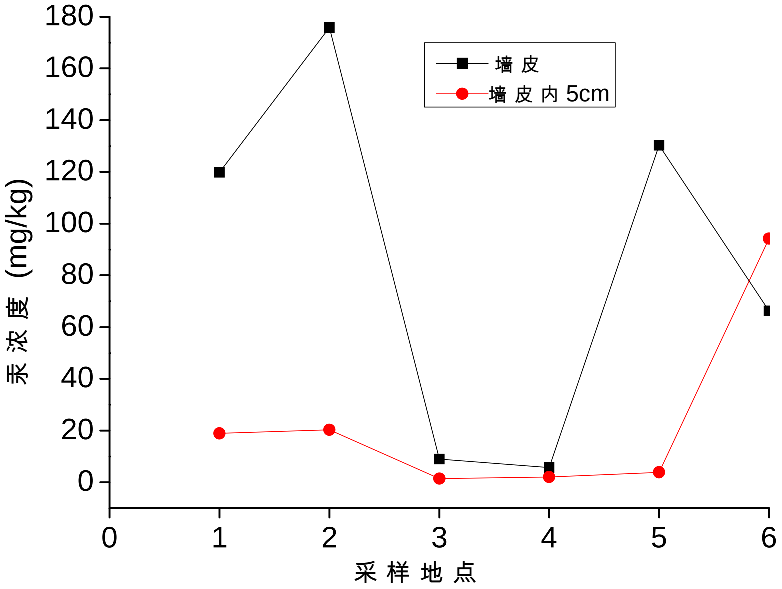

Fig.5 Variation of total Hg concentration (mg/kg) in 1 meter high (m) at the wall of the pump maintenance room

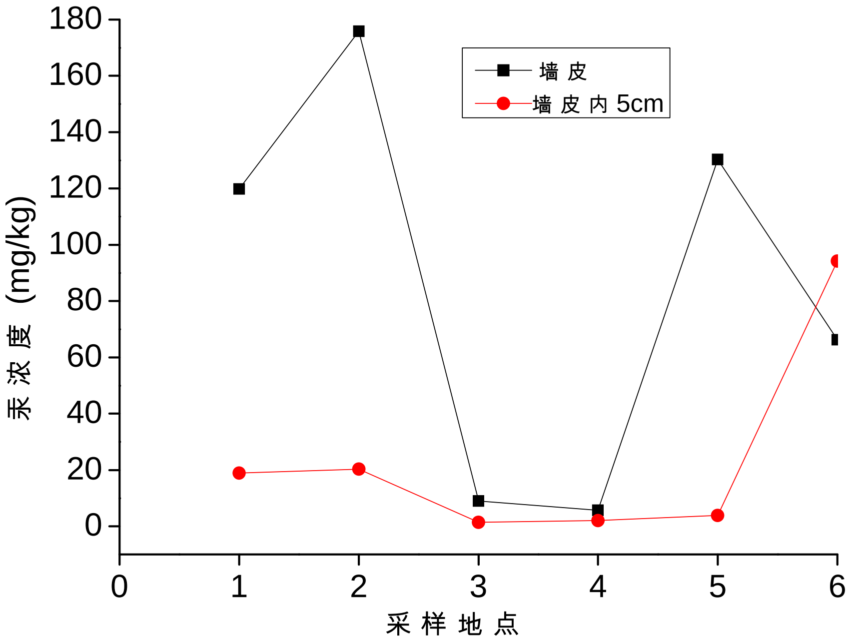

Fig.6 Variation of total Hg concentration (mg/kg) in 1 meter high (m) at the wall of the mercury storeroom

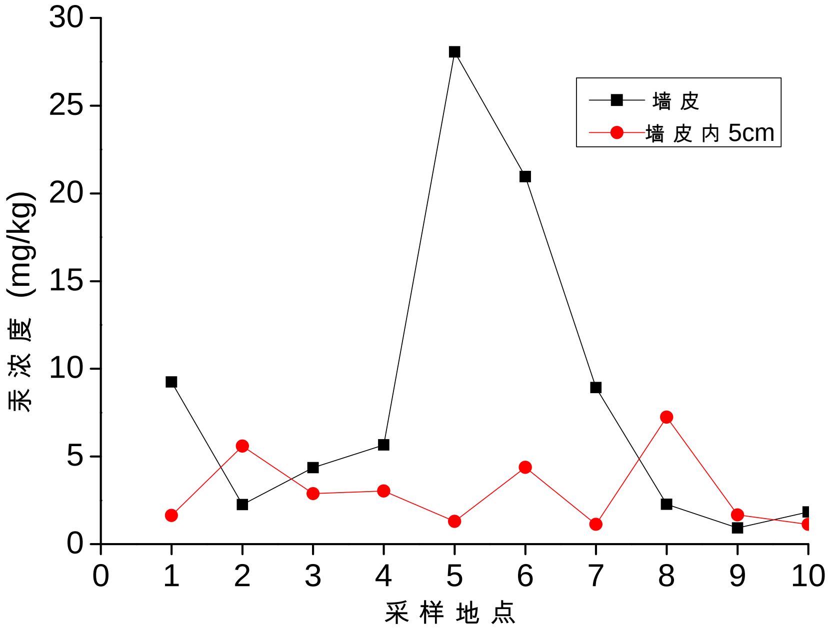

Fig.7 Variation of total Hg concentration (mg/kg) in 1 meter high (m) at the wall of the 7.2- meter deep rare mental storeroom

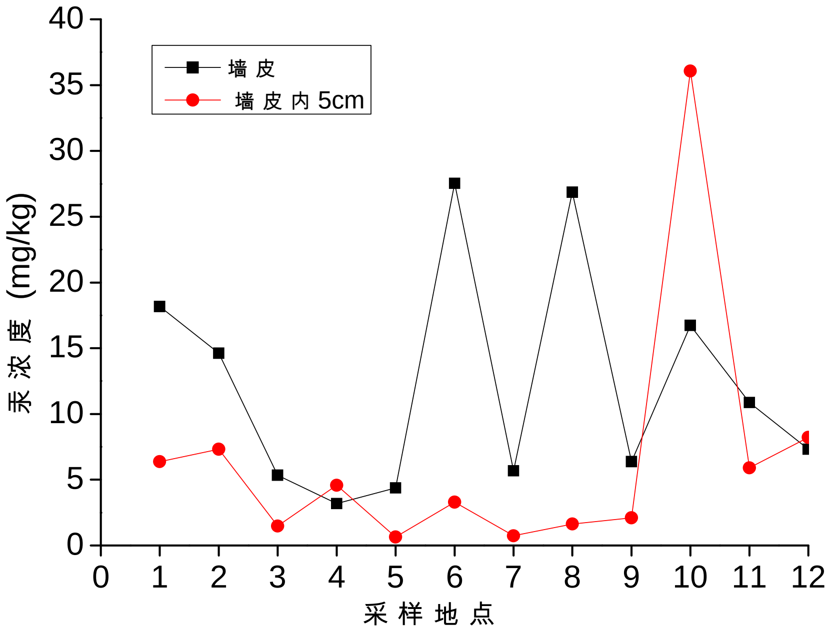

Fig.8 Variation of total Hg concentration (mg/kg) in 1 meter high (m) at the wall of the southeast factory

Mercury concentrations in water at the sampling sites

Fig.9-11 shows that the mercury concentration varies among different area during 2002 -2006.

As shown from Fig.9 to Fig.11, the whole production area, the drainage area and the residential area, the mercury concentration of the water body had far exceeded water body mercury water quality III standard of surface water (GHZB 1-1999) (0.1ug/L), and the biggest concentration of air mercury at residential area was 3.88 ug/L in February 2006.

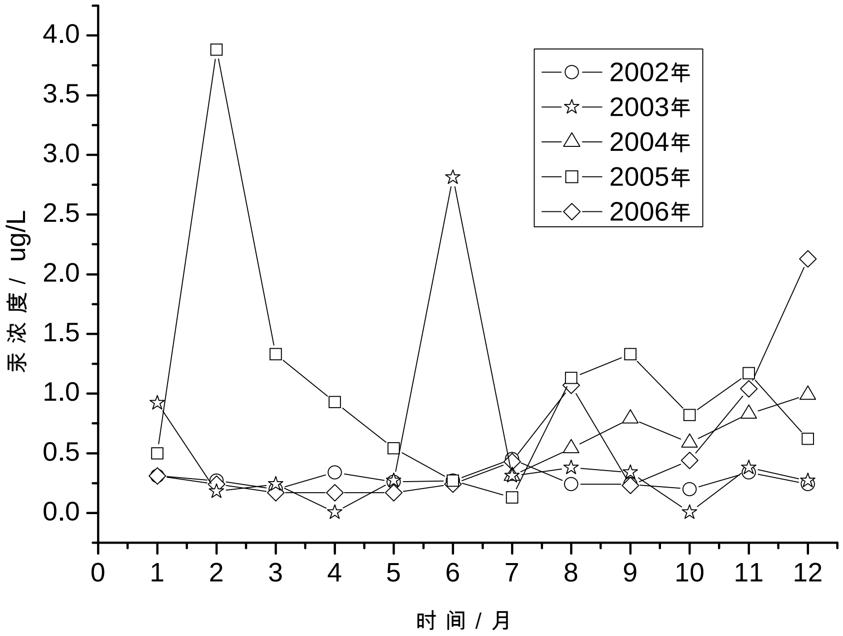

Fig.9 Total mercury concentration in water from the residential area during five years

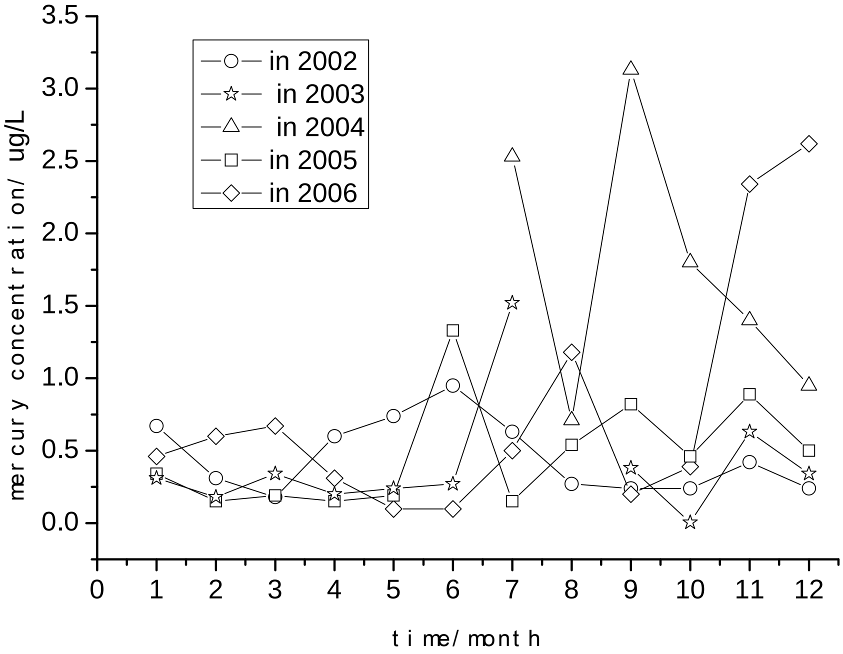

Fig.10 Total mercury concentration in water from the whole production area during five years

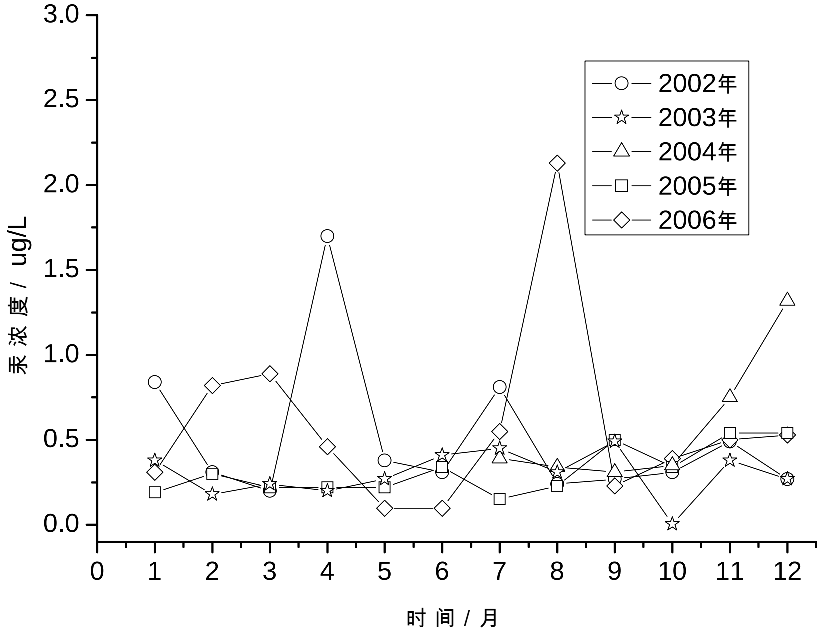

Fig.11 Total mercury concentration in water from the whole drainage area during five years

Mercury concentrations of air at sampling sites

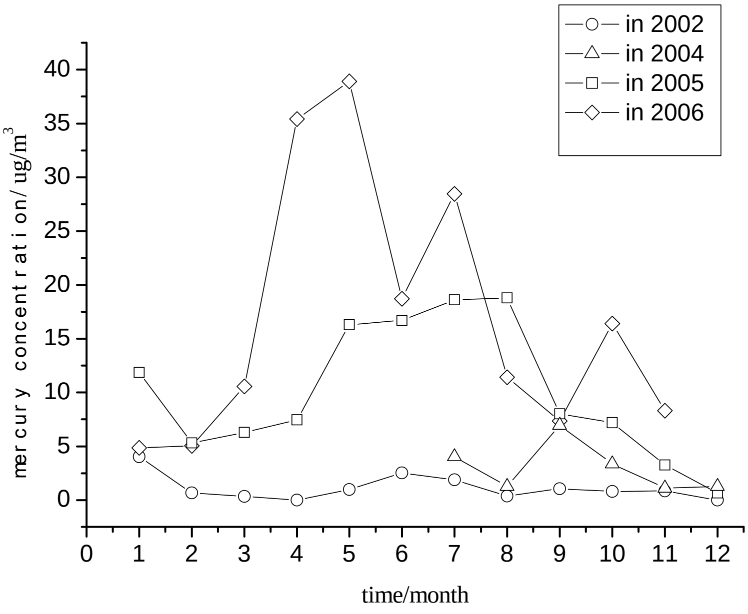

Fig.12 Variation of total air Hg concentration (ug/m^3) in the 7.2- meter deep rare mental storeroom during four years from 2002 to 2006

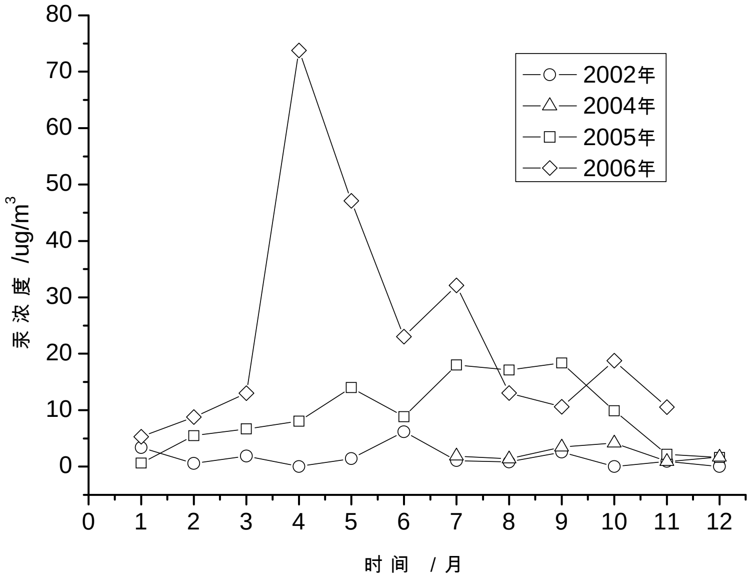

Fig.13 Variation of total air Hg concentration (ug/m^3) in the mercury storeroom during four years from 2002 to 2006

From the Fig.12 and Fig.13, it is apparent that the mercury pollution in air is very heavy, especially in spring and summer, because mercury vapor is easily evaporable, the mercury concentration in air increased to 73.8 ug/L, which had far exceeded air quality standard of 0.3 μg/m^3.

TCLP test

Typical TCLP leach results are summarized in Table 1. Untreated mercury from the platform of the mercury storehouse resulted in TCLP concentrations is 9.787 mg/l (pH=8.3) which is more than 195 times the SHWC's (Identification standard for hazardous wastes of China) current allowable limit of 0.05 mg/l.

In order to determine whether the stabilization reaction was complete, the concentrations of leachable mercury in the stabilized soil ranged from cement treated samples with no additive consistently result in acceptable levels of mercury in TCLP leachates during 25 days, all of them are less than 50 ug/L (Table 2).

Table 1: Concentration of Hg in TCLP leachate

	Wastewater pool	Platform of the mercury storehouse	hall	East wall of the mercury storehouse
pH	mg/L			
5.0	0.941	8.381	0.898	0.077
6.3	0.58	6.344	0.691	0.19
8.3	0.771	9.787	0.933	0.104

However, with the leaching time prolong, increase of mercury release imply that a modified process is needed. However, it is still difficult to predict the long-term releases of mercury.

Table 2: Release of Hg from cement solidified waste

Leaching time	On-site mercury waste （μg/L）	Clay Sticky soil （μg/L）	Sandy soil （μg/L）
5	11.26	<5	<5
10	12.19	<5	<5
15	38.72	<5	<5
20	37.07	<5	<5
25	39.12	<5	<5

Note: 20 g from each of three batches of treated mixed-waste mercury. Analysis performed on October 2007.

Table 3: Mechanical performance of the cemented wastes

	Breaking stress（Mpa)	Compressive stress (KN)	Compress strength (Mpa)
On-site mercury waste 1	3.7	52.4	32.8
		50.6	31.6
On-site mercury waste 2	5.7	51.2	32
		50.9	31.8
Sticky soil-1	1.7	8.4	5.2
		＜8	N/A
Sticky soil-2	1.7	＜8	N/A
		＜8	N/A
Sandy soil 1	5.3	39.2	24.5
		40.3	25.2
Sandy soil 2	5	40.2	25.1
		29.9	18.7

Conclusions

A stabilization/solidification process for both hazardous and mixed-waste mercury metal was tested using a set of laboratory-scale processing equipment. When elemental mercury and cement are mixed, the process reduces leachable mercury, meeting ISHWC criteria. Long-term leaching behavior of the processed waste, as determined by the GB-5085 method, indicates that mercury releases are controlled well during 28 days and the release rates are low.

4 Conclusions

Mercury-contaminated sites potentially represent an important source of mercury emission into the atmosphere due to evaporation of mercury from contaminated land and waters. They constitute an important source for transboundary movement of mercury. Contaminated sites in ecosystem-sensitive areas may represent a considerable health and ecosystem risk due to direct and indirect exposure to mercury and its compounds.

In response to the UNEP Governing Council decisions the German Federal Ministry for the Environment together with German and Chinese partners organized a workshop on remediation of mercury-contaminated sites in Guiyang, China. The aim of the workshop was to address, discuss and understand relevant issues and problem areas related to remediation of mercury-contaminated sites. Its objective had been to exchange knowledge on the characterization and identification of mercury-contaminated sites, the demonstration of the state of the art in science and technology on remediation technologies and strategies as well as the procedure of the development of inventories with respect to mercury.

First, individual aspects were reported and brought up for discussion to work out differences and to identify possibilities for the knowledge exchange/transfer. On the basis of the following topics, the information and approaches available in the Federal Republic of Germany/Europe and China were compared:

- Legal Background in Germany, Europe and China
- Register of Contaminated Sites
- Characterisation of Mercury-Contaminated Sites
- Risk Assessment and Risk Management of Harmful Substances
- Remediation Techniques and Strategies
- Remediation of Chemical Production Facilities

In Germany, the awareness of contaminated sites being a major environmental problem came up around 1980 together with some severe cases of soil and groundwater pollution. In 1999, the Federal Government put the Federal Soil Protection Act (BBodSchG) and the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) into force, which established nationally standardised regulations for the registration and remediation of contaminated sites.

Common European efforts aimed in a Soil Thematic Strategy and a proposal for a Soil Framework Directive with the objective to protect soils across the European Union. The European Framework Directive sets out common principles, objectives and actions to prevent further contamination, to establish inventories of contaminated sites and draw up national remediation strategies. The legal framework in China has just been revised by the Chinese authority. At present the valid limit values for contaminants in soil are from 1988. On the basis of Cr and DDT as leading substances, nationally standardized regulations for the registration and remediation of contaminated sites will be established.

For the successful treatment of contaminated sites, a huge number of steps for the registration of potentially contaminated sites must be implemented to obtain a comprehensive base of information and documentation. The registration of a potentially contaminated site in Vietnam could be demonstrated as an example of the development of a register within the Asian-Pacific region.

Chemical and physical extraction methods serve in addition to quantify Hg and unsolved Hg-species as basic data for a risk assessment. There was a broad consensus that the state of the art in science and technology for the characterization and quantification of Hg in soils is far advanced. Special attention was paid to the combination of different remediation technologies („treatment train“) as well as the strategic approach to remediation of contaminated sites, especially for mega sites. Due to the huge number of factors, strategies can be developed taking into account cost optimization.

A software for the development of remediation strategies was introduced by the German side. Spatial Analysis and Decision Assistance (SADA) is free software that incorporates tools from environmental assessment fields into an effective problem solving environment. These tools include integrated modules for visualization, geospatial analysis, statistical analysis, human health risk assessment, ecological risk assessment, cost/benefit analysis, sampling design, and decision analysis. The freeware SADA 5 can be downloaded on the website: http://www.tiem.utk.edu/~sada/download.shtml.

The presented approach to use trigger-values as basic data for a risk assessment to analyze the need for the realization of remediation measures was brought to the attention of the Chinese side. In this area knowledge transfer and further support was assured, e. g. by an exchange of literature.

The example of the chemical factory of Marktredwitz (CFM) demonstrated the successful remediation of a contaminated site in Germany. In view of the follow-up, a case study was given by the Chinese side and discussed at the workshop. First, the quantification of Hg at different hot spots was carried out. The following discussion showed that at present there is still not enough information available to develop a remediation strategy. As a follow-up to the workshop, a questionnaire will be addressed to the Chinese colleagues to provide site-specific parameters of their case study for the development of a remediation strategy.

Finally, all participants agreed that all topics had been introduced and discussed extensively. In future, a huge number of cooperation possibilities can be developed from the common exchange of ideas and approaches. Participants appreciated and recognized the added value of debating the issues in a truly multidisciplinary context and expressed interest in remaining involved in future proceedings.

5 Follow up

The workshop generated action items and recommendations that can be implemented along with the UNEP Governing Council initiative. Numerous new areas of cooperation possibilities on different levels were identified which are to be addressed shortly:

- At ministerial level, the drafting of new or adaptation of the present legislation could be supported in an advisory capacity by the German authority.
- Support of the Chinese authorities in the development of guidelines/procedural instructions/regulations for Cr and POP (DDT)
- Calculation and application of trigger values
- An urgent need seems to lie with the strategies for contaminated sites from chemical production processes ("hot spots").
- Plenary discussion of the example of the Chinese case study has shown that there is a great need for knowledge exchange/transfer.
- Other examples of successful remediation projects should be presented to the Chinese side: Mirror factory in Bavaria, Chemical plant Buna-Bitterfeld.
- The answers to a questionnaire by the German side will provide the necessary specific parameters for a mercury-contaminated site in China (see next page) to conduct a strategy analysis. The questions of the questionnaire are aimed to assess:
    - Remediation objectives and plan
    - Regulatory requirements
    - Specific parameters of the contaminated site
- Strategies with regard to mega sites, as they also exist in the southwest of China, are also of great interest for China. There is the possibility to download a freeware program http://www.tiem.utk.edu/~sada/download.shtml..
- In the follow-up to the workshop, the extended summary will be published e.g. on the EUGRIS or the UFZ/TASK homepage.
- To build on the success of this workshop, it was recommended to continue with a workshop on “Remediation of a mercury contaminated site – elaboration of the remediation concept of a contaminated site in China” with participants from German and Chinese authorities, facility owners, engineering offices and science. The workshop should expand beyond the discussions of the Chinese case study and take place in Germany in 2009/2010.

Questioner on the remediation concept for the remediation of a Chinese facility

- What are the remediation objectives?
- Risk reduction / risk management or risk elimination
- What type of future land use is planned?
- Are there any clean up values / levels of clean up for soil and / or groundwater given or proposed by the authorities?
- Who (which authority) will decide about the remediation plan?
- Are there other regulatory requirements?
- Have there been talks or negotiations about the acceptance of stakeholders?
- Which time scale is available to start and to complete remediation
    - Is there an urgent political, social or economical need to remediate?
    - Is there a risk for human health?
- Is therefore a high rate or flow of treatment needed?
- Is it preferred to have high invest/ capital cost and low or no cost for operating and maintenance or the other way round? Who is going to pay for the remediation?
- What has been assed / is known about the chemical, physical, and biological properties of the contaminants and their distribution?
- What has been assed / is known about the properties of the contaminated media (soil, groundwater, concrete)?
- Systematic soil assessment (grid, depth, sampling)
- What analytical SOP was used?
- What has been assed / is known about the hydrogeological / geological conditions? Are there any monitoring wells (depth, diameter, period of monitoring, parameters assessed)?
- Is there enough space for constructing onsite treatment facilities, or a containment technology?
- What are the distances to off site treatment / disposal facilities?
- Are there any restrictions concerning environmental effects (emissions, waste, consumption of energy and materials)?
- What are the regulations for the protection of community and workers during remediation?

6 Acknowledgement

The Federal Ministry for the Environment, Nature Conservation and Nuclear Safety of Germany through the guidance of Reiner Arndt and Andreas Bieber provided the impetus and primary support of this workshop. Additional financial support was provided by the Tsinghua University of Beijing, China.

7 Workshop impressions


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8 Participants of the workshop

Dr. Thorsten Meyer, Head of delegation Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH Theodor-Heuss-Str. 4 38128 Braunschweig, Germany Phone: +49 531 8012 249 Fax: +49 531 8012 200 E-mail: Thorsten.Meyer@grs.de	
Andreas Bieber, Head of delegation Federal Ministry for the Environment, Nature Conservation and Nuclear Safety Division WA II 7 - Soil Conservation and Management of Contaminated Sites Robert-Schuman-Platz 3 D - 53175 Bonn , Germany Phone: +49 0228 99 305 3431 E-mail: andreas.bieber@bmu.bund.de	
Prof. Jianlong Wang, Head of delegation Tsinghua University, Beijing Phone: +8610-6278 4843, Fax: +49 531 8012 200 E-Mail: wangjl@mail.tsinghua.edu.cn	

Jörg Frauenstein Federal Environment Agency - Soil Protection Measures - Wörlitzer Platz 1 D-06844 Dessau-Roßlau, Germany Phone: +49 340 2103 3064 Fax: +49 340 2104 3064 E-Mail: joerg.frauenstein@uba.de	
Martin Bittens Contaminated Site Management Group (CoSiMaG), Department Groundwater Remediation, Helmholtz Centre for Environmental Research - UFZ Permoserstrasse 15 04318 Leipzig, Germany Phone: +49 341 235 1682 Fax: +49 341 235 451682 E-mail: martin.bittens@ufz.de	
Dr. Harald Mark MSP - Dr. Mark, Dr. Schewe & Partner GmbH Hasenwinkeler Str. 139 44879 Bochum, Germany Phone: +49 234 5 86 51 00 Fax: +49 121266 5 86 51 06 E-mail: mark@msp-dortmund.de	

Dr. Gernot Huber Bavarian Environment Agency , Unit 95 - Contaminated Sites, Harmful Soil Changes Hans-Högn-Str. 12 D – 95030 Hof, Germany Germany Phone: +49 9281 1800 4950 Fax: + 49 9281 1800 4519 E-mail: gernot.huber@lfu.bayern.de	
Dipl.- Ing. Christian Weingran HIM GmbH – Department Remediation of Contaminated Sites Plausdorfer Weg D – 35260 Stadtallendorf, Germany Phone: + 49 6428 9235 0 Fax: + 49 6428 9235 35 E-mail: asg.stadtallendorf@t-online.de	
Dr. Andreas Zeddel Landesamt für Natur und Umwelt des Landes Schleswig-Holstein Hamburger Chaussee 25 24220 Flintbek, Gemany Germany Phone: +49 4347 704 602 Fax: +49 4347 704 112 E-mail: azeddel@lanu.landsh.de	

Prof. Dr. Harald Biester

Technical University of Braunschweig, Institute of Environmental Geology

Pockelsstraße 3

D-38106 Braunschweig, Germany

Phone: +49 531-391-7240

Fax: +49 531-391-8130

E-mail: h.biester@tu-bs.de

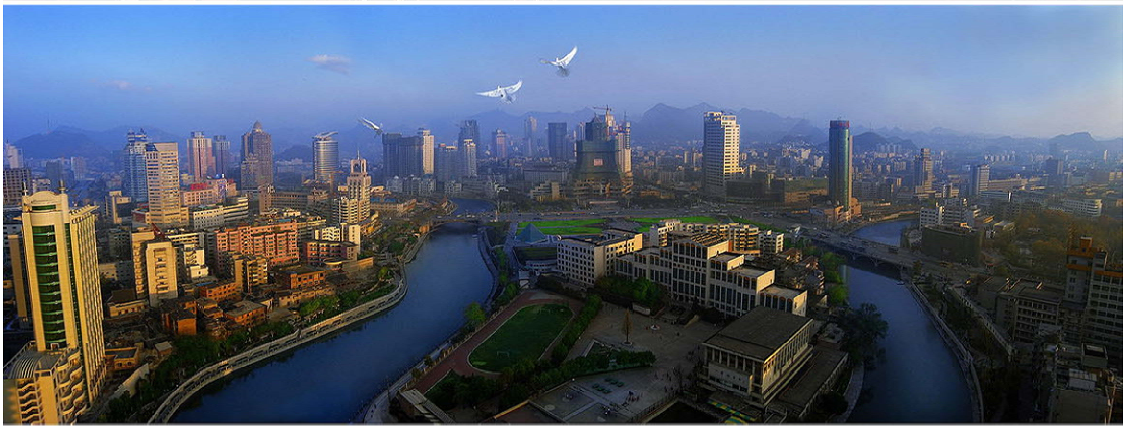
D-38023 Braunschweig

Name	Address	Postcode	Telephone	E-mail
Thorsten Meyer	Gesellschaft für Anlagen- und Reaktorsicherheit (GRS)	38542	05318012249	Thorsten.Meyer@grs.de
Bieber, Andreas	Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (BMU)	53424	0228993053431	Andreas.Bieber@bmu.bund.de
Andreas Zeddel	LA für Umwelt und Naturschutz SH	24161	04347704535	azeddel@lanu.landsh.de
Jörg Frauenstein	Umweltbundesamt (Federal Environment Agency) (UBA)	15732	030 8903 2285	Joerg.frauenstein@uba.de
Gernot Huber	Bayerisches Landesamt für (LfU) Bayern	92674	0928118004950	Gernot.huber@lfu.bayern.de
Harald Biester	Technische Universität Braunschweig	38104	05313917240	h.biester@tu-bs.de
Harald Mark	MSP GmbH	44879	02341495788	mark@msp-dortmund.de
Martin Bittens	UFZ, Permoserstrasse 15, 04318 Leipzig / Germany	04318	03412351682	Martin.Bittens@ufz.de
Weingran, Christian	Plausdorfer Weg, 35260 Stadtallendorf	35260	06428192350	asg.weingran@t-online.de
Hanjun WANG	CNFC, China	014035	13500628102	
Ren DIAO	CNFC, China	014035	13327199870	
Chenghe WEI	CNFC, China	014035	13327199896	
Jianglong WANG	INET, Tsinghua University	100084	861062784843	wangjl@mail.tsinghua.edu.cn
Jun HU	INET, Tsinghua University	100084	861062796427	hujun@mail.tsinghua.edu.cn
Xinbin FENG	State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang, China	550002	13984097217	fengxinbin@vip.skleg.cn

Xianglian PAN	State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang, China	550002	13885188756	xiangliangpan@163.com
Daoyong ZHANG	State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang, China	550002	13511948277	zhang-daoyong@163.com
Fanglin LI	CNPE, China	450052	13663807552	lifanglin@21cn.com
Fanghau YAO	CNPE, China	450052	037167726510	hancinann2000@yahoo.com.cn
Sarah Rothenberg	Institute of Geochemistry, CAS,	550002	15086012462	srothenb@gmail.com
Jonas Sommar	Institute of Geochemistry, CAS,	550002	13885090277	jonas@mail.gyie.ac.com
Xuemei ZHU	Chinese Research Academy of Environmental sciences	100012	13521239182	zhuxm@craes.org.cn
Jing ZHU	Institute of Geochemistry, CAS,	550002		
Heng YAO	Institute of Geochemistry, CAS,	550002	13984866122	yaoheng28@gmail.com
Zhonggen LI	Institute of Geochemistry, CAS,	550002	13608518010	lizhonggen@gyig.ac.cn
Bo MENG	Institute of Geochemistry, CAS,	550002	13608518010	mengbo05@gmail.com
Xuewu FU	Institute of Geochemistry, CAS,	550002	13037866465	xuewu-fu@hot.mail
Haiyu YAN	Institute of Geochemistry, CAS,	550002	13984309502	yanhaiyu@vip.skleg.cn
Xin ZHAO	Institute of Geochemistry, CAS,	550002	13984119832	xin0124@163.com
Chunxiao CHEN	Institute of Geochemistry, CAS,	550002	13985041286	fayechan@163.com
Yinxia SONG	Institute of Geochemistry, CAS,	550002	13985041286	songyingxia@163.com

9 Location - GUIYANG

The city was first constructed as early as 1283 AD during the Yuan Dynasty. Under the Ming (1368–1644) and Qing (1644–1911) dynasties, the town became the seat of a superior prefecture named **Guiyang**. Guiyang has subsequently become a major provincial city and industrial base.



The city is situated on the Nanming River, a headstream of the Wu River, which eventually joins the Yangtze River at Fuling in Sichuan province. Guiyang is a natural route center, with comparatively easy access northward to Sichuan and northeast to Hunan province.

Coal is mined in the locality of Guiyang and Anshun, and there are large thermal generating plants at Guiyang and Duyun, supplying electricity for the city's industry. A large iron and steel plant came into production in Guiyang in 1960, supplying the local machinery-manufacturing industry.

Large deposits of bauxite have been discovered to the north, and by the 1970s Guiyang had become a major producer of aluminum. Guiyang also manufactures industrial and mining equipment, as well as railway vehicles and equipment. It has a large chemical industry, producing fertilizers, and a rubber industry, manufacturing automobile tires. Guiyang also has textile plants and makes glass, paper, and other consumer goods.

10 Abstracts

Legal Background in Germany and European Perspective

Andreas Bieber

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Germany

The awareness of contaminated sites being a major environmental problem came up in Germany around 1980 together with some severe cases of soil and groundwater pollution. The regions (Laender) began to register the sites where contamination was suspected: industrial sites, waste disposal sites and military sites. Today, about 290,000 sites are registered as suspected to be contaminated. It is estimated that 10 to 20 % of them will need to be remediated. About 500 million Euro are spent every year for the clean up of contaminated soils and groundwater in Germany.

In 1998, the German Federal Government issued a Federal Act on Soil Protection. The main obligations are:

- to protect the soil from pollution and degradation and
- to clean up contaminated sites and polluted groundwater.

In 2006, the European Commission issued a Soil Thematic Strategy and a proposal for a Soil Framework Directive with the objective to protect soils across the European Union.

The Strategy is intended to intensify research on soil and to raise public awareness.

The Framework Directive sets out common principles, objectives and actions. It requires the 27 Member States to adopt a systematic approach to identify and combat soil degradation, to tackle precautionary measures and to integrate soil protection into other policies. Member States shall identify areas where there is a risk of erosion, organic matter decline, compaction, salinisation and landslides. They must set risk reduction targets for those areas and establish programmes of measures to achieve them. They will also have to prevent further contamination, to establish an inventory of contaminated sites on their territory and draw up national remediation strategies. Finally, the Member States are required to limit or mitigate the effects of sealing, for instance by rehabilitating brownfield sites. The proposal passed the European Parliament and is negotiated in the Council of the Member States.

Recent legal developments in Germany and a European Soil Framework Directive – Prospects for Management and Remediation of Contaminated Land

Jörg Frauenstein

Federal Environment Agency, Soil Protection Measures,Germany

The management of contaminated land and groundwater was one of the key pressures for federal soil protection law in Germany. In 1999, the Federal Government put the Federal Soil Protection Act (BBodSchG) and the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) into force, which established nationally standardised regulations for the registration and remediation of contaminated sites. The purpose of the Soil Act is to protect or restore the functions of the soil on a permanent and sustainable basis. Actions entail the prevention of soil changes which are harmful to the soil; the rehabilitation of the soil and water resources at contaminated sites; and precautions against negative soil impacts, such as the disruption of its natural functions and its function as an archive of natural and cultural history.

One important focus of the act is to prevent soil contamination and to regulate the clean-up of abandoned contaminated sites. The Federal Soil Protection and Contaminated Sites Ordinance supplements the Act and specifies requirements in respect of site investigation, sampling strategy and laboratory approach, evaluation and remediation. The laboratory approach and the methods for soil analysis are furthermore determined according to German Industry Standards (DIN) and European Standards (CEN).

This legislation has established a national assessment framework for the evaluation of soil quality in relation to the “Soil-Man”, “Soil-Plant” and “Soil-Groundwater” paths of action.

Since 1999, the individual States have been responsible for the enforcement of Act and Ordinance. Now the Federal Environment Ministry is preparing an update of the Federal Soil Protection and Contaminated Sites Ordinance. It is to take the experience gained over several years with the implementation of the BBodSchV adequately into account and adapt its technical and methodological requirements to the advanced state of knowledge. In particular, it is necessary to incorporate methodological developments, which have noticeably accelerated with the introduction of soil protection legislation and the results of a broad range of soil-related research into an updated Soil Protection Ordinance and implementation practice.

However, more than 270.000 suspected contaminated sites registered in Germany in 2007. To handle this huge number of sites, a stepwise risk assessment procedure was developed to filter out the sites where there is urgent call for action because of their risks for humans and the environment. In the past 20 years, considerable efforts have been made to clean up and redevelop contaminated sites. Public funding to research as well as to industry has contributed significantly to the development of soil treatment technologies at a high standard. The technologies used are best demonstrated for the treatment of typical industry-originated substances. Current research and development efforts are rather concentrated on the setting up of cost-efficient clean-up techniques and strategies.

The remediation process will become more complex and interdisciplinary in which the actual clean-up procedure must contribute by effective technologies at reasonable prices. This is also the focus of ongoing national research.

In 2006, the European Commission presented a Thematic Strategy for soil protection and a Proposal for a Directive establishing a framework for the protection of soil (SFD).

The Strategy sets out a series of actions aiming at defining a comprehensive strategy with the overall objective of protection and sustainable use of soil by preventing further soil degradation, preserving its functions and restoring degraded soils to a level of functionality consistent at least with current and intended use. The SFD is an important chance to regulate soil protection on the same level like water and air. However, it was not possible so far to attain the qualified majority needed to reach political agreement on a draft directive establishing a framework for the protection of soil.

Nevertheless, among most member states several communities express the crucial interest to come forward with a European Soil Framework quickly. Within the Common Forum (the network of contaminated land policy makers and advisors from national ministries in EU member states and EFTA countries), it was announced that France will pick up the SFD back on the political agenda for the upcoming EU-Presidency. Reflecting the statement given by the French Minister during the Deliberation of the Environment Council, we expect that the technical discussion about content will shift the political arguments against a European Soil Framework.

Register of Contaminated Sites

Dr. Harald Mark, MSP GmbH, Germany

A successful treatment of contaminated sites requires a systematic and gradual procedure - such as it has proved its worth in Germany for many years. The first step of treatment is the registration of contaminated sites. Registration contains investigation in the sense of collecting information, various steps of assessment and documentation in maps and text. Main target is the complete registration of all abandoned landfills and industrial sites within an area municipality. Normally already existing, but widespread information is collected and systematically analysed. The methods of area-wide registrations are mainly based upon historical sources like documents, plans, aerial photographs and maps. The procedure of area-wide registrations is fairly complex and requires considerable skill. It is important to divide the steps of investigating industrial sites from those, which refer to abandoned landfills.

In order to investigate abandoned industrial sites, historical address books, trade-indices and license-documents are normally important sources as well as historical maps. After the investigation of data the registered industrial sites must be located in an actual topographical map of large scale. The most important source for detecting landfills (and also contaminated sites caused by military action) are historical aerial photos (analysis of time-lapse anal photos). In order to get all relevant information aerial photos should be analysed stereoscopically.

All results are read in a database. The main purposes of using a database are storing, retrieving and modifying data. These data are also spatially represented corresponding directly with a Geographical Information System (GIS). Geographical information systems combine spatial data with subject data. This means that e.g. the information „storage building“ contained in the data bank of the Geographical Information System is represented as an area (polygon) exactly as regards its position and contours. That means that the storage building – equally as all other (partial) uses recorded – is represented in the GIS with its contours on the background of a(n) actual) topographical basic map (or if this is not available: of an aerial photo) and may be thus exactly localized on the terrain. This graphical information together with the entries into the data bank provide an important basis for planning and carrying out further measures as they may be concentrated on areas showing a high contamination risk owing to their actual and/or historical use.

Characterization of Mercury Contaminated Sites – The Role of Speciation Analyses

Harald Biester

Technical University of Braunschweig, Germany

Mercury is known to be released by a large number of industrial processes including energy production and has caused contamination of soil and aqueous ecosystems on local to global scale. The volatility of mercury at ambient temperature and the high toxicity of most of its compounds make it unique among the heavy metals released by anthropogenic activities. Moreover, more than any other heavy metal, mercury in natural environments undergoes various species transformation processes, which may enhance or diminish its mobility, bioavailability and thus its risk potential. Due to this, determination of Hg species or Hg binding forms in soils, sediments and waters is essential to evaluate environmental risks of Hg contaminated areas. The presentation will show examples of Hg contaminated sites of different scale such as Hg mining areas, chlor-alkali plants and wood preservation sites, where soils and aqueous ecosystems have been heavily polluted over decades or even centuries. Examples of a pyrolytic solid phase Hg speciation method are shown, which allows to distinguish most inorganic Hg compounds such as Hg(0), HgS, HgO, $HgSO_4$ and humus bound Hg forms in soils and sediments. Case studies from Hg mining areas will demonstrate the importance of distinguishing insoluble Hg ores (cinnabar) from humus bound Hg species. In contrast to cinnabar, organically bound Hg formed in soils after deposition of Hg(0), which has been emitted from the smelter, is mobile and has a high potential to become bioavailable in aqueous environments. Similar examples are shown from soils in the vicinity of chlor-alkali plants, where originally deposited Hg(0) is quantitatively transformed to organically bound forms or re-released to the atmosphere.

Other case studies of former wood preservation sites, where soils and groundwater were contaminated by discharge of large quantities of $HgCl_2$-solution show that Hg mobility in aquifers can be drastically diminished by natural reduction of Hg-Chloride to Hg(0) through changing redox condition in the saturated zone. In addition, operational defined methods of Hg speciation in aqueous samples are demonstrated, which allow to distinguish soluble reactive Hg forms from soluble organic Hg complexes. Here, it will be shown that soluble humic complexes are the most common Hg binding forms released from polluted soils into the aqueous environment and the most important Hg species in the pathway to bioavailability.

Besides their important role for the characterization of contaminated sites, Hg speciation measurements will be shown to play an important role for remediation strategies, especially if based on Hg transformation processes such as immobilization through the formation of HgS or the use of reactive barriers for groundwater clean-up.

Mercury Pollution in Guizhou, Southwestern China
- an overview -

Xinbin Feng, Guangle Qiu

State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China

Mercury (Hg) is a global pollutant and poses a worldwide concern due to its high toxicity. Guizhou province is recognized as a heavily Hg-polluted area in China due to both the special geochemical background and human activities. Here an integrated overview of current knowledge on the behavior of Hg in environments, as well as human health risk with respect to Hg contaminations in Guizhou was presented.

Two key anthropogenic Hg emission sources in Guizhou were coal combustion and metals smelting, which dominantly contributed to the high levels of Hg in local ecosystems and high fluxes of Hg deposition. The annual Hg emission from anthropogenic sources ranged between 22.6 and 55.5 t, which was about 6.3-10.3% of current total Hg emissions in China.

Meanwhile, Hg enriched soil in the province serves an important natural Hg emission source to the ambient air. The local environment of Hg mining and zinc smelting areas are seriously contaminated with Hg. It is demonstrated that rice growing in Hg contaminated soil can accumulate methylmercury (MeHg) to a level to pose health threat to local inhabitants whose staple food is rice.

Local inhabitants in Hg mining areas are exposed to Hg through inhalation of Hg vapor and consumption of rice with high level of MeHg. Rice intake is indeed the main MeHg exposure pathway to local inhabitants in Hg mining areas in Guizhou, which is contrary to the general point of view that fish and fish products are the main pathway of MeHg exposure to humans.

Key words: Emission; Coal combustion; Methylmercury exposure; Mining; Smelting

The investigation of the mercury contamination in a Chinese plant: a case study

Jun Hu & Jianlong Wang,

Laboratory of Environmental Technology, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, 100084, P.R.China

For investigating the current situation and the mercury contamination and remediation measurement in a Chinese plant, the samples of soil, water and air in this area had been taken and analyzed. The result showed that the mercury concentrations in soil were 1349.26, 25.52, 342.2, 360.79, 73.57, 175.86, 28.07 and 36.06 mg/kg at eight different sampling sites, respectively, and the maximal mercury concentration in surface soil was 4179.26 mg/kg.

The mercury concentration in water body exceeded the water quality III standard of surface water (GHZB 1-1999) (0.1 ug/L). The range of mercury concentration of air samples is 5.3 ug/L- 73.8 ug/L in 2006 and pollution is very serious.

From the mercury data collected from the soil, water and air in this region, we can conclude that the soil in that area has been contaminated heavily.

Keywords: elemental mercury, environmental pollution, TCLP, stabilization/solidification

Risk Assessment and Risk Management of Harmful Substances in Germany in the Framework of the Soil Protection Ordinance Example - Mercury

Dr. Andreas Zeddel

Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, Germany

The soil protection ordinance encloses trigger-values for the soil-to-human, soil-to-groundwater and soil-to-edible plant exposure-pathways to identify “harmful changes to the soil-functions”. Trigger-values are used for risk-assessment in the exploratory investigation phase to diagnose the need for further investigations. Because of the hazard-based nature of these values – especially for the soil-to-human-pathway – they can release remediation measures in certain cases. The derivation of these values is well documented and the exposition conventions are as realistic as possible concerning the ‘realistically worst case’. The derivation of trigger-values for the soil-to-human and soil-to-groundwater pathway for mercury and the conventions used was presented.

The starting point in derivation of trigger-values for the soil-to-human pathway is the tolerable resorbed doses (TRD) achieved from experimental or epidemiological data. Due to different toxicities, inorganic (especially $HgCl_2$) and organic (especially Methyl-Hg) mercury-species are discriminated. Toxicological effects on humans were observed especially in neuronal disorders as well as nephro- and immunotoxical effects (TRD-value for inorganic mercury: 15 ng/kg*d for oral ingestion, 30 ng/kg*d for inhalativ ingestion; TRD (oral) for organic mercury: 50 ng/kg*d). By calculating a TRD-value, safety-factors are required to get a safe distance to the lowest observed adverse effect concentration (LOAEL) and the no-effect level (NOAEL), respectively. In this manner e.g. the TRD-value - oral - for organic mercury was derived from a LOAEL of 700 ng/kg*d (neurotoxical effects on children, whose mothers are exposed to these concentrations in pregnancy). A safety-factor for the extrapolation of a NOAEL from the LOAEL (SF_b=5) and a safety-factor for especially sensitive persons (SF_d=3) are chosen in this case. Safety-factors are an important tool for the calculation of hazard-based trigger values. A so called hazard-factor was achieved by building a geometrical mean of these safety-factors. In the case of oral ingestion of organic Hg the hazard-factor is SQR(5*3)=3,9 resulting in a hazard-based body dose of 195 ng/kg*d.

To get a trigger-value, information about the background exposure by food, drinking water and air is necessary. The background exposure in Germany by oral ingestion was assessed to 30-300 ng/kg*d. Due to special researches the convention of a contingent of 80 % of the TRD by the (food) background was chosen in the case of mercury.

Conventions about the exposure of men, especially children, to contaminated soil are the second stand for calculation trigger-values (e.g. a soil incorporation rate of 33 mg soil/ kg*d for children). From these data a primary trigger-value for (organic, oral) mercury was calculated with 4,7 mg/kg. From all calculation approaches this was the most sensitive one. Keeping in mind the ratio of inorganic and organic mercury in ‘worst case’, the trigger-value was fixed with 10 mg/kg for playgrounds. Trigger-values for all usages are to discuss.

It will be presented what sort of investigations can be done if trigger-values for this pathway are exceeded in the exploratory investigation phase (bioavailability, the real inorganic/organic ratio) and why there are no action values for mercury for this pathway.

Trigger-values for the soil-to-groundwater pathway and “insignificance thresholds” for groundwater are based on different conventions. The derivation of “insignificance thresholds” also includes ecotoxicological agreements.

Remediation Techniques

Christian Weingran

HIM, Germany

There are two basic approaches to remediation:

- Elimination of the risks by removing or destroying contaminants
- Control of risks (reduction / management) to an acceptable level by reducing contaminant concentrations or by containing the contaminants, such as installing barriers between the contaminants and potential receptors.

In the past cleanup was very often based on civil engineering approaches aiming at maximum risk control (excavation/containment) or risk elimination. Groundwater remediation has focused on the removal of contaminated water form the subsurface and treating it at the surface (P&T)

From a technical point of view these approaches are still the fastest way to solve the problem. If there is an urgent need to reuse the sites or to solve a problem this is an advantage. The high costs associated with these methods are a big disadvantage and were prohibitive in many projects.

As a consequence concepts which focus on the control of the groundwater plume or the containment of the source rather than the elimination of the source have received increasing attention during the recent years.

A lot of active and passive in-situ technologies have been developed, that address the contamination of soil and groundwater and avoid the (effects and cost of) excavation and the above ground environmental impacts but require more time. They have less predictable results and may require long time monitoring and aftercare.

The selection of the appropriate technology is critically dependent upon:

- the goals which are set for site remediation. Goals can be defined on various levels, e.g. reduction of potential or reduction of actual risk.
- the remediation strategy: e.g. a risk reduction/management strategy may suggest the use of pump and treat systems, physical and/or hydraulic containment systems.

The remediation strategy developed for a particular site may combine both approaches and several different methods. Different mobility of the components of a mixture of contaminants will require different methods, strategies and priorities of remediation.

Integrated strategies consisting e.g. of P&T for hydraulic control and dissolved plume mass removal combined with source targeted technologies have been determined to be a most effective long term solution in many cases and may lead to cost-effective remediation measures specifically suitable to large industrial areas, where the source zones are often poorly defined or hardly accessible.

Selection and integration of technologies should use the most effective contaminant transport mechanisms to arrive at the most effective treatment scheme. To assess the applicability and potential performance of technologies, information is required on the contaminants present and the physical, chemical, and biological properties of the material to be treated.

Treatment technologies capable of contaminant destruction by altering their chemical structure are thermal, biological, and chemical treatment methods.

Treatment technologies used for extraction and separation of contaminants from environmental media include soil treatment by thermal desorption, soil washing, solvent extraction, and soil vapor extraction (SVE) and water treatment technologies.

Treatment technologies that immobilize the contamination include stabilization, solidification, and containment technologies, such as placement in a secure landfill or construction of treatment walls. No immobilization technology is permanently effective, so some type of maintenance is desired.

Some technologies can be applied ex-situ (after contaminated soil or groundwater has been removed for the treatment) or in-situ (without removing the contaminated media). Ex-situ treatment may be performed on-site using mobile or transportable treatment systems or off-site fixed treatment facilities.

The processes are frequently combined in treatment trains. A treatment train is a sequential combination of technologies or unit processes which treat recalcitrant matrices more effectively than any single technology could. E.g. soil washing becomes the prelude to chemical or biological treatment.

Remediation of Contaminated Sites – Strategies

Martin Bittens,

Helmholtz Centre for Environmental Research – UFZ, Department of Groundwater Remediation, Germany

In Germany and other European Countries, a large number of regions exist where industrial, military and mining activities during the past century have led to vast contaminations in soil, groundwater and surface waters.

Large-scale contaminated sites may severely affect human health, the environment and the economy. Currently some 20,000 of these so called megasites exist in Europe (including CEE States) with estimated costs for revitalization measures that exceed the amount of 100 Billion Euros. The figures clearly demonstrate that revitalization of megasites demands innovative site investigation and remediation strategies to make it economically feasible.

Streamlining site investigations and cleanup decision a dynamic framework is needed that allows site managers to achieve defined project objectives. According the TRIAD approach which is being recommended by the U.S Environmental Protection Agency elements such as systematic planning, dynamic work plan, on-site analytical tools need be integrated in such an approach (EPA, 2005).

In preparation of effective site investigation measures a series of factors need to be considered. These include technology selection, identification of potential exposure pathways, hot-spot detection, assessment of risks for human health and the environment, design of a conceptual site model (CSM), calculation of clean-up levels, as well as estimation and evaluation of costs for site improvement, operation, and maintenance. Some of the factors are of particular relevance in developing an appropriate remediation strategy for large scale contaminated sites, among them the CSM and the delineation of contaminant sources in the subsurface.

The CSM is one of the primary planning tools that can be used to support the decision making process managing contaminated land and groundwater on a large scale. The CSM organizes available information about a site in a clear and transparent structure and facilitate the identification of data and information gaps. Once the CSM is established, additionally needed data can be gathered and integrated in the CSM, followed by a revision of the CSM and a refinement of decision goals, if required. Thus, the CSM matures and enables an improved understanding of the site characteristics, such as contamination status, receptor profiles, etc., and the re-adjustment of decision criteria.

The detection of hot spots is essentially for the design of source removal measures. Particularly on contaminated sites of large extent, the hot spot search would cause enormous costs if it is performed on basis of soil and/or groundwater samples taken from a regularly grid mesh. A more cost effective approach is the application of geostatistical methods which allow the hot spot identification under definite boundary conditions (probability of hitting or missing hot spots, maximum size of hot spots that would be hit, a grid of samples based on finding a hot spot of a defined size with a distinct probability).

Remediation of the Chemical Production Facility (CFM) of Marktredwitz

Dr. Gernot Huber

Bavarian Environment Agency, Germany

Introduction

For nearly 200 years, products containing inorganic and organic mercury were processed in the Chemical Production Facility in Marktredwitz (Chemische Fabrik Marktredwitz), the oldest chemical manufacturing facility in Germany. The plant caused serious environmental pollution before it was closed down in 1985. This is an overview of the measures performed between 1986 until now for environmental risk assessment, decontamination and restoration of the contaminated site and its surrounding area.

Basic studies

A research project on risk assessment for the mercury-contaminated site in Marktredwitz was realised prior to the remediation of the CFM. Analytical methods for the determination of mercury, especially the differentiation of inorganic and organic forms of Hg, have been derived, and the Hg content of soil, water and air was measured in Marktredwitz and surrounding areas. Transport pathways for mercury by air and water have been specified.

CFM premises

On the premises of the chemical production facility, the concrete and the brick-structures of the buildings as well as the subsurface soil and soil- and groundwater were severely contaminated with mercury (up to 5 000 mg/kg in subsurface soil and up to 200 mg/l in soil water). For the protection of the nearby river (Kösseine) a vertical groundwater barrier was installed; for the decontamination of the site, technical facilities and buildings were demolished. Soil excavation of material containing more than 10 mg mercury per kg and a groundwater pump-and-treat system (remediation target < 1 µg/l Hg) were employed until 1996. About 55 000 metric tons of contaminated debris and soil were treated in an off-site soil treatment facility and cleaned up to concentrations of mercury below 50 mg/kg by soil washing and vacuum distillation. The treated soil was deposited in a mono-landfill (4-ply mineral base seal). 35 000 metric tons of excavated soil were land filled directly. Another 5 000 metric tons containing chemical wastes and treatment residuals from the manufacturing process were deposited in a subsurface landfill.

Revitalisation of the CFM premises

The premises in the centre of Marktredwitz were completely decontaminated and could thus been made available for different types of uses. Today an office and shopping centre – now an important part of the townscape - is located on the site.

City centre of Marktredwitz

Soil sampling and analysis were done in the nearby city centre in order to characterise the contamination in this area. Mercury content up to 180 mg/kg soil was determined. Furthermore, water, sediment, air, dust and food samples were analysed for mercury. Based on specific exposure scenarios, environmental health risk assessments for residents living in the municipal area were carried out. Consequentially, in gardens with more than 33 mg mercury per kg soil (trigger value for housing areas with gardens case-specifically deduced for Martkredwitz), soil excavation and backfilling with clean soil were done. Human bio-monitoring (sampling of blood and urine) was performed as well. The scientific research carried out indicates that there is no fundamental threat to human health.

River and flood plains downstream the CFM

Mercury-contaminated effluents have been discharged into the rivers Kösseine and Röslau without any effective pre-treatment for about 190 years. Analyses of water and sediment showed that for more than 15 km downstream of the CFM, river bed sediments were contaminated up to 700 mg mercury per kg and flood plains contained up to 170 mg mercury per kg agriculturally used soil. Highest concentrations in river sediments were measured in backwaters from weirs; from these zones and a cooling water pond of a power plant, about 34 000 metric tons of river sediments were removed. Thus more than 900 kg Hg were recovered from the river system. The risk for groundwater and drinking water quality was assessed, no adverse effects were predicted. Forage (grass) from the flood plains is regularly analysed, reassessed for mercury content and evaluated for the foodstuff use Human uses in the flood plains (i.e. playgrounds, allotment gardens) were mapped, soil sampled and case specific measures carried out. A bio-monitoring program has been installed in order to monitor the effects of the site remediation on the aquatic ecosystem (fish, macro-invertebrates, macrophytes). An enormous reduction of Hg content in the river ecosystem over a wide area due to closing down and remediation of the CFM and its environment could be achieved, but contamination still exists in future.

Transboundary commission for water quality protection

In the river system mercury has been transported across the national border to the Czech Republic and transfer of mercury, but in considerable lowered amounts after close down and remediation is still going on. Further measures are realised in close contact to the Czech neighbour country due to coordination by a transboundary commission for water quality protection.

11 Transparencies

The transparencies of the workshop presentations are available on the attached CD.