NICOLE

NETWORK FOR INDUSTRIALLY CONTAMINATED LAND IN EUROPE

RISK-BASED MANAGEMENT

OF MERCURY-IMPACTED SITES

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INTRODUCTION & REGULATORY CONTEXT

This technical booklet has been prepared on behalf of the Network for Industrially Contaminated Land in Europe (NICOLE) Mercury Working Group to share case studies and best practice related to the characterisation and management of industrial sites impacted by Mercury (Hg). NICOLE was formed in February 1996 for the stimulation, dissemination and exchange of knowledge regarding industrially contaminated land. Its 100 members from 20 European countries come from industry, trade organizations, service providers, technology developers, universities, independent research organizations and governmental organizations. More information about NICOLE can be found at www.nicole.org.

Only for specific industries is Hg typically found as a principal pollutant, often at relatively-high concentrations (e.g. 100 to 1 000 mg/kg). A common example is chlor-alkali sites, where the majority of the Hg impacts identified in surrounding soils typically comprise the original elemental form of Hg. Mercury has also been used as a key reactant in the production of organic compounds, such as the synthesis of vinyl chloride and acetaldehyde from acetylene. At other industrial sites, Hg is often present as a secondary pollutant at relatively low concentrations (i.e. not the primary risk driver)[1]. A typical example is the presence of Hg at 1 to 10 mg/kg levels in coal tar contaminated soils at gas and coking works, originating from low levels of Hg in the coal that is co-condensed with the tarry substances.

Recent legislative texts and government policies restrict the industrial use of Hg in Europe and could lead to the closure and redevelopment of some industrial operations using Hg. Most of these affected facilities will need to be investigated and management measures may subsequently be required. This concerns not only chlor-alkali plants using the Hg cell process, which are the majority industrial user of Hg in Europe, but also other industrial activities, such as wood impregnation, precious metals recovery, oil and gas production, and the manufacture and/or recycling of batteries, thermometers, and electrical switches.

Two recent policy developments include the United Nations Environmental Programme (UNEP) Global Mercury Convention (*Minamata Convention on Mercury*)[2] and an updated version of the European Commission's Best Available Techniques Reference Document (BREF) for the chlor-alkali industry[3].

The Minamata Convention is a multilateral environmental treaty agreed by over 140 countries on 19th January 2013, addressing several Hg-related industrial activities. It will require signatory nations to:

- Phase out Hg in some manufacturing processes (acetaldehyde production by 2018 and chlor-alkali production by 2025) and restrict its use elsewhere;
- Reduce and, where feasible, eliminate the use of Hg in other industries, such as artisanal gold mining, and also reduce air emissions from point sources such as coal burning, cement production, smelting of non-ferrous metals and waste incineration; and
- Phase-out or reduce Hg use in products, such as batteries, switches, lights, cosmetics, pesticides and measuring devices and dental amalgam.

The historic use of Hg is also addressed in the Convention, as each signatory nation must develop appropriate strategies to identify and assess sites impacted by Hg or Hg compounds. In addition, the Convention addresses the supply and trade of Hg, and safer storage and disposal.

UNEP MINAMATA CONVENTION ON MERCURY

The European Commission BREFs are one of the main reference documents used by EU Member States when issuing operating permits and establishing emission limits for industrial installations. The updated BREF for the chlor-alkali industry (CAK BREF) was finalised in December 2013, supplementing the existing European legislative framework related to the chlor-alkali industry. The CAK BREF states that Hg cells are no longer considered as Best Available Technology (BAT). As such, Hg cell technology can no longer be used in EU-based chlor-alkali sites permitted under the Industrial Emissions Directive (IED) beyond 11th December 2017. The BAT conclusions (Chapter 5 of CAK BREF) were published in the EU Official Journal and are legally binding[4].

The updated European Commission BREF supplements existing EU Directives (EC 1102/2008 and 2011/97/EU), which ban the export of recovered metallic Hg outside of the EU, restrict Hg re-use, and specify requirements for transportation, storage and disposal. Some countries (e.g. France) are considering the development of country-specific guidelines for the management of Hg-impacted sites.

Though Hg exhibits a unique combination of physical and chemical properties compared to other metals, NICOLE believes that the management principles for Hg-impacted land should be the same as for other contaminants, applying the principles of Risk-Based Land Management (RBLM)[7], Sustainable Remediation[8] and Net Environmental Benefit Analysis[9].

JRC SCIENCE AND POLICY REPORTS

Best Available Techniques (BAT) Reference Document for the Production of Chlor-alkali

Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control)

Thomas Brinkmann, Germán Giner Santonja, Frauke Schorcht, Serge Roudier, Luis Delgado Sancho

2014

L 332/34 EN Official Journal of the European Union 11.12.2013

COMMISSION IMPLEMENTING DECISION

of 9 December 2013

establishing the best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions, for the production of chlor-alkali

(Text with EEA relevance)

(2013/732/EU)

The challenge with Hg-impacted sites is to acquire sufficient representative data to build a robust conceptual site model (CSM) and determine the most appropriate site management measures. We have prepared this booklet in light of the recent regulatory developments to share current information, case studies and best practice related to the characterisation and management of Hg-impacted industrial sites. The focus of the technical booklet is on the management of Hg-impacted soil and groundwater. Whilst surface water, air emissions, sediments and other media are discussed generically, they are not the primary focus.

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MERCURY PROPERTIES AND INFLUENCE ON FATE & TRANSPORT

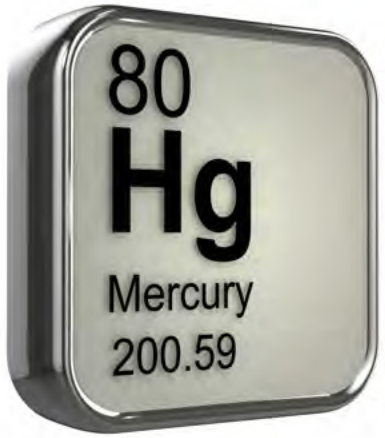
Hg exhibits unique physical and chemical properties which are critical to understand during the characterisation and management of Hg impacts at industrial sites. There are three primary forms of Hg:

- Elemental Hg (Hg^0), which can occur in liquid and gaseous states;
- Inorganic Hg species (e.g. mercurous [Hg^+] chloride, mercuric [Hg^{2+}] chloride, mercuric oxide, mercury sulphate); and
- Organic Hg species (e.g. methyl-Hg).

These Hg forms can be present in the environment as metallic pure-product (elemental), aqueous phase, gaseous phase and/or bound to the soil or other solids (e.g. concrete).

Knowing the speciation of the Hg forms present, as well as the ambient and anthropogenic geochemistry, provides insight into the long-term behaviour of Hg, potential migration pathways, receptors, risks and the appropriate management measures to control such risks sustainably.

Understanding past industrial practices, such as the chemical processes, types of Hg used, and how raw materials, wastes and effluents were managed, is the first step to identifying the Hg forms and species potentially released, as well as the likely migration pathways into the surrounding environment. Site sampling and innovative laboratory analysis, such as selective sequential extraction and solid-phase Hg pyrolysis/thermal desorption, can then be used to quantify the Hg species present in site soils and groundwater.



Elemental Hg (Hg^0)

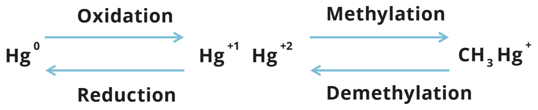
Elemental Hg is relatively insoluble in water, forming dense droplets that can migrate laterally along sub-surface utility corridors, drainage systems and surrounding backfill. The high density of elemental Hg enhances the risk of downward migration, typically along preferential pathways (e.g. coarse backfill around pilings/foundations, rootlets, cracks/fissures) and during drilling or ground-disturbing activities that create voids or ground vibrations.

The density and surface tension of elemental Hg are high, approximately 13.5 g/cm^3 and 470 dyn/cm at 20°C, compared to 1 g/cm^3 and 73 dyn/cm for fresh water. Elemental Hg and some organic Hg species are also volatile, which can lead to air dispersion and potential vapour intrusion.

Once released to ground, elemental Hg can also remobilise through volatilization and subsequent condensation or deposition. This transport mechanism has been shown to be most prevalent in warmer climates and areas with large temperature variations . This can lead to lateral dispersion of Hg from source areas and lead to the accumulation of elemental Hg beneath impermeable slabs and buildings and on top of concrete foundations.

Inorganic Hg (Hg^+, Hg^{2+})

Depending on the ambient geochemistry, Hg released to the environment can transform into other Hg fractions with varying mobility and toxicity. The key conditions that control Hg transformation include pH, temperature, organic matter, redox potential, cation exchange capacity, grain size and porosity. The main processes that can increase Hg mobility are redox changes (e.g. oxidation, reduction) and methylation:



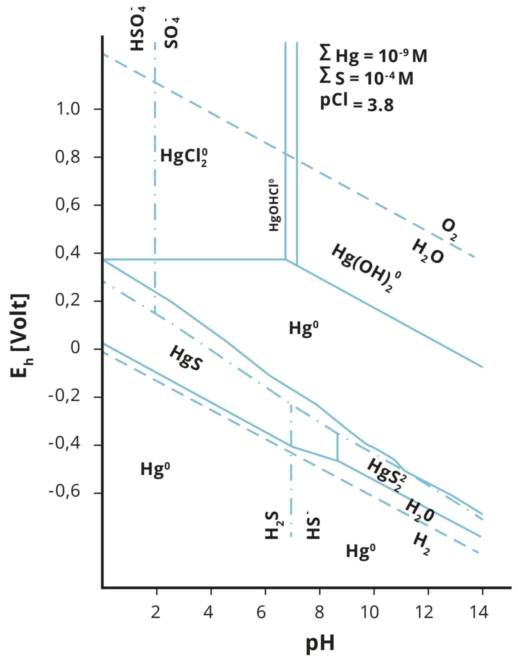
Oxidation can occur under acidic or basic conditions. The primary oxidant is typically oxygen, with the following reactions occurring:

Acidic conditions:
$4Hg + O_2 + 4H^+ \rightarrow 2Hg_2^{2+} + 2H_2O$
$2Hg + O_2 + 4H^+ \rightarrow 2Hg^+ + 2H_2O$
$2Hg_2^{++} + O_2 + 4H^+ \rightarrow 4Hg^{2+} + 2H_2O$
Basic Conditions:
$2Hg + O_2 \rightarrow 2HgO$

Residual chlorine can also oxidise Hg:

Acidic conditions:
$2Hg + Cl_2 \rightarrow Hg_2Cl_2$
$Hg + Cl_2 \rightarrow HgCl_2$
$Hg_2Cl_2 + Cl_2 \rightarrow 2HgCl_2$
Basic Conditions:
$Hg^+ + ClO^- \rightarrow HgO + Cl^-$

Hg can form salts with variable solubility in combination with various anions. For example, in the presence of excess chloride (e.g. salt water), Hg forms more soluble chloride species. One such species, mercuric chloride ($HgCl_2$), has a solubility of 6 % at 20 °C. Mercury can also form soluble complexes with dissolved organic matter.



Hg Pourbaix Diagram with Cl and S

Organic Hg (Methyl-Hg).

The biogeochemistry of Hg is complex, having both aerobic and anaerobic pathways. The primary processes are methylation and de-methylation. Methylation is a complex process that generally occurs under anaerobic conditions but is difficult to predict. Current research indicates that the methylation process is mediated by sulphate-reducing bacteria[11].

Methyl-Hg is of concern due to its mobility, toxicity and because it may be bio-accumulated in aquatic/marine animals in the food chain. Bioaccumulation in aquatic species has been shown to be influenced by pH and dissolved oxygen content[12]. While sulphate-reducing bacteria can promote methylation, which enhances Hg mobility and toxicity, sulphate reduction can also form sulphide, which then precipitates the highly-insoluble cinnabar (HgS).

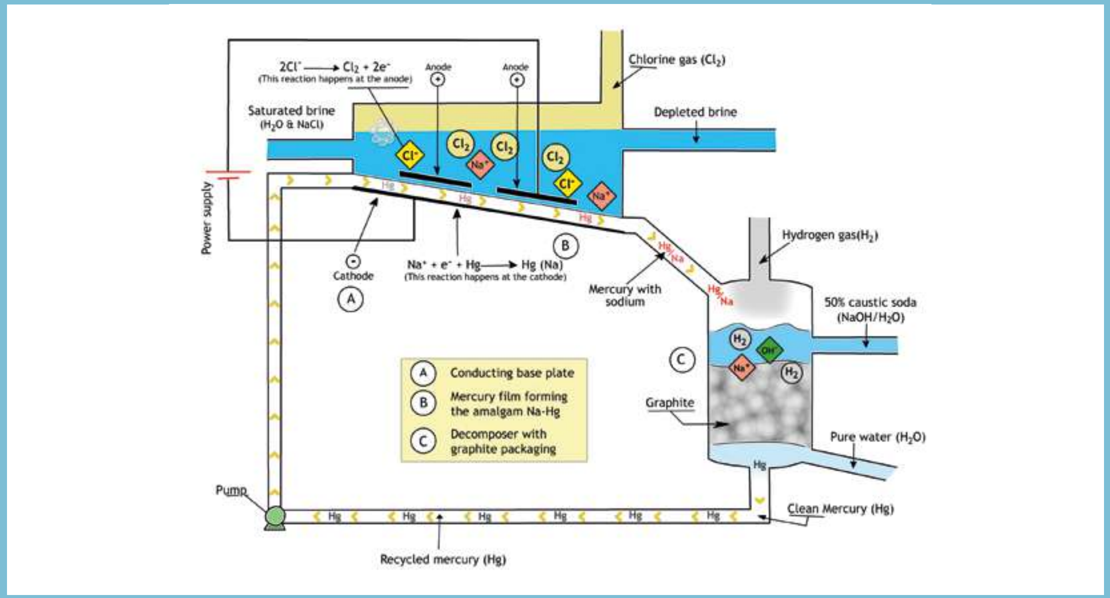
De-methylation is a process that generally occurs under oxidative conditions. However, there are also reductive de-methylation pathways:

Oxidative Pathway: $CH_3Hg \rightarrow Hg^{++} + CO_2$
Reductive Pathway: $CH_3Hg \rightarrow Hg^0 + CH_4$

Various bacteria show the capacity to reduce ionic Hg and/or methyl-Hg to elemental Hg[13], and de-methylation has been demonstrated with anaerobic bacteria[14]. In fact, it has been shown that some of the same bacteria that are responsible for methylation are also implicated in de-methylation, depending on the ambient geochemical conditions.

CASE STUDY 1:
CHLOR-ALKALI PLANTS

A LARGE INDUSTRIAL COMPANY THAT HAD RECENTLY CEASED OPERATING THEIR MERCURY-CELL CHLOR-ALKALI PLANTS WAS DECIDING A STRATEGIC APPROACH FOR MANAGING THE PORTFOLIO.



Key learnings

- Understanding the prior industrial processes, including management of raw materials, waste and effluents is critical for anticipating Hg distribution and speciation:
    - Cell rooms → relatively low solubility but volatile elemental Hg
    - Brine and Hg-Na amalgam treatment → more soluble ionic forms (e.g. $HgCl_2$, $Hg(OH)_2$)
- Hg plumes in groundwater are typically relatively short, with moderate concentrations (typically 10s of µg/l), although local geochemistry can affect this. Migration to depth can be an issue, particularly when in association with dense brine solutions.
- Effluent streams and air dispersion can lead to secondary impacts and off-site migration.
- Direct measurement (e.g. surface water, sediments, air, fish, arable crops, egetables) is the most effective way to convince stakeholders of true impacts and potential risk levels.

Identification of Hg Species

The Hg present in soil or sediment can be fractionated according to its chemical reactivity, mobility and potential bioavailability using analytical techniques such as Selective Sequential Extraction (SSE), performed by some commercial labs (e.g. Brooks Applied Labs[15]). Selective Sequential Extraction uses a variety of extractants ranging from water to *aqua regia* (HCl/HNO_3) to differentiate the Hg forms present, from water-soluble compounds to highly insoluble compounds such as cinnabar. This analytical methodology allows a quantitative assessment of the different Hg species, including potentially bioavailable species and the proportion of Hg that is semi-mobile or non-mobile.

Fraction	Description	Typical Compounds	Extractant
F1	water soluble	$HgCl_2$	deionized water
F2	weak acid soluble	HgO $HgSO_4$	pH 2 HCl/HOAc
F3	organo complexed	Hg-humics Hg_2Cl_2 CH_3Hg	1M KOH
F4	strongly complexed	mineral Lattice Hg_2Cl_2 Hg^0	12M HNO_3
F5	mineral bound	HgS m-HgS HgSe HgAu	aqua regia

Source: Brooks Applied Labs (www.brooksrand.com)

As with most inorganic compounds, metals will typically seek a stable geochemical endpoint when released into the environment. In an aerobic environment, SSE fractions F1, F2 and F3 typically dominate. Conversely, in a reducing environment, the F3, F4 and F5 fractions dominate in most cases. The F1, F2 and F3 fractions are more mobile and therefore typically drive the need for remediation. The SSE fractions F4 and F5 are relatively immobile.

Other Considerations

The fate and transport of Hg in the environment is also affected by sorption onto soil, sediment and other materials (e.g. concrete). As with many other contaminants, Hg sorption is strongly dependent upon the organic content[12] of the soil or sediment. In water, inorganic Hg and methyl-Hg can bind strongly to organic matter. The bound Hg can then be transported as particulates or colloids in surface water or groundwater. The transformation and mobilization of Hg from the soil or sediment particles to which it is adsorbed may then occur by chemical or biological reduction to elemental Hg or by microbial conversion to methyl-Hg.

To illustrate this, a recent US study showed the transport and distribution of inorganic Hg in particulate form from mine wastes to nearby reservoir sediment, and its subsequent conversion into methyl-Hg within the reservoir[16]. Higher methylation activity was seen in sediments subjected to wet/dry conditions resulting from seasonal water level fluctuations.

CASE STUDY 2:
CHLOR-ALKALI PLANT, TROPICS

CHLORINE AND CAUSTIC PRODUCTION FOR > 30 YEARS USING HG CELL TECHNOLOGY. PRIMARY RECEPTOR IS ADJACENT WATERWAY. SEDIMENTS WERE PREVIOUSLY DREDGED, BUT THEN RE-CONTAMINATED BY SITE RUNOFF.

Source: ERM

Key learnings

- Tropical climate, strongly aerobic subsurface conditions.
- Selective sequential extraction analysis (SSE) on residual Hg → primarily ionic:
  - 34 % water-soluble Fraction 1 ($HgCl_2$, $HgSO_4$)
  - 36 % acid-soluble Fraction 2 (HgO)
  - 0.4 % strongly-complexed Fraction 4 (Hg^0)
  - Remaining 29 % Fraction 3/Fraction 5 (majority likely organo-complexed)
  - No methyl-Hg
- Proposed risk-based remediation → Dredge hotspots, consolidate and stabilise on-site.

3

TECHNIQUES AND CONSIDERATIONS FOR RISK ASSESSMENT

The SNOWMAN Network[17] recently undertook a comprehensive Europe-wide review of current approaches for the assessment of risk at Hg-impacted sites and provided best practice suggestions as part of the IMaHg Project *(Enhanced Knowledge in Hg Fate and Transport for Improved Management of Hg Soil Contamination)*[18]. Based on their review, the primary human health exposure pathways for Hg-impacted sites include:

- Inhalation of indoor air;
- Soil ingestion; and
- Ingestion of vegetables or fish from impacted sites.

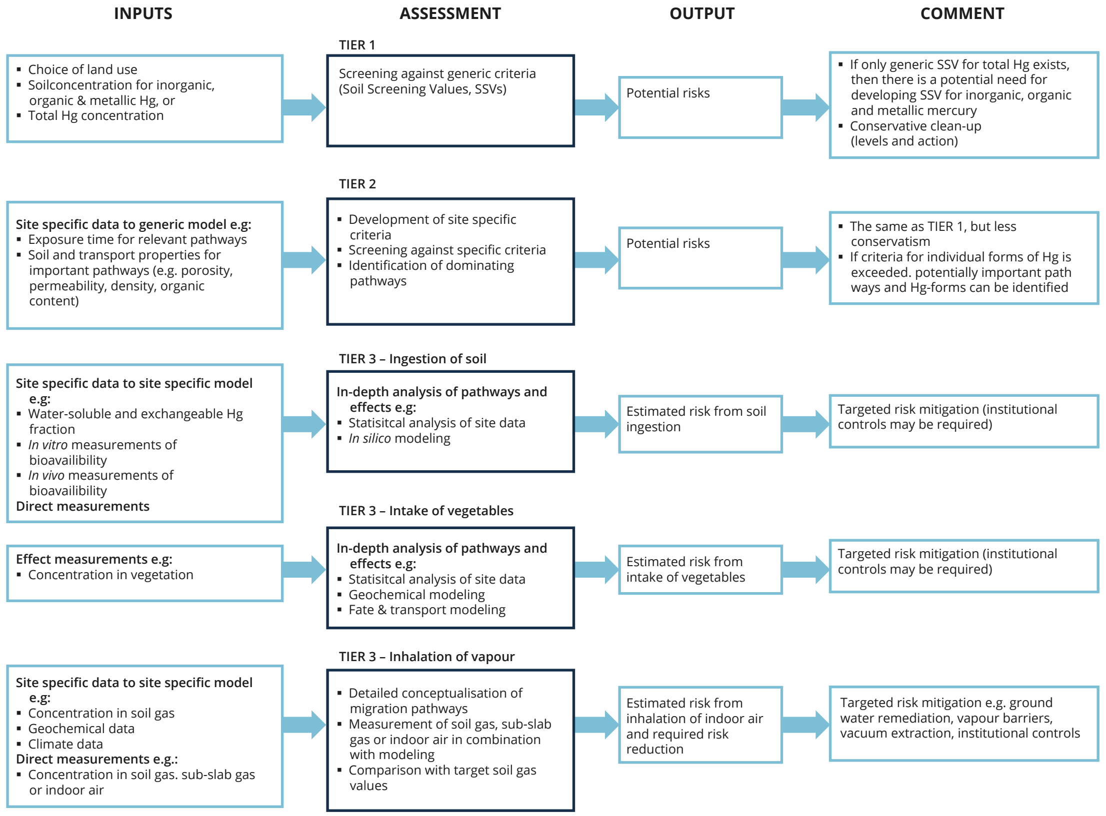
Through consultation with European contaminated land experts, IMaHg found that the risks associated with Hg exposure are generally assessed similarly in different countries, but the specific approaches used can differ. Some European countries (e.g. England & Wales, Belgium [Flanders], the Netherlands and Sweden) have developed and use their own generic models as a basis for establishing soil guideline values, with the same models often made available and used for site-specific assessments (by incorporating site-specific data). However, other countries, such as Spain, have selected and utilise a variety of generic exposure models and data developed elsewhere.

The SNOWMAN Network recommends assessing the Hg species present and their associated bioavailability in order to support a robust site-specific human health risk assessment and to identify efficient and effective risk-based remediation options. NICOLE supports this recommendation, so that site-specific, risk-based, sustainable and cost-effective management measures are identified and implemented.

SNOWMAN NETWORK
Knowledge for sustainable soils

Due to the variable and complex properties of the different Hg species, NICOLE recommends that exposure pathways and the Hg fractions be assessed individually and not lumped together to consider only total Hg. Consideration of just total Hg can result in the over- or under-estimation of risk levels (more commonly over-estimation). As a best practice, it should be clear from the risk assessment which pathway(s) could pose an unacceptable risk and to what extent risk reduction is needed to protect human health.

The SNOWMAN Network's findings support NICOLE's recommendation to use a combination of direct field measurements and geochemical modelling to efficiently characterise the different Hg forms and species present and assess the potential risks associated with a specific site.



INPUTS	ASSESSMENT	OUTPUT	COMMENT
▪ Choice of land use ▪ Soilconcentration for inorganic, organic & metallic Hg, or ▪ Total Hg concentration	TIER 1 Screening against generic criteria (Soil Screening Values, SSVs)	Potential risks	▪ If only generic SSV for total Hg exists, then there is a potential need for developing SSV for inorganic, organic and metallic mercury ▪ Conservative clean-up (levels and action)
Site specific data to generic model e.g: ▪ Exposure time for relevant pathways ▪ Soil and transport properties for important pathways (e.g. porosity, permeability, density, organic content)	TIER 2 ▪ Development of site specific criteria ▪ Screening against specific criteria ▪ Identification of dominating pathways	Potential risks	▪ The same as TIER 1, but less conservatism ▪ If criteria for individual forms of Hg is exceeded. potentially important path ways and Hg-forms can be identified
Site specific data to site specific model e.g: ▪ Water-soluble and exchangeable Hg fraction ▪ *In vitro* measurements of bioavailibility ▪ *In vivo* measurements of bioavailibility **Direct measurements**	TIER 3 – Ingestion of soil **In-depth analysis of pathways and effects e.g:** ▪ Statisitcal analysis of site data ▪ *In silico* modeling	Estimated risk from soil ingestion	Targeted risk mitigation (institutional controls may be required)
Effect measurements e.g: ▪ Concentration in vegetation	TIER 3 – Intake of vegetables **In-depth analysis of pathways and effects e.g:** ▪ Statisitcal analysis of site data ▪ Geochemical modeling ▪ Fate & transport modeling	Estimated risk from intake of vegetables	Targeted risk mitigation (institutional controls may be required)
Site specific data to site specific model e.g: ▪ Concentration in soil gas ▪ Geochemical data ▪ Climate data **Direct measurements e.g.:** ▪ Concentration in soil gas. sub-slab gas or indoor air	TIER 3 – Inhalation of vapour ▪ Detailed conceptualisation of migration pathways ▪ Measurement of soil gas, sub-slab gas or indoor air in combination with modeling ▪ Comparison with target soil gas values	Estimated risk from inhalation of indoor air and required risk reduction	Targeted risk mitigation e.g. ground water remediation, vapour barriers, vacuum extraction, institutional controls

***Fig1. Three Common Exposure Pathways for Hg (IMaHg Project)**, This chart and full IMaHg report can be found at www.snowmannetwork.com*

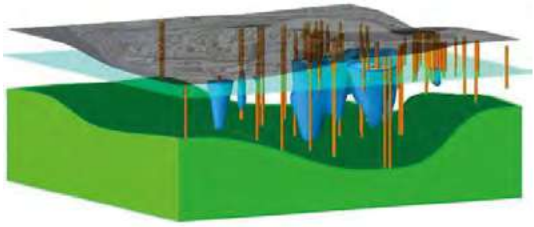
Within the IMaHg project, a first version of a new geochemical model, HP1[19] was developed to support Hg risk assessments by modelling the partitioning of Hg between soil, pore water, pore gas and elemental phases. This model currently requires validation of the hypotheses by experimental work. In particular, to experimentally study the behaviour of liquid Hg in porous media, with variable factors such as moisture content, organic matter and grain size distribution.

4 SITE CHARACTERISATION TECHNIQUES

As for any impacted site, the selection of appropriate investigation techniques for Hg-impacted sites will depend upon the site setting, geological context and the specific objectives and rationale for investigation. However, the unique physicochemical properties of Hg often present additional technical challenges and health and safety constraints for site characterisation.

Planning for Site Characterisation

Prior to mobilising into the field, available information related to past industrial activities, waste management practices, potential Hg sources, background concentrations, the desired future land use, potential receptors, and the site geological, hydrogeological and geochemical setting should be compiled and evaluated to the extent possible. As described above, understanding the potential speciation of the Hg forms present can also provide key insight into the Hg fate and transport to help focus the investigation and identify possible health and safety risks during site works. Site plans and other information related to site infrastructure, such as the locations of subsurface pilings/foundations and drains, are also important for identifying potential preferential migration pathways. This information should be used to develop an initial CSM that outlines potential source-pathway-receptor linkages in order to focus subsequent site investigation.



3-D Virtual site model showing mercury plume. Source: ERM

The lateral extent of potential Hg contamination in soils, sediment and surface water is typically a function of the duration and quantity of elemental Hg lost to the environment and the direction and strength of the prevailing winds. Therefore, meteorological factors that can influence Hg fate and transport (as well as measurements of Hg in the environment) should be recorded throughout the site characterisation programme to support data interpretation, including atmospheric pressure, wind speed/direction, temperature, humidity and recent rainfall.

The "Nugget Effect"

Elemental Hg contamination is often sporadically distributed within soils and building structures as small beads. Even when site soil conditions are fairly homogenous, close inspection of the soil fabric frequently shows Hg beads distributed unevenly within small voids, fissures and cracks created by rootlets (or other objects) and surrounding gravel and cobbles.

Source: ERM

lemental Hg can collect in features such as subsurface drains, and the foundations, walls, floors and metallic structures surrounding industrial processes can incorporate Hg through adsorption. As a result, the selected site investigation techniques should be tailored to account for non-uniform contaminant distribution (so-called "nugget effect").

Ground Penetration Techniques

When conducting intrusive sampling programmes at suspected Hg sites, it is important to consider that the vibrations from typical investigation and drilling methods can further mobilise elemental Hg into deeper soil horizons. Therefore, the use of techniques with high vibrations should be minimised in areas suspected of significant elemental Hg contamination. As with all impacted sites, rigorous decontamination procedures should be employed between sampling locations and at the end of the investigation programme.

Test pits and excavator trenches can be effective for the visual characterisation and assessment of shallow soil strata (e.g. for Hg droplets) and to facilitate the collection of shallow soil samples. However, slow advancement and clear decision-making is required to avoid penetration of low permeability layers and increased risk of vertical migration. A combination of visual inspection for Hg droplets and the scanning of samples/soil cores with a hand-held vapour monitor is recommended during all intrusive investigation activities. Further information regarding in-situ and ex-situ characterisation techniques are described below.

Source: ERM

Following investigation, any environmental boreholes must be properly backfilled with expandable grout (e.g. bentonite) to avoid creating preferential pathways, and all investigations should consider the importance of maintaining the integrity of low permeability layers.

In-situ Site Characterisation Techniques

Due to its volatility, elemental Hg will partition into the vapour-phase and can thus be detected in air and soil-gas. As such, various passive and active soil-gas sampling techniques can be used to rapidly and cost-effectively obtain large numbers of field measurements across a site, in order to evaluate the distribution of elemental Hg and to identify potential hot-spots or areas for further investigation. In comparison to active soil-gas sampling, passive sampling techniques are typically well-suited for use in shallow soil with low-permeability or high moisture-content or where access for more intrusive investigation techniques is limited.

Passive soil gas sampling modules are currently offered by suppliers including Beacon Environmental and Amplified Geochemical Imaging, LLC. However, Amplified Geochemical Imaging LLC does not currently offer analysis of Hg. The sorbent-based modules are typically installed in a grid pattern within the shallow soil horizon and left for a specified period of time (typically 30 to 60 days). The modules are then retrieved and returned to the supplier or laboratory for analysis. Although resulting data cannot be directly compared with regulatory standards or exposure thresholds, passive soil gas sampling programmes have been effective in identifying potential Hg hot-spots[20].

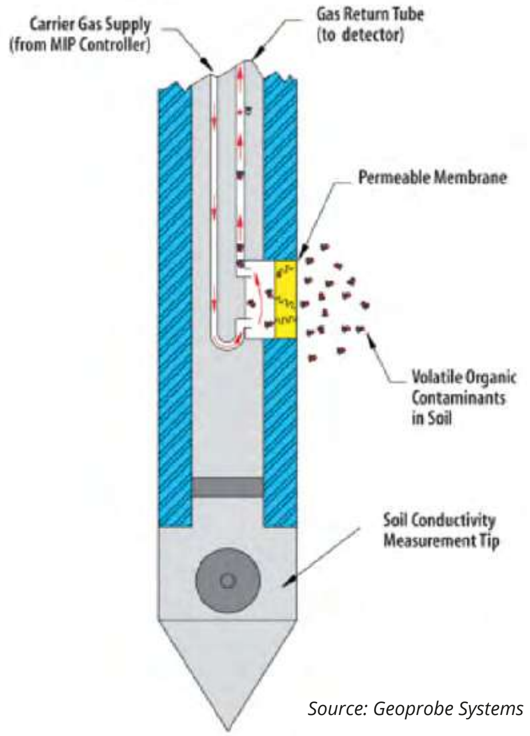
Active soil gas sampling for elemental Hg can be conducted using direct-push drilling technologies and portable Hg vapour analysers (for real-time data) or sorbent tubes (for subsequent laboratory analysis). Specially designed soil gas probes (such as the Geoprobe® Post Run Tubing System) are now available for use with direct push drilling rigs to increase sampling efficiencies and reduce potential issues due to rod leakage and contamination. Alternatively, dedicated soil-gas sampling points can be installed for one-off sampling or repeat monitoring events.

Source: Geoprobe Systems

Small portable Hg vapour analysers, such as those offered by Jerome® (e.g. J405) or Lumex® (e.g. RA915+), have been used successfully during soil investigations and soil-gas sampling activities to provide real-time quantitative elemental Hg vapour measurements.

If sorbent tubes are used, sulphide-activated charcoal tubes are considered to provide better data than normal activated carbon[21]. It should be noted that ensuring reliable measurements of Hg vapour can be problematic in some soil types as the pump rates on many instruments can draw up more vapour than is readily replenished through the soil pores, which can lead to overly conservative data being used in subsequent exposure modelling. Using passive capture devices such as the side cell on the Lumex can help to avoid this.

The Membrane Interface Probe (MIP) has also recently been demonstrated to be effective in providing rapid real-time vertical profiles of elemental Hg in soil and sediment[22]. The MIP is mounted onto a direct push rig and driven into the subsurface. The heated probe volatilises elemental Hg in the direct vicinity and the Hg vapour permeates the MIP's porous membrane and is transported in an inert carrier gas to a real-time detector at the surface. The MIP probe typically includes a tip that measures soil conductivity and other parameters at a known distance below the membrane, which can help to correlate contaminant concentration changes in soil stratigraphy.



Source: Geoprobe Systems

Ex-situ Characterisation Techniques and Sampling Considerations

Portable Hg analysers can be used for the ex-situ screening of building infrastructure and debris, as well as solid or liquid environmental samples. Hand-held vapour analysers, such as the Lumex® or Jerome® analysers described above, or other available hand-held detectors such as the Ion Science MVI, can be used to scan the head-space above a sample or site feature suspected of elemental Hg contamination or for the direct analysis of air or other gas streams. There are also mobile analysers available for the direct analysis of solid or liquid samples in the field.

Some of the more commonly-used analysers in Europe for the field analysis of soil, debris, sediment, organic materials and liquid samples include the Jerome® J405, Lumex® RA-915+ (with attachments such as the RP-91, 91C or PYRO-915+) and portable X-ray fluorescence (pXRF) analysers that are available from several suppliers, including Thermo-Scientific (Niton), Bruker GmbH, Oxford Instruments and Olympus. A summary of the main analysers is provided in the table on the next page.

Table 1. Commonly-used Portable Hg Analysers

Instrument Name	Manufacturer	Analytical Method	Range	Reported Interference	Dimensions	Image
Jerome® J405	Arizona Instruments, LLC	Gold film sensor	0.5 – 999 $\mu g/m^3$	None identified	2.4 kg 27.9 x 15.2 x 16.5 cm	
Lumex RA 915	Ohio Lumex Co.	Atomic adsorption spectrometer, Zeeman correction of background	0.05 – 200 $\mu g/m^3$	None identified	3.3 kg 29.0 x 21.0 x 11.0 cm	
Mercury Vapour Indicator (MVI)	Ion Science	Dual beam ultraviolet adsorption module	0.1 – 200 $\mu g/m^3$ 1.0 – 1999 $\mu g/m^3$	None reported	3 kg 14.5 x 29.5 x 8.0 cm	
NIC EMP-2	Nippon Instruments	Atomic adsorption spectrometer	0.1 to 1 000 $\mu g/m^3$	None reported	1.8 kg 26.5 x 12.8 x 11.0 cm	
Tekran Model 2537X	Tekran Instruments Corporation	Gold trap preconcentration with atomic fluorescence detection	0.001 to 2 $\mu g/m^3$	None reported	Weight not reported 48.3 (w) x 22.9 (h) cm	
DELTA Handheld XRF	Olympus	X-ray fluorescence	2 to 4 and 10 to 15 $\mu g/m^3$	None reported	1.5 kg (w/o battery) 26 × 24 × 9 cm	

Source: Data obtained from the respective manufacturer's published instrument specifications.

The currently-available portable detectors provide varying detection ranges, resolution, calibration requirements, accuracy, battery life/power requirements, size/weight, interference issues etc., and should be selected based on the specific project needs, site conditions and regional availability. For example, there is a potential to obtain false negative results when using pXRF detectors to screen materials with high concentrations of elemental Hg, due to the fact that X-rays do not effectively penetrate Hg droplets.

Although direct field measurements can typically be made with minimal sample preparation, it is often recommended that solid samples are dried, sieved, and homogenised before analysis. Preliminary tests conducted by the BRGM comparing Hg concentrations in split samples dried in a small non-ventilated oven at 38 °C (max) to the original wet (non-dried) samples showed differences were less than the normal observed sample heterogeneity. However, the pre-drying allowed more efficient and effective sieving prior to analysis. (Proper health and safety procedures should be implemented during such activities). An alternative drying method that could be tested, would involve placing the sample within a closed volume in the presence of a non-reactive water absorbent (e.g. silicate, anhydrous $CaCl_2$).

As described in Sections 2 and 3, identification of the different Hg species present is critical for evaluating the potential risks posed by a site to human-health or the environment and for developing an effective CSM and risk-based management strategy. This should be backed up by analyses focussed on the exposure media (e.g. ambient air) and migration pathways (e.g. soil-gas, groundwater, leachate samples) to establish a robust "lines-of-evidence" approach to the CSM.

Additionally, a solid understanding of other physicochemical parameters, such as pH, total/dissolved organic content, grain size distribution, clay content, redox potential, cation exchange capacity (CEC), soil moisture and iron content, is important for evaluating the Hg distribution, fate and transport. The collection of samples for laboratory analysis is therefore recommended in addition to the use of field screening techniques, in order to obtain sufficient coverage across the site as well as the low quantification limits, supporting parameters and Hg speciation data needed for robust site characterisation and management. The sample preparation performed in the laboratory prior to analysis (e.g. drying, homogenization, grinding) is conducted under more-controlled conditions, thereby increasing the reliability and reproducibility of the measurements compared to field screening techniques.

Considering these factors, the SNOWMAN network recommends at least one laboratory analysis for every ten samples collected for total Hg (and other relevant parameters), with a subset of those samples showing elevated Hg concentrations also submitted for speciation analysis[18]. Although few accredited analytical laboratories currently provide Hg speciation analyses, Brooks Applied Labs is a laboratory

CASE STUDY 3:
MERCURY WASTE CELL, GERMANY

AN UNDERGROUND SANDSTONE GALLERY USED TO STORE 80 METRIC TONS OF HG CONFISCATED FROM GERMAN ARSENALS DURING WWII. CORROSION OF STORAGE CONTAINERS RELEASED LARGE QUANTITIES OF HG INTO THE GALLERY AND CONTAMINATION OF GROUNDWATER SEEPAGE.

Source: ERM

Key learnings

- A robust investigation of the gallery, and surrounding groundwater, surface water and sediment was conducted to assess potential human and ecological risks.
- Human and ecological risk assessments supported a pragmatic remediation approach that was accepted by the regulatory authorities.
- Stringent H&S protocols, monitoring and the use of well-trained sub-contractors allowed work within the gallery to be safely executed with no recordable incidents.
- Management strategy included removal of parts of gallery walls and floor, treatment of water seepage with poly-sulphides, and immobilisation of the remaining elemental Hg as HgS.

in the US that provides trace metals analysis for sites worldwide, including Hg speciation through sequential extraction[23].

The collection of soil samples from undisturbed soil cores is preferred to minimise potential Hg losses due to volatilization, and when collecting samples for laboratory analysis, suitable laboratory-supplied sampling containers and preservatives should be used. Polyethylene bottles, for example, have been shown to allow Hg losses through volatilization. Analysis of groundwater and surface water samples should be performed on both filtered and un-filtered samples, so as to assess Hg levels in both dissolved and particulate/colloidal forms.

Other Impacted Media

Material cost during the remediation of Hg-impacted sites is often associated with other impacted media, such as sludges, concrete, surface water and sediments. Assessment of these media during site characterisation is essential to establish a full CSM, robust reserves and minimise the risk of additional works during remediation implementation.

Health & Safety Challenges During Site Characterisation Activities

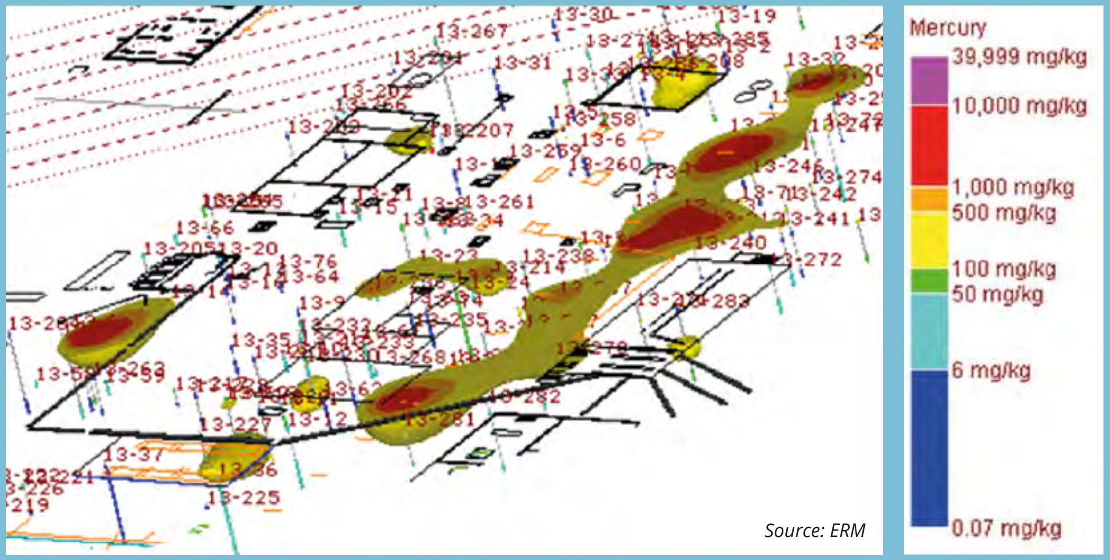
The main Hg exposure routes for human health are inhalation and ingestion. Therefore, strictly-controlled site-specific personal protective equipment (PPE) and health and safety procedures are critical during site characterisation (e.g. use of Hg-specific respirators, protective suits, full skin coverage). The use of hand-held vapour analysers and/or ambient air monitoring stations is also recommended. Stringent decontamination procedures, waste handling/disposal and good hygiene should be implemented. If the site is located within a residential area or near sensitive receptors, it might be necessary to enclose work areas to prevent unacceptable air emissions during ground-disturbing activities. Routine medical monitoring (e.g. urine testing) is advisable before, during and after investigation programmes.


Source: ERM


Source: ERM

CASE STUDY 4:
ACETALDEHYDE PLANT, FRANCE

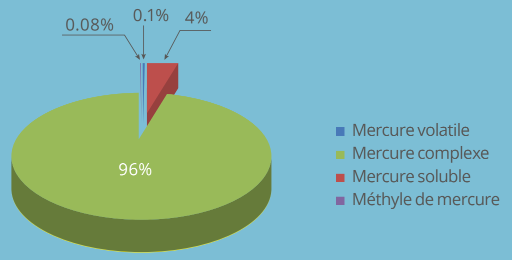
A LARGE CHEMICAL COMPLEX DEVELOPED IN THE 1960S AND CLOSED IN 2009, COMPRISING FORMER ACETALDEHYDE AND VINYL CHLORIDE PRODUCTION UNITS USING HG CATALYSTS.



Source: ERM

Key learnings

- Innovative investigation techniques applied, with Hg speciation by Brooks Applied Labs. Results showed high proportion of complexed Hg, low levels of Hg^0 and negligible methyl-Hg.



- No impact to groundwater, ambient air, or off-site surface soils, surface water, or river sediments provided further lines of evidence for the risk assessment.
- Robust characterisation and risk assessment facilitated negotiation of favourable clean-up goals: 80 % mass removal, acceptable risk for future industrial use.
- Pan-European bid process in 2013 to select most qualified contractor.