



NETWORK FOR INDUSTRIALLY CONTAMINATED LAND IN EUROPE

RISK-BASED MANAGEMENT OF MERCURY-IMPACTED SITES

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1 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 industry³.

1. INTRODUCTION & REGULATORY CONTEXT

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.



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 binding⁴.

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 Remediation⁸ and Net



Environmental Benefit Analysis⁹. 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.

2 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.



2. MERCURY PROPERTIES AND INFLUENCE ON FATE & TRANSPORT

Elemental Hg (Hg⁰)

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.

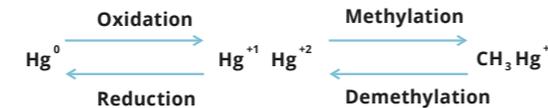
The density and surface tension of elemental Hg are high, approximately 13.5 g/cm³ and 470 dyn/cm at 20°C, compared to 1 g/cm³ and 73 dyn/cm for fresh water. Elemental Hg and some organic Hg species are also volatile, which can lead to air dispersion and potential vapour intrusion.

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⁺, Hg²⁺)

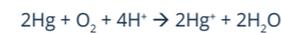
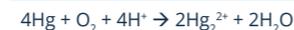
Depending on the ambient geochemistry, Hg released to the environment can transform into other Hg fractions with varying mobility and toxicity. The key conditions that control Hg transformation include pH, temperature,

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:

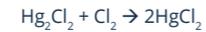
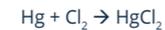
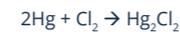


Basic Conditions:

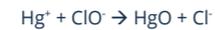


Residual chlorine can also oxidise Hg:

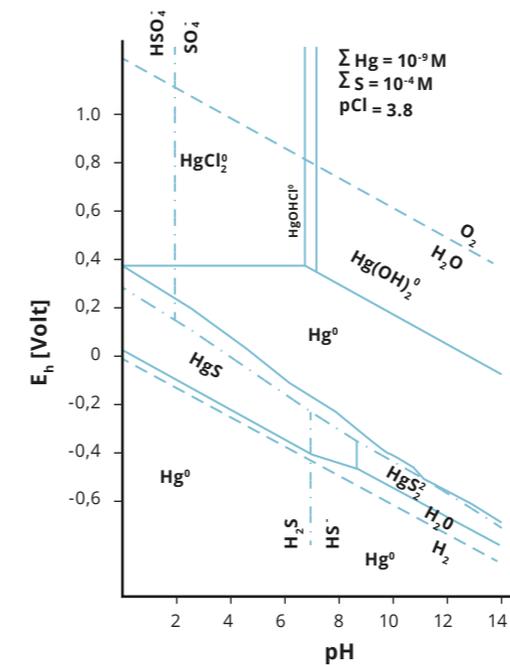
Acidic conditions:



Basic Conditions:



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 (HgCl₂), has a solubility of 6 % at 20 °C. Mercury can also form soluble complexes with dissolved organic matter.



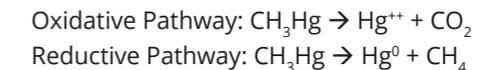
Hg Pourbaix Diagram with Cl and S

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 bacteria¹¹.

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 content¹². 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).

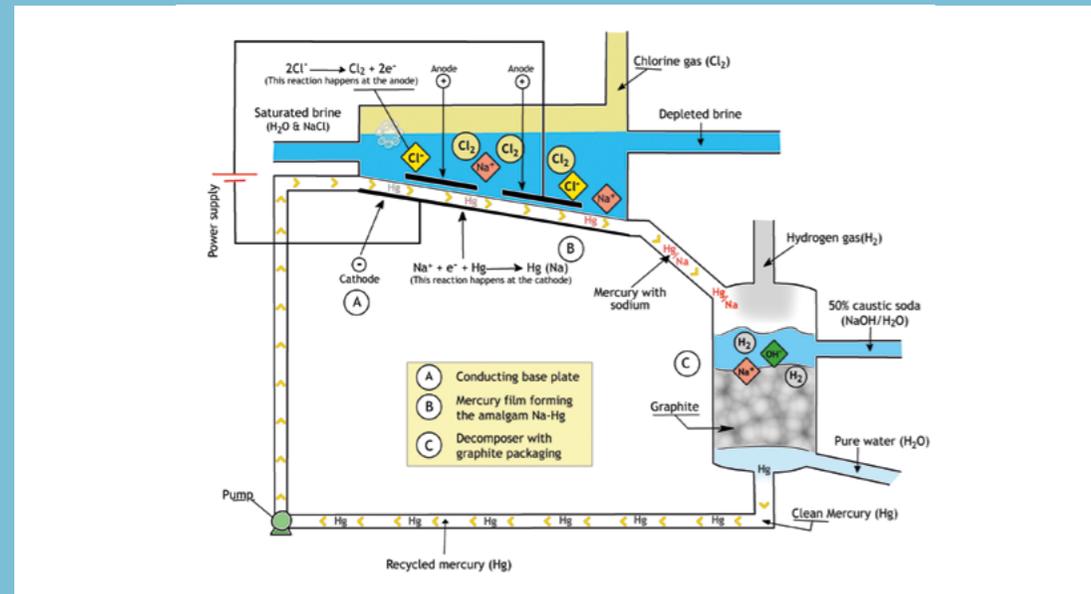
De-methylation is a process that generally occurs under oxidative conditions. However, there are also reductive de-methylation pathways:



Various bacteria show the capacity to reduce ionic Hg and/or methyl-Hg to elemental Hg¹³, and de-methylation has been demonstrated with anaerobic bacteria¹⁴. 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 $\mu g/l$), 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, vegetables) 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 Labs¹⁵). 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 content¹² 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 reservoir¹⁶. 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 (HgCl₂, HgSO₄)
 - 36 % acid-soluble Fraction 2 (HgO)
 - 0.4 % strongly-complexed Fraction 4 (Hg⁰)
 - 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 Network¹⁷ 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



3. TECHNIQUES AND CONSIDERATIONS FOR RISK ASSESSMENT

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.

Within the IMAHg project, a first version of a new geochemical model, HP1¹⁹ 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.

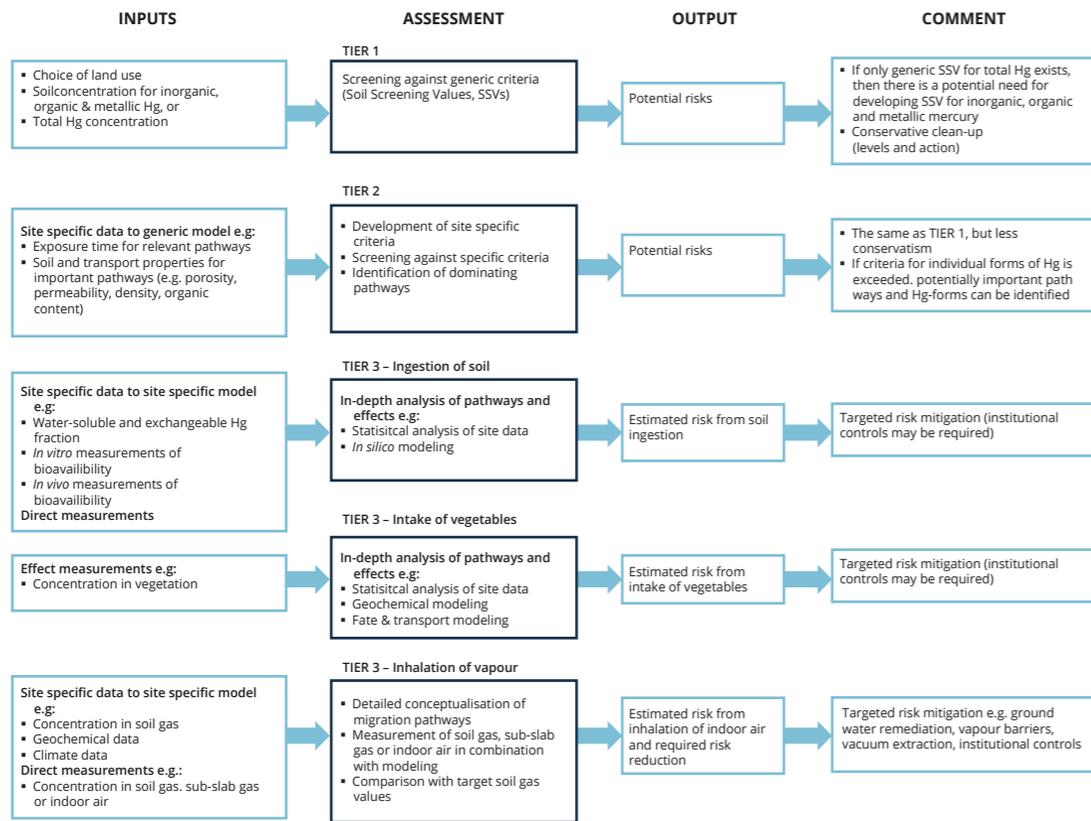


Fig1. Three Common Exposure Pathways for Hg (IMaHg Project), This chart and full IMAHg report can be found at www.snowmannetwork.com



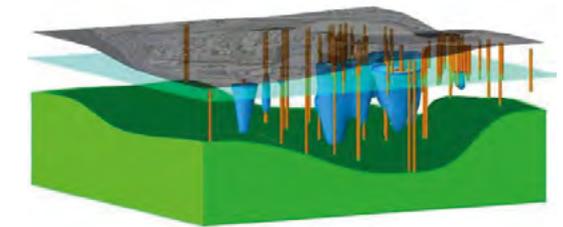
4 SITE CHARACTERISATION TECHNIQUES

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.

4. SITE CHARACTERISATION TECHNIQUES

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.



Elemental 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.



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-spots²⁰.

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.



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 carbon²¹. It should be noted that ensuring reliable measurements of Hg vapour can be

4. SITE CHARACTERISATION TECHNIQUES

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 sediment²². 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.

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.

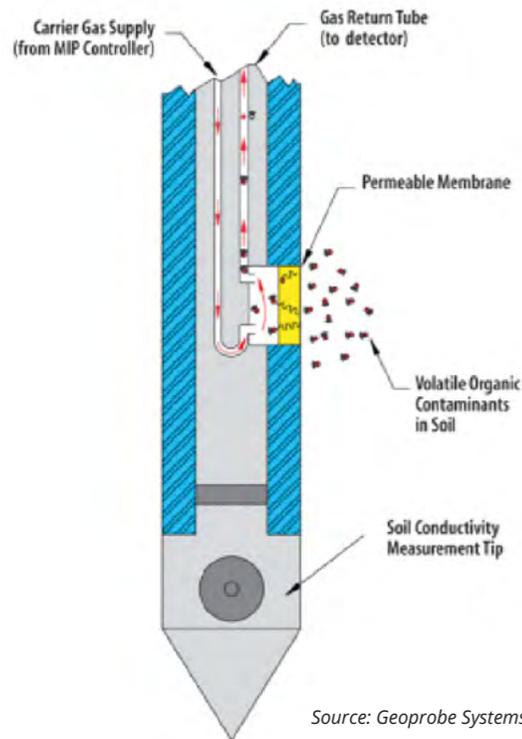


Table 1. Commonly-used Portable Hg Analysers

Instrument Name	Manufacturer	Analytical Method	Range	Reported Interference	Dimensions	Image
Jerome [®] J405	Arizona Instruments, LLC	Gold film sensor	0.5 – 999 µg/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 µg/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 µg/m ³ 1.0 – 1999 µg/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 µg/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 µg/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 µg/m ³	None reported	1.5 kg (w/o battery) 26 x 24 x 9 cm	

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

4. SITE CHARACTERISATION TECHNIQUES

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 CaCl₂).

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 analysis¹⁸. 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.
- 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.
- Human and ecological risk assessments supported a pragmatic remediation approach that was accepted by the regulatory authorities.
- 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.

4. SITE CHARACTERISATION TECHNIQUES

in the US that provides trace metals analysis for sites worldwide, including Hg speciation through sequential extraction²³.

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.



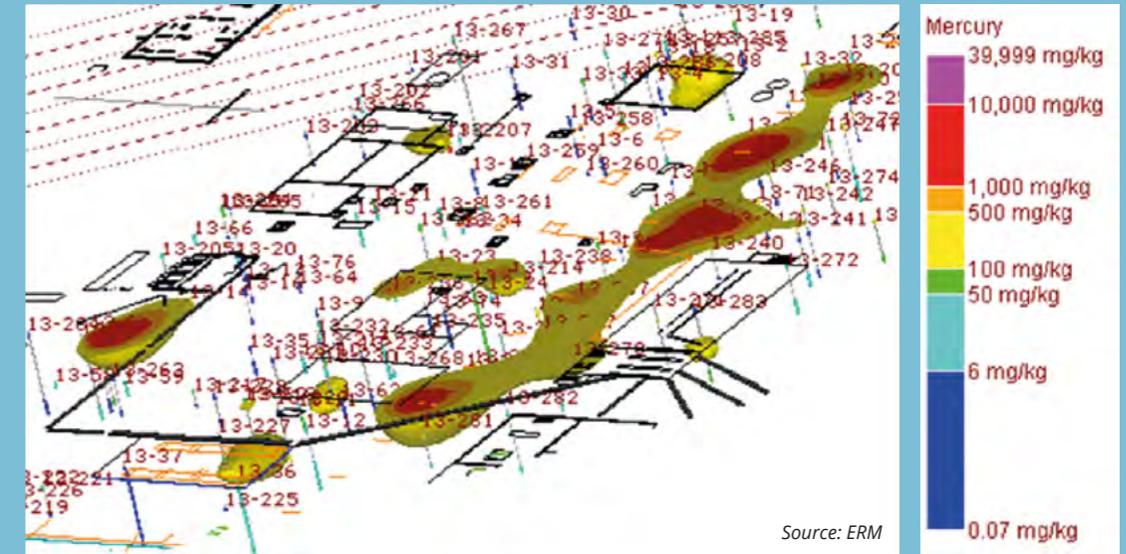
Source: ERM



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 Hg⁰ 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.



CASE STUDY 4: ACETALDEHYDE PLANT, FRANCE

- Developed a robust H&S culture during bid process and at start of remediation works and implemented appropriate monitoring (air & biological).
- Rate of excavation was slower than for other pollutants to effectively segregate soils and avoid vertical migration of elemental Hg.
- Coarse alluvial deposits allowed the optimization of off-site disposal volumes/ costs by mechanical sorting (circa 60% reduction in disposal volumes).
- Impacted fines were stabilised and disposed of in the Bellegarde landfill in south-eastern France or drummed and stored in the UEV salt mine in Germany. Recovered elemental Hg was refined at the Hg Industries site in France.
- Remediation complemented by other risk management measures: covering of residual concentrations, deed restrictions, sale contracts.



SOURCE: K+S ENTSORGUNG, GMBH, HESSEN, GERMANY

5 SITE MANAGEMENT TECHNIQUES

If site characterisation and risk assessment conclude that management measures are required to control unacceptable risks, the appropriate approach should be defined via assessment of cost-benefit and sustainability indicators, taking into account risks to human health and the environment and site-specific constraints, future site-use and stakeholder expectations^{24,25}.

This section presents case studies and a summary of remedial approaches that have been applied at Hg-impacted sites, both for in-situ and ex-situ soil treatment and

groundwater remediation.

Although the main focus of this section is on remediation techniques, NICOLE highlights the importance of other tools (e.g. deed restrictions, monitoring, robust sales contracts) that can be employed to complement remediation and achieve the most sustainable management approach for Hg-impacted industrial sites.

The site management techniques covered by this booklet are summarised in the table below:

	Soil	Groundwater
Most commonly employed	<ul style="list-style-type: none"> ■ Soil excavation & off-site disposal (section 5.1) ■ Soil washing (5.2) ■ Solidification/stabilisation (5.3) ■ Thermal treatment (5.4) 	<ul style="list-style-type: none"> ■ Hydraulic containment (5.6) ■ Pump & treat (5.6) ■ Permeable reactive barriers (5.6) ■ Funnel & gate (5.6)
Emerging and/or unproven	<ul style="list-style-type: none"> ■ In-situ electro-remediation (5.5) ■ Bio-treatment (Fixed-bed bioreactors) (5.5) ■ Phyto-extraction (5.5) 	<ul style="list-style-type: none"> ■ Immobilised algae (5.7) ■ Biochar (5.7) ■ Chelating agents (5.7) ■ Nanotechnology (5.7) ■ Chemical Reduction & stripping (5.7) ■ Copper/brass shavings (5.7)

Table 2. Summary of Site Management Techniques Summarized in this Booklet

5. SITE MANAGEMENT TECHNIQUES

5.1. SOIL EXCAVATION AND OFF-SITE DISPOSAL

Although soil excavation and off-site disposal is a long-established remediation approach for impacted sites, the unique properties of Hg mean that excavation methodologies need to be refined and the off-site disposal options are more limited and costly.

Soil Excavation

Excavation of Hg-impacted soils needs to be performed in a controlled manner, so as to: 1) optimise soil volumes needing off-site disposal (the primary cost for this remediation approach); and 2) minimise the risk of increasing impacted soil volumes, primarily by avoiding coalescence and downward migration of elemental Hg.

Full-time supervision of excavation works by trained personnel is advised, as this enables visual inspection and soil monitoring (using field instruments – see Section 4) to optimise waste volumes by effective segregation of clean and impacted soils. On-site instruments also support the mitigation of Health & Safety risks and validation of the base and sides of the excavations prior to confirmatory laboratory analysis.



Supervising staff should identify Hg-impregnated structures (slabs, walls, foundations), which have the potential to re-contaminate surrounding soils if left in place, and maintain the integrity of low permeability horizons (e.g. clay layers) to prevent downward migration of elemental Hg. They should also direct excavation efforts to impacted horizons and preferential Hg-migration pathways (e.g. cracks/fissures, granular backfill, rootlets), thereby minimizing excavated volumes and the remediation time and costs.

Although labour-intensive, manual removal of elemental Hg (e.g. using hand tools, syringes, suction pumps), when discovered during excavation, is typically cost-effective, as the pure Hg represents significant mass and it will reduce the costs of soil treatment and disposal.

The characteristics of Hg and the issues described above inevitably lead to longer excavation times than for soils impacted by other pollutants. However, if these best practice measures are employed, the volumes of soil requiring treatment and off-site disposal can be materially reduced, leading to lower remediation costs.



As excavation forms the basis for all ex-situ technologies, the careful control of excavation and minimisation of waste volumes are equally applicable during the early phases of both soil stabilisation and thermal remediation projects discussed in subsequent sections.

A well thought out project plan is essential to ensure that the excavation works proceed in an orderly manner. The need for robust Health & Safety controls, including appropriate PPE, air monitoring and regular medical testing (including baseline tests) is also an important aspect during the works, and specific plans should be prepared to identify risks and implement appropriate mitigation measures.

On-site treatment before off-site disposal

If granular soils are present (e.g. alluvial deposits), soil sorting (e.g. by griddle bucket, hydrocyclone or mechanical screener) can materially reduce soil volumes requiring off-site disposal, as Hg is typically concentrated in the finer soil fraction. Air capture and treatment should be considered to minimise Hg-impacted air emissions from the treatment. Mechanical screening of Hg-impacted soils during remediation of the acetaldehyde site in France (see Case Study 4) reduced volumes of waste soil requiring off-site disposal by circa 60%.



To ensure acceptance at some off-site disposal facilities, other forms of pre-treatment can be necessary prior to consignment of the waste materials. As described further in Sections 5.2 and 5.3, several treatment technologies have been patented, trialled or taken to full implementation for this purpose. The majority of these technologies aim to solidify/stabilize the materials by converting elemental Hg and Hg compounds into stable sulphide-rich forms of Hg.

Off-site treatment/recovery and disposal facilities

As mentioned previously, off-site disposal represents the main cost associated with this remediation approach, typically ranging from 250-500 €/T, or potentially higher for heavily-impacted materials.

If limit values for Hg relating to leach testing can be achieved, then landfilling within an appropriate class landfill is an applicable disposal route. During the remediation works performed in 2014 (Case Study 4), the Bellegarde Landfill operated by SITA FD was permitted to accept pre-stabilised Hg-impacted soils with leachable Hg of up to 0.2 mg/l, which corresponded to circa 5 000 mg/kg total Hg at the site in question. These soils were stabilised at the Bellegarde site prior to disposal to a specific landfill cell.

Other treatment and disposal options available within Europe for more heavily-impacted materials are summarized in the table on the next page.

5. SITE MANAGEMENT TECHNIQUES

Company	Location	Description	Comments	Web Address/ Contact Information
Offsite Disposal				
SITA FD	Bellegarde, France	Hazardous waste landfill	Accept soil/debris. No liquid metallic Hg and no radioactive waste. Hg thresholds of 5 000 mg/kg total and 2 mg/kg leachable. Other threshold values on TOC and metals also apply.	+33 04 66 01 13 83
Minosus (Veolia Environmental Services)	Cheshire, UK	Underground disposal in industrial salt mine	Accept soil/debris, but cannot accept liquids (including liquid metallic Hg), sludges, gases or radioactive waste. Waste must be non-flammable, non-explosive, non-volatile, non-odorous, non-deliquescent, non-radioactive and non-reactive upon exposure to air, salt or moisture within the mine. Total Organic Carbon (TOC) threshold of 3% and the facility conducts biodegradability testing prior to acceptance.	http://veolia.co.uk/
Umwelt, Entsorgung und Verwertung GmbH (UEV)	Heilbronn, Germany	Underground disposal in former salt mine	Accept soil, debris, but cannot accept liquids or waste with significant free moisture. No liquid metallic Hg and radioactive waste is generally refused.	http://www.uev.de/
K+S Entsorgung, GmbH	Hessen, Germany	Underground disposal in former salt mine	Accept soil/debris, but cannot accept liquids or waste with free moisture (including Hg droplets). No liquid metallic Hg and no radioactive waste. Hg threshold of 5% Hg by weight. Materials would be refused if methyl-Hg is potentially present.	http://www.ks-entsorgung.com/
Glückauf Sondershausen Entwicklungs- und Sicherungsgesellschaft mbH (GSES)	Sondershausen, Germany	Underground disposal in former salt mine	Accept soil, debris, but cannot accept liquids or waste with significant free moisture. No liquid metallic Hg and radioactive waste is generally excluded.	http://gses.de/
Miljøteknikk Terrateam AS	Mo i Rana, Norway	Underground disposal in rock caverns of former steel works	Facility has a permit to receive 70,000 metric tons of inorganic hazardous waste per year. The waste must be stabilised/solidified before placement into the rock cavern. Maximum allowed leaching of 0.01 mg Hg/l based on the US TCLP63 test.	http://www.terrateam.no/
NOAH	Langøya Island, Norway	Stabilisation with lime and gypsum and disposal below sea level in former limestone quarry	Accept high-concentration waste (> 1000 mg/kg Hg), but not liquid metallic Hg. Upper TOC limit of 1% for high-concentration waste and 5% for less-contaminated waste. NICOLE expresses concern about the hydrological and hydrogeological setting of this facility (photo below).	http://www.noah.no/

Table 3. Treatment and Disposal Facilities for Highly-Impacted Mercury Contaminated Waste

Company	Location	Description	Comments	Web Address/ Contact Information
Offsite Treatment				
Nordische Quecksilber Rückgewinnung GmbH (NQR)/Remondis	Dorsten, Germany	High-capacity thermal desorption/recovery	Former DELA facility recently acquired by Remondis and is undergoing re-startup/permitting. Previously able to accept large volumes of waste (e.g. commercial products, soil, debris and free elemental Hg). Dioxins possibly an issue and testing required.	http://www.remondis-industrie-service.de/ris/loesungen/nqr-mercury/
Hg Industries (Aurea)	Voivres-lès-le-Mans, France	Batch thermal desorption/recovery	Former MBM facility. Typically handles shipments of 20-25 tons (max) high-concentration waste (e.g. commercial products, soil, debris, and liquid metallic Hg).	+33 679 013 625
BATREC Industries (Veolia Environmental Services)	Switzerland	Batch thermal desorption/recovery	Typically handles shipments of 1-50 ton high-concentration (> 10,000 mg/kg) waste (e.g. batteries, soil, debris, and free elemental Hg).	+33 637031265
Gesellschaft für Metallrecycling mbH (GMR GmbH)	Leipzig, Germany	Batch thermal desorption/recovery as well as an immobilisation process with geopolymers	Typically handles small batches of slurries, sludges and other residues containing natural radioactivity and/or Hg as well as free elemental Hg.	http://www.gmr-leipzig.de/
Ophram Laboratoire	Saint Fons, France	Batch thermal treatment/ Hg recycling	Specializes in the recycling and refining of pure metallic Hg. Supplies high-purity Hg in sealed ampoules to microelectronics and optronics sector for semiconductor production.	http://www.opfram.com/



SOURCE: K+S ENTSGUNG, GMBH, HESSEN, GERMANY

Special packaging and handling requirements are required for most of the disposal facilities listed above, including the use of sealed drums, bulk bags or steel containers.

Given the high cost and relatively low throughput of several of the batch thermal treatment and recovery facilities listed in Table 3, they are typically only used for recovered free metallic Hg and/or the most highly-impacted soils and waste that cannot be accepted in other storage or treatment facilities. At the time of publication of this booklet, the former

5. SITE MANAGEMENT TECHNIQUES

high-capacity DELA thermal desorption facility in Dorsten, Germany, had been acquired by Remondis and undergoing permitting/start-up as Nordische Quecksilber Rückgewinnung GmbH (NQR). Once operational, it is anticipated that this facility will likely offer a lower-cost, higher-capacity treatment option for highly-impacted Hg wastes.

Cross-Border Waste Shipments

Another important consideration with respect to waste handling is compliance with export requirements during cross-border shipment of wastes to their final disposal site. Chlor-alkali producers have a legal responsibility under EC Directive 1102/2008 to report the amount of >95 % pure Hg recovered during the decommissioning of chlor-alkali plants. To arrange export and comply with the EU Waste Directive 2008/98/EC, the consignee must apply to the competent authority of the country where the waste is produced and obtain consent from the relevant exporting and importing countries and pay any fees. In 2007, close to 700 000 T of waste (coded as 170503-Contaminated soil and stones) was transported across EU borders, with the biggest recipient being Germany.

Due Diligence of Disposal / Treatment Facilities

Appropriate due diligence is recommended when considering off-site treatment and disposal facilities. Key questions to answer include:

- Is the facility fully permitted to accept your waste materials?

- Does the operator of the facility assume full responsibility for the waste?
- If cross-border transfer is required, does it comply with EU Directives?
- For long-term storage solutions, how geologically secure is the facility?
- For treatment facilities, what does the facility do with the recovered Hg?

5.2. SOIL WASHING

Soil washing techniques utilise physical and/or chemical processes to reduce the Hg content in solid materials (soil, sediment or sludge). There are three commonly-used approaches to soil washing. The most common is particle-size beneficiation. This is based on the premise that contamination is associated with surface area. Fine-grained materials have the greatest surface area and therefore the highest concentration of contaminants. Separation of the fines from the coarser fractions (which generally have lower contaminant levels) can significantly decrease the volume of soil requiring treatment and/or disposal. The second approach often used for Hg-impacted soils, especially materials impacted with elemental Hg (Hg⁰), is density separation. The density of elemental Hg is 13.5 g/cm³ compared to the density of soil, which is generally about 2 to 3 g/cm³. This density difference provides a basis for separating elemental Hg from soil and reducing the overall mass of material requiring treatment/disposal. The third approach comprises chemical leaching of Hg from the soil. For this approach, liquid solutions such as nitric acid, hydrochloric acid and potassium iodide/iodine are used to remove Hg from the solid matrix.

Comprehensive information regarding the origin of the Hg impacts will provide a good basis for understanding the species of Hg likely present at a site. However, it is important to consider that the physicochemical nature of the contamination can change slowly over time due to various phenomena like oxidation, complexation, methylation, adsorption, etc. The Hg species present and the physicochemical nature of the soil will strongly effect the efficiency of a treatment process such as soil washing^{28,29,30,31}.

Summary of Recent Soil Washing Projects

Conventional physical separation techniques are the most typically applied in Europe and North America, comprising steps such as screening, sieving, hydrocycloning, attrition scrubbing, froth flotation, magnetic separation, etc²⁸. These techniques can be relatively simple, and therefore cost-efficient, as proven by the extensive track record in the last 25 years. Physicochemical soil washing techniques, including chemical extraction, entails (simplified) hydrometallurgical methods, generally making them more complex, lower in throughput and currently more expensive^{29,32,33}. This is reflected in the scarce number of projects and their small size, often at pilot scale only.

The existence of competitive solutions, such as controlled landfilling (up to concentrations of 5,000 mg/kg Hg in Europe) and specific thermal treatment techniques, impose a financial boundary condition on the applicability of soil washing for Hg-impacted soils. Practically this means that conventional soil washing techniques are typically applied primarily for the

removal of elemental Hg, for which bespoke washing plants have been designed.

In 1993, approximately 10,000 m³ of coarse sandy soil impacted with various metals including Hg was treated by washing (consisting of screening, hydrocycloning, attrition scrubbing and froth flotation) at the King of Prussia superfund site (New Jersey, USA). Throughput of the plant was 25 T an hour. Although it is described in the project report for this site³³ that Hg concentrations could be reduced from 100 mg/kg to 1 mg/kg, the report does not provide any actual performance data regarding Hg.

During the remediation of a former chlor-alkali plant operated by Nexus in British Columbia, Canada, approximately 24,000 T of soil were reportedly treated by washing between 1999 and 2003. The soil washing plant had a capacity of 14 T an hour, and reduced the Hg concentration down to 40 mg/kg. The initial concentrations were not specified. The process used at this site was reportedly the basis for the Orica Botany transformation project in Australia³³.

A former chlor-alkali plant near Syracuse was identified as one of the primary sources of contamination to the Onondaga lake (New York State, USA). Concentrations of elemental Hg up to 19,000 mg/kg were found in soil at this site. In 2003, about 8,500 T of soil were treated by soil washing, which reportedly removed about 7 T of Hg. However, no technical data regarding the soil washing plant or the soil composition were published.

5. SITE MANAGEMENT TECHNIQUES

During the remediation of the former EKA chlor-alkali site in Bengtsfors, Sweden, in 2007, large volumes of Hg-impacted gravels were found. These were treated on-site by simple drum washing of the fraction >20 mm, with a throughput of 100 T an hour. The re-use target was 5 ppm. Although the undersized fraction was potentially washable, the environmental permit did not allow on-site washing and the undersize had to be landfilled. The recycled oversize fraction made up about 70 % of the total soil volume³¹.

In 2010, 13,000 T of sandy soil were washed off-site in a treatment centre in Antwerp. The soil came from a former felt production site in Lokeren, Belgium, and was impacted by Hg, mainly in the form of Hg nitrate. Initial Hg levels of up to 50 mg/kg were washed to below 5 mg/kg. As expected, the removal efficiency of highly water soluble Hg nitrate salt was high.

After some years of laboratory scale and pilot testing, a bespoke soil washing plant (simple screening, drum washing) was built for the Orica project (Botany Bay, Australia)³⁴. The plant was erected in a hall with air extraction and monitoring. The former chlor-alkali site was heavily impacted with Hg (80 to 15,000 mg/kg Hg). The plant had to stop operations after only a few months of production in 2011. The specific reasons for stopping the plant were not published, but issues with Hg vapour emissions and poor performance are mentioned. Only 2,900 T of soil were treated, 1,350 T re-used, and 1.2 T of Hg removed. The treatment target level was 70 mg/kg.

A former chlor-alkali site operated in the Netherlands contained 60,000 T of impacted sandy soil, with Hg levels up to 1,200 mg/kg³⁴. Extensive laboratory research showed that reductions in Total Hg concentrations between 70 and 80% could be achieved through soil washing. Although the re-use target was set at a relatively-low 7 mg/kg total Hg, it was decided to carry out on-site soil washing with the aim of recycling as much soil as possible. In total, 20,000 T of soil were washed. Although the lab-scale removal rates were achieved in the full-scale process, only 3,000 T of the washed soil met the 7 mg/kg target.



During the bidding process for the remediation of an Hg-impacted site in France, lab-scale soil washing tests were conducted by DEC (part of DEME Group). The site soil consisted mainly of gravel (55 %) and sand (35 %), with 10 % fine materials. Initial concentrations were generally in the order of 100 to 10 000 mg/kg, with some visible Hg droplets. During the test, the gravel was effectively separated and washed to below the established re-use levels (28 mg/kg). However, cleaning the sand fraction was more difficult. The operator opted for a dry gravel sorting process, with sand and fine materials

considered as residue and landfilled off-site. Laboratory tests carried out on soils from several sources, mainly chlor-alkali facilities^{29,30,35}, typically show that medium to high concentrations of elemental Hg (100 to 10,000 mg/kg) in sand could be effectively reduced to below 50 mg/kg. Further decreases require intensive conventional soil washing steps (e.g. attrition scrubbing or froth flotation) and/or alternative techniques (ultrasonic scrubbing or chemical complexation). Characterisation of the residual Hg after physical washing by visual inspection or microscopy and by sequential leaching tests showed that microscopic Hg droplets were absorbed within fissures of the sand grains, and some Hg oxides were still present.

Conclusions

Physical soil washing can materially reduce Hg concentrations in soil, with the gravel fraction effectively cleaned to relatively-low concentrations. The sand fraction, however, is generally much more difficult to treat, and requires intensive techniques (e.g. scrubbing, flotation, chemical cleaning) in order to reach concentrations of 10–20 mg/kg total Hg. As with any soil washing, the fines (clay + silt fraction) should be below about 30 % of the total soil mass.

A disadvantage of soil washing is that the residue of fines (filter cake) can be very concentrated in Hg, making it difficult and expensive to transport and dispose off-site.

For Hg impacted sites, two types of soil washing applications can be considered:

firstly reducing elemental Hg concentrations to moderate levels, for example below 1 000 mg/kg in Europe to allow landfilling. Secondly, more intensive soil washing can reduce Hg concentrations to lower levels (10-50 mg/kg), which is often sufficient to comply with site-specific risk-based standards.

5.3. STABILISATION / SOLIDIFICATION

Stabilisation/solidification (S/S) is a frequently-used technology for the treatment of Hg-impacted soil and waste²⁸. A wide range of Hg-impacted material can be treated by various S/S processes, including soils, sludge, liquid wastes, industrial waste and elemental Hg. Stabilization/solidification can be applied either in situ or ex situ, although it is most commonly implemented ex situ.

Stabilization/solidification is a well-established remediation technology in the USA, Japan and several European countries. It originates from the construction, mining and nuclear waste industries and was later applied to soil remediation. The uptake of S/S as a remediation technique in Europe was relatively slow compared to other technologies prior to enactment of the EU Landfill Directive, mainly due to the lack of technical guidance, performance uncertainties, previous poor practice and potential residual liabilities. In the UK, for example, this changed following the publication of guidance from the Environment Agency in 2004 supporting a risk-based framework for the management of land contamination.

5. SITE MANAGEMENT TECHNIQUES

Application of S/S to impacted soils and wastes is supported by a body of scientific evidence gathered over several decades, and Hg-specific techniques and innovations are continuing to be developed. Stabilization/solidification can be used on its own or combined with other management approaches as part of a remedial strategy. However, the different species of Hg can, under certain conditions, display complex behaviour presenting potential challenges to the use of S/S.

A significant proportion of the available literature is focused on the S/S or pre-treatment of Hg-containing waste (including hazardous and radioactive waste) for landfill disposal, rather than re-use on site. Although this research merits consideration, the review provided herein focusses on S/S treatment of Hg-impacted soils.

Stabilization/solidification relies on the reaction between a binder and/or reagent with soil/waste to reduce contaminant mobility. These techniques do not reduce the contaminant concentration, but instead reduces its mobility through chemical or physical changes. The key S/S processes currently used for Hg-impacted soils include:

- **Stabilisation** – involving the addition of reagents to an impacted soil to chemically fix the soluble species, producing a more chemically stable, less soluble material.
- **Solidification** – involving the addition of binders to a impacted soil to change its physical nature in order to contain or encapsulate contaminants into a solid and robust low-permeability matrix.

- **Amalgamation** – considered a sub-set of the S/S techniques, and involving the dissolution of Hg in other metals (e.g. copper or zinc) and solidification to form a non-liquid, semi-solid alloy called an amalgam. The technique is also commonly used to supplement more traditional cement-based S/S techniques^{39,40}. Hg stabilisation with sulphur or sulphur polymer cement (SPC) is also sometimes referred to as amalgamation⁴¹. However, combining Hg with sulphur results in Hg sulphide, a stable ionic compound, not an amalgam or alloy⁴².

Bench-scale testing followed by pilot-scale application are important elements of the design process, thereby providing confidence in full-scale operation.



Stabilisation / Solidification Techniques

A range of ex-situ and in-situ techniques have been successfully applied for S/S of Hg-impacted soils, although ex-situ methods are more commonly used³⁸. Mobile plant and reagent delivery systems can be configured to meet most site conditions and deliver the right mix of binders and reagents. However, several S/S reactions can partially volatilise Hg and so require adequate control measures and associated health and safety precautions.

Compared to in-situ S/S techniques, ex-situ techniques can be more onerous on-site with several material handling stages needed, but can provide higher production rates, better quality control over binder delivery and mixing and improved verification of the stabilised material. This is especially important to ensure complete encapsulation in the S/S material of elemental Hg, which is dense and can be difficult to mix.

Physical pre-treatment, including processing and screening, can be an effective first step prior to ex-situ stabilisation, so as to prepare a homogenised medium and optimise mixing, and to concentrate the Hg compounds given their affinity for the finer soil fractions. Wet screening is not recommended prior to S/S, as the dense Hg droplets can behave as a separate liquid phase⁴³.

Recovery of elemental Hg prior to S/S application can be advisable to reduce contaminant loading, especially when on-site re-use/retention of the treated material is planned. Breaking up larger Hg globules to provide a larger surface area to react with the binder/reagent is another key pre-treatment step. Some technologies include a mechanical system for breaking the elemental Hg into fine spherical particles (prills)⁴⁴. As described below, a suitable reagent (e.g. sodium sulphide) can also be initially added to produce either Hg oxides or Hg sulphides and once mixed sufficiently, the cement is added⁴⁵.

In-situ stabilisation is well established in geotechnical applications, for which specialised injection/mixing equipment have been developed. However, in-situ mixing or injection is less established for environmental application, as homogenous treatment can be difficult to ensure and validate⁴⁴. These techniques are most often used to stabilise sludge lagoons, deeper soil contamination or soil under infrastructures. It can produce a “monolith” in the ground, which needs to be carefully designed to avoid localised flooding and to minimise constraints for future site-use. This approach continues to be developed, as demonstrated by some case studies presented in NICOLE’s Summary Report⁹ and the US EPA²⁸, including the use of innovative nanoparticles.



In situ stabilisation of sediment and soils impacted with Hg and PAHs in a former effluent treatment pond using binder agents. Source: ARCADIS

5. SITE MANAGEMENT TECHNIQUES

Treatment rates for S/S vary significantly based on the form of Hg present, and the number of processes and reagents used. However, rates of 300 to 600 m³ per day should be achievable. Rates where chemical processes such as amalgamation are undertaken may be considerably lower.

Binders and Reagents

Several binders and reagents can be used in the S/S of Hg-impacted soils and waste (US EPA²⁸). The most commonly used include Portland Cement, enhanced by additional binders such as ground granulated blast furnace slag (GGBFS), pulverised fly ash (PFA), asphalt or bitumen⁴⁴. Elemental sulphur and various sulphide additives have also been used successfully^{43,67,69}.

Some elemental Hg and organic Hg compounds can prove difficult to stabilise and additional chemical or physical pre-treatment is needed to ensure effective S/S. Common stabilizing agents include elemental sulphur, sodium sulphate, reactivated carbon, or ferric-lignin derivatives prior to solidification.^{45,46,47}. Other additives containing sulphur such as GGBFS have also been successfully applied. With adequate blending, such additives have been shown to successfully convert the Hg compounds into less soluble forms, such as mercuric sulphide (cinnabar and metacinnabar)⁶⁸.

The two main chemical S/S approaches applied to soils or wastes containing elemental Hg are: 1) conversion of the elemental Hg to Hg sulphide; and 2) amalgamation. Some

techniques combine both and include the use of a cement-based mix enhanced with GGBFS and copper powder^{40,41}.

The ratio of binders/reagents to soil will depend on detected concentrations and the soil's chemical composition (i.e. Hg species, but also other contaminants or naturally-occurring substances that could interfere with the S/S process). The choice of binder/reagent should be site-specific, and subject to bench tests and pilot trials. Several case studies relating to laboratory and site-scale applications are provided by the US EPA²⁸ and GRS⁴⁰.

The choice of binder/reagent and the dosage used will lead to variable stability of the materials treated and also influence the curing time, compressive strength, costs and treatment process applied on-site²⁸.

Influencing Factors and Considerations

Key factors commonly affecting the effectiveness of S/S include good characterisation of the materials to be treated, selection of the best binder and reagent, effective contact between the contaminants and binder/reagent, good physical and chemical consistency of feedstock, appropriate mixing equipment and binder delivery, control over external factors (e.g. temperature and humidity) and the control of other inhibitive substances.

The applicability of S/S to treat Hg-impacted soils depends on the Hg species present, its mobility and concentrations, together with the soil pH and moisture content⁴⁸. The presence

of more than one Hg species may complicate the process and reduce the effectiveness unless characterised and designed appropriately. Typically, the solubility of Hg increases in more acidic conditions, although some studies suggest that some soluble Hg compounds (e.g. Hg sulphate) may form at higher pH⁴⁹.

Certain non-Hg compounds in the soil may also interact with the S/S reagents, thus affecting their performance. For example, high concentrations of chloride may render phosphate additives ineffective⁵⁰. For certain binders to be effective, the treated material needs to have a specific moisture content and therefore material may need to be pre-treated to adjust the moisture.

Typical doses for binders are 5 to 15 % of the Hg-containing soils by weight. However, doses where high levels of elemental Hg are present can be higher.

Performance

The performance of S/S in soils is often linked to meeting risk-based remedial targets associated with leachability testing and also physical strength tests if the S/S material is to be re-used on-site. However, there is little precedence of S/S-treated Hg-impacted soils being re-used on-site (unless in-situ techniques have been applied) and as such the strength testing requirements may be of less importance. The leachate performance of ex-situ S/S-treated Hg-impacted soils is regularly linked to meeting landfill acceptance levels.

Successful S/S pre-treatment of Hg-impacted soils in the US and Canada are reported to regularly meet the associated non-hazardous landfill leachability acceptance criteria of 0.025 mg/l and 0.2 mg/l, respectively. For comparison, the European Waste Acceptance Criteria (WAC) leaching limits using BSEN 12457-3:2002 at a cumulative liquid:solid ratio of 10 for granular wastes for inert, non-hazardous and hazardous landfills are 0.001 mg/l, 0.02 mg/l and 0.2 mg/l, respectively³⁸.

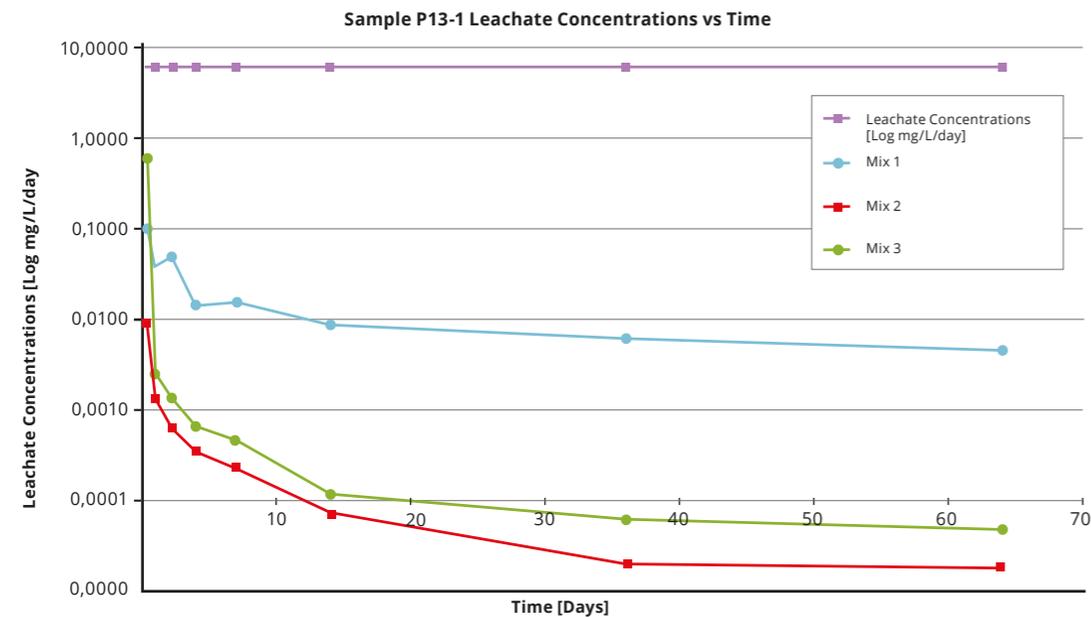
Various bench and site trial case studies^{28, 40} show that Hg concentrations in soil of 1,000 to 4,000 mg/kg can be successfully treated by S/S, achieving leachable concentrations between 0.002 mg/l and 0.0139 mg/l (using the Toxicity Characteristic Leaching Procedure test). Celtic (wholly-owned subsidiary of EnGlobe) have performed in-house tests that found that material with up to 200 mg/kg total Hg is readily stabilised and could be re-used on-site.

The Mercury Amalgamation Stabilization/Solidification white paper prepared by the Oak Ridge National Laboratory⁴¹ provides a comprehensive discussion of the impact of elemental Hg spikes (up to 10,000 mg/kg) on leachate and the performance of various slag-cement based binders and reagents.

Long-Term Performance

A limitation in the published literature is an apparent lack of appropriate long-term data on the chemical behaviour of Hg-impacted soils treated by S/S, particularly where the material has been in contact with water. In-situ techniques that create monoliths in the ground

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Source: Celtic (subsidiary of EnGlobe)

may meet their agreed leachability remedial targets, but consideration of the long-term performance of the S/S material remains to be tested. There is a significant amount of performance data for other S/S materials, which suggest that Hg-containing materials should be stable in the long-term. However, this is an area requiring further research in real environments.

The current understanding of long-term performance is generally based on predictive models focused on leaching mechanisms and have been applied to Hg wastes, stored either in landfill cells or dedicated storage facilities. However, these models are still being developed and refined. They are becoming more sophisticated to consider the complexity

of contaminated soils and numerous site-specific factors that could affect the long term performance of the S/S process.

The credibility of S/S treatment of Hg-impacted soils, as with all remediation technologies, is dependent on thorough design (including interpretation of site or re-use conditions), bench or pilot trials, optimised on-site application and verification reporting to demonstrate clear lines of evidence based on the works undertaken. In particular, confidence in the long-term performance and the use of credible verification processes are essential when used as part of a risk-based remediation strategy.

CASE STUDY 5: PULP AND TISSUE MILL, WASHINGTON STATE, USA

A FORMER PULP AND TISSUE MILL OPERATED FROM 1926 TO 2007, INCLUDING A FORMER CHLOR-ALKALI PLANT. THE SITE IS SITUATED ADJACENT TO A MARINE SHORELINE IN A POPULATED AREA, AND IS PLANNED FOR MIXED-USE REDEVELOPMENT. IN THE CHLOR-ALKALI PORTION OF THE SITE, THE REMEDIAL INVESTIGATION IDENTIFIED SHALLOW GROUNDWATER AND FILL SOILS THAT WERE IMPACTED WITH HG, AS WELL AS A COMPARATIVELY SMALL VOLUME OF HIGHLY-IMPACTED VADOSE ZONE SOIL CONTAINING FREE-PHASE HG IN LOCATIONS WHERE ELEMENTAL HG WAS PREVIOUSLY HANDLED.



Source: Anchor QEA, LLC

Key learnings

- Supported by laboratory treatability testing, on-site stabilization and off-site landfill disposal was selected as the far more cost-effective option relative to off-site thermal treatment for managing the highly-impacted soils containing free-phase Hg.
- Bench-scale testing evaluated the effectiveness of S/S with Portland cement, Portland cement with elemental sulphur, and Portland cement with ferrous sulphate, including an evaluation of Hg vapour release due to heat generation during stabilization (cement hydration). The results supported the selection and development of an optimized S/S protocol using Portland cement with elemental sulphur for full-scale application⁶⁶.

CASE STUDY 5: PULP AND TISSUE MILL, WASHINGTON STATE, USA

- Full-scale application of S/S using Portland cement with elemental sulphur achieved the required treatment standards for off-site landfill disposal without exception (166 individual treatment batches).
- Subsurface impacts from caustic solutions resulted in geochemical conditions favoring either elevated Hg concentrations in groundwater or soil (but typically not both), as Hg mobility in groundwater increases at high pH while soil adsorption and uptake decreases. In down-gradient areas where the groundwater pH values decrease towards neutral, dissolved Hg concentrations also decline but soil concentrations increase.
- Further bench-scale testing evaluated amendments for their Hg removal efficiency from high pH groundwater, increased uptake capacity of amended soil, and long-term stability of the sequestered Hg. Long-term effectiveness was tested by subjecting treated Hg-loaded soils to leaching under both aerobic and anaerobic conditions. Overall, ferrous sulfate and GAC were found to be the most effective amendments for remediation of site groundwater, while a Portland cement-ferrous sulfate mixture was the preferred amendment for minimizing leaching from site soils^{28,70,71,72}.
- Based on the bench-scale testing results, full-scale implementation in the near future is anticipated to include a combination of approaches including in situ injection/soil mixing and reactive barriers to address Hg in groundwater and soil across the site.



Source: Anchor QEA, LLC



Source: Anchor QEA, LLC

5.4 THERMAL TREATMENT

Mercury's chemical properties (see Table 4 below) allow the application of various thermal technologies for the effective treatment of Hg-impacted soil and other solid wastes. Experience over the last decade has shown that thermal treatment is often the most cost-effective method for removing Hg from solid waste, especially for fine-grained materials such as silty and loamy soils. Common co-contaminants, such as PAHs, PCBs, dioxins, furans, TPH and organo-lead compounds, can also be effectively removed and/or destroyed within properly designed thermal treatment units.

Table 4. Chemical Properties of Hg

Melting Point	- 38.8 °C
Boiling Point	357.1 °C (225 °C at 50 mbar)
Vapour Pressure	0.00163 mbar at 20 °C

A number of ex-situ thermal technologies have been developed and tested in recent years for the treatment of Hg-containing solid wastes, with varying levels of success:

- Heated screw conveyors/continuous mixers;
- Vacuum retorts;
- Vacuum thermal desorption (indirectly heated batch vacuum mixers); and
- Rotary kilns (direct-fired or indirectly heated).

The last two technologies (vacuum thermal desorption and rotary kilns) have been proven effective and economically viable for the treatment of Hg-containing soil and

solid waste. Thermal desorption is also being developed for the remediation of impacted soils in-situ, with recent studies indicating successful treatment of both in-situ soil and biopiles.

Ex-situ Thermal Treatment - Vacuum Thermal Desorption (Batch Vacuum Mixers)

At the core of the batch vacuum mixer is an evaporation chamber, which uses heat and a controlled vacuum to volatilise contaminants with boiling points below 450°C (at atmospheric pressure). The system is typically heated by circulating synthetic thermal oil in an external heating jacket and through a rotating central shaft, which also mixes the waste during treatment (Figure 2).



Batch vacuum mixer with solidification unit for treated material. Source: ECON Industries GmbH

The treatment process is conducted in stages to allow entrained water and target contaminants to be recovered separately. In the initial stage, operating temperatures of c.150°C and a low vacuum (c.800 mbar absolute) are applied for water removal. Following evacuation of the water vapour,

5. SITE MANAGEMENT TECHNIQUES

the operating temperature is increased to c.370°C and the pressure lowered to c.50 mbar (absolute) for the removal of Hg and other co-contaminants.

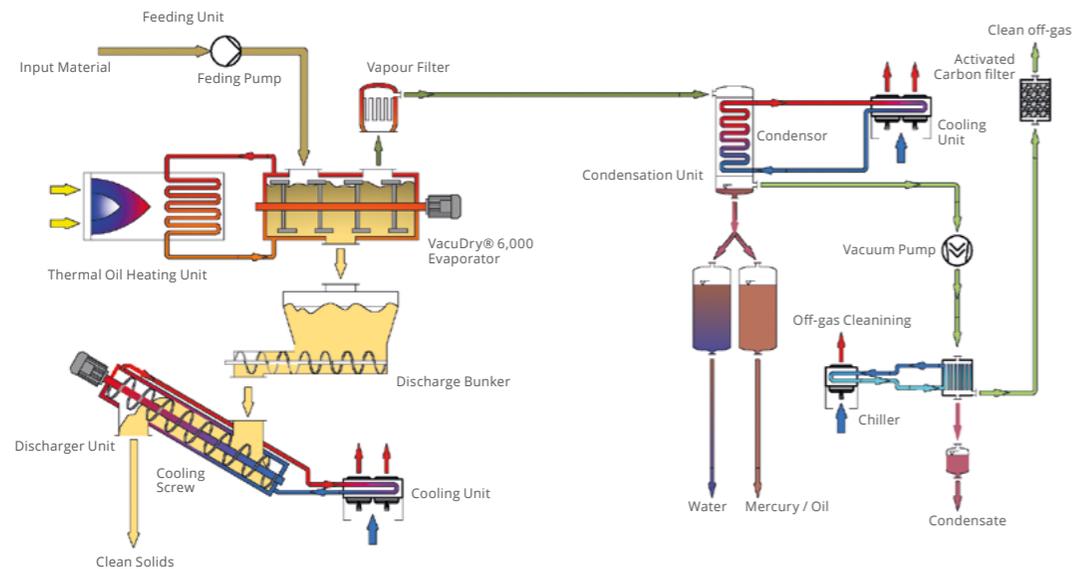
The resulting vapour stream is filtered to remove entrained particulates, and then run through a condensing unit for contaminant recovery (Figure 2). The subsequent exhaust gas stream is passed through a secondary vacuum unit and an activated carbon filter before discharge to the atmosphere. The treated solids are discharged (hot) via a discharge flap into a cooling bunker, and subsequent treatment batches are initiated while the prior batch cools.

Figure 3. Batch Vacuum Mixer Products



Source: ECON Industries GmbH

Figure 2. Typical Batch Vacuum Mixer Process (Indirectly Heated)



Source: ECON Industries. See process animation @ www.youtube.com/watch?v=3i_jxWDX2sY

Ex-situ Thermal Treatment - Rotary Kilns

Rotary kilns provide continuous treatment under minimal vacuum (Figure 4). The waste material is continuously fed and conveyed through the rotating kiln by a screw conveyor, where it is heated to the desired treatment temperature (typically 650 to 1,100°C). Additional mixing blades can be installed in the kiln to enhance mixing and increase retention time. The treated material drops out of the rotary kiln and is cooled on a cooling conveyor before discharge.



Source: ECON Industries GmbH

The off-gas is first directed through a cyclone for particulate removal, and then processed in an after-burner chamber where it is exposed to oxidizing conditions at 850°C for approximately 4 seconds to avoid formation of toxic substances (e.g. dioxins). Following treatment, the water and Hg in the off-gas is condensed, and the off-gas is then scrubbed and filtered before being treated by activated carbon and discharged to the atmosphere.

Direct-fired rotary kiln units are equipped with a refractory lining or a layer of heat-resistant concrete and the waste material is heated directly by a front-mounted burner. Although rarely used, the indirectly-heated rotary kilns typically consist of a steel cylinder without an inner refractory lining. In this case, the kiln is indirectly heated by the hot exhaust gases from a gas burner.

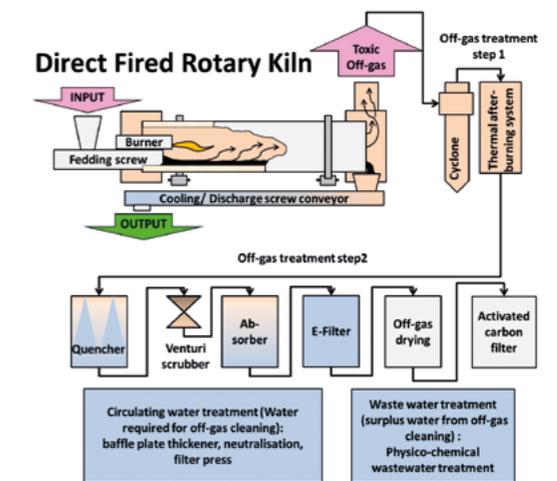


Figure 4. Direct-fired Rotary Kiln including Off-Gas Treatment

5. SITE MANAGEMENT TECHNIQUES

Ex-situ Thermal Technology Comparison

A comparison of the batch vacuum mixer and rotary kiln technologies is provided in Table 5. Due to the lower operating temperatures, the indirectly-heated batch vacuum mixer is typically used when no cinnabar (HgS) or Hg(I/II)chloride is present in the waste material to be treated, including:

- Excavated soils and demolition waste from industrial sites;
- Sediments from lakes and streams; and
- Sludge from gas exploration and production.

There are no limitations with respect to the water content, or concentrations of hydrocarbons or Hg for treatment in a batch vacuum mixer. The process is a closed system, and so can usually be permitted for use in sensitive areas.

In comparison, the rotary kiln technology can be applied to waste containing all Hg species, including HgS and Hg(I/II)chloride, and has been used to treat the following waste streams:

- Catalysts from petro-chemical processes;
- Disposed activated carbon;
- Some types of impacted soil (e.g vinyl chloride production sites); and
- HgS-rich sludges from industrial wastewater treatment processes.

The rotary kiln process is generally more energy-intensive than batch vacuum mixers, and is therefore less economical for materials with elevated water content. Wastes with hydrocarbon content greater than 5 % can cause overheating of the kiln.

Rotary kilns typically produce more air emissions than batch vacuum mixers, require sophisticated off-gas treatment systems and monitoring, and can be difficult to permit for use within sensitive areas. The process can also produce significant quantities of wastewater (c.0.5-1.0 T of wastewater per T of treated waste) due to the need for off-gas scrubbing.

	Batch Vacuum Mixer (Indirect Heating)	Rotary Kiln (Direct Fired)
Typical Application		
Elemental Mercury	✓	✓
Methyl Mercury	✓	✓
Mercury (I/II) Chloride	X	✓
Mercury Sulphide/Cinnabar (HgS)	X	✓
Hydrocarbons	(No Limit)	(Up to 5 % Max)
PAHs, TPH, PCBs, Dioxins, Furans, Organo-lead	✓	✓
Elevated Water Content	No Limit	Up to 25 % (Max)
Elevated Mercury Content	No Limit	No Limit
Waste characteristics	Sludge, soil, filter cakes, including poorly-conveyable and highly-viscous materials	Sludge and soil (up to 25 % moisture)
Mobile installation for on-site treatment	✓	(with appropriate air emissions controls)
Typical plant throughput capacities	10 000-50 000 T/annum	30 000-50 000 T/annum
Treatment Efficiencies and Other Considerations		
Hg levels after treatment	< 1 ppm	< 1 ppm
Typical Max Process Temperatures	Up to 370°C	650°C to 1,150°C
Off-gas Stream	100 – 1 000 Nm ³ /hr	5 000 – 25 000 Nm ³ /hr
Distillates	Distillates can be recovered separately (no combustion)	Mercury is recovered
Off-gas treatment	Vapour filter, two-stage condensation unit, and activated carbon filter	Cyclone, post-combustion chamber, gas-scrubber, e-filter, and active carbon filter
Air emissions	Minimal	Typically > batch vacuum mixer. Requires sophisticated off-gas treatment system and monitoring
Additional produced wastewater	None	~ 0.5 -1 T wastewater per T material treated (from off-gas scrubbing)
Approx. Energy consumption per ton soil treated (sandy; 15% moisture)	~ 210 kWh/t	~ 700 kWh/t
Safety	Operation under vacuum (50 mbar absolute), inert atmosphere	Limited vacuum (3 mbar differential), oxidizing atmosphere
Environmental permitting	State of the art technology, permitting often possible in sensitive areas (closed system)	State of the art technology, permitting can be difficult in sensitive areas

Table 5. Comparison of Ex-situ Thermal Treatment Methods

5. SITE MANAGEMENT TECHNIQUES

In-situ Thermal Desorption

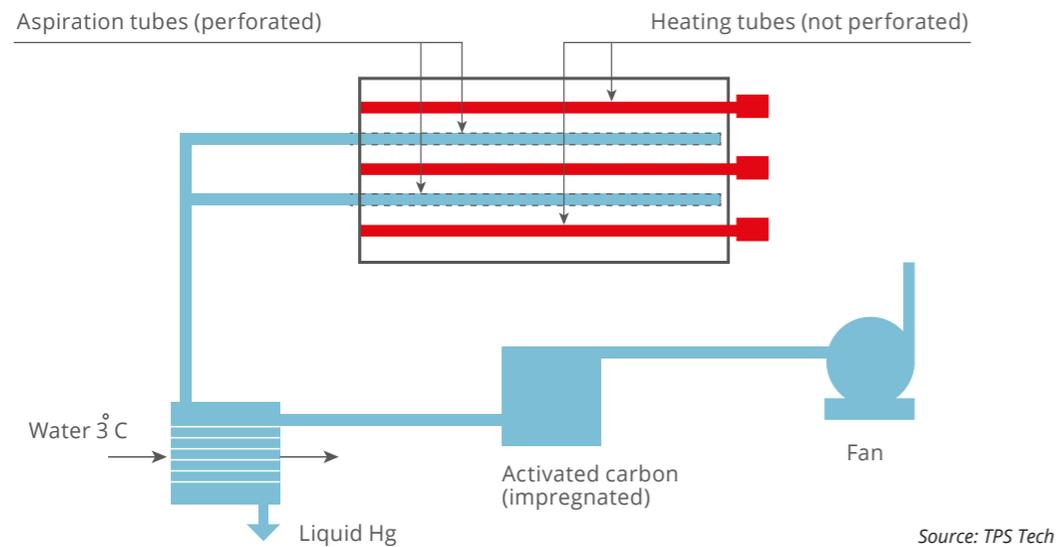
In recent years, thermal desorption has been developed and is being applied to in-situ remediation of impacted soils and biopiles. As for the ex-situ treatment methods described above, the temperature of the impacted soil is raised using a network of heating tubes to achieve the appropriate temperature, pressure, and residence time for contaminant desorption from the soil matrix. The tubes are typically heated through the circulation of high-temperature combustion gases in a closed loop (Figure 5). The mobile combustion burners are typically run on either propane or natural gas.

Compared to conventional ex-situ thermal desorption technologies (e.g. rotary kilns, batch vacuum mixers), where the soil residence

times are typically around 20 minutes, the heating time for the in-situ process takes much longer (e.g. several weeks). However, the treatment “batches” can be substantially higher, allowing potentially similar monthly treatment capacities.

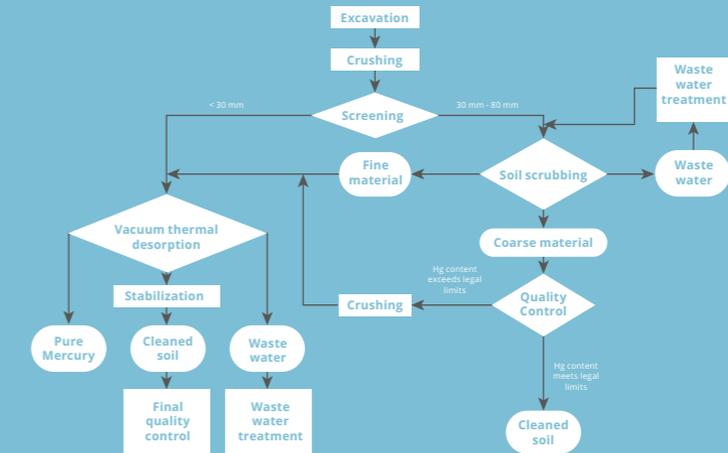
In-situ thermal desorption is an emerging technology for the management of Hg impacted sites. In this application, desorbed Hg (and other volatile co-contaminants) are collected within collection pipes under negative pressure and condensed/recovered. Exhaust gas treatment is often required (e.g. sulphur-enriched activated carbon). However, one concern associated with in-situ thermal treatment is the potential for un-controlled condensation of elemental Hg in areas of relatively lower temperature..

Figure 5. Schematic of In-situ Thermal Remediation Unit



CASE STUDY 6: MIRAMAS INDUSTRIAL SITE, SOUTHERN FRANCE

INDUSTRIAL SITE SINCE 1918, INCLUDING THE PRODUCTION OF LIGHT ISOTOPES THROUGH LITHIUM-MERCURY AMALGAM ISOTOPE SEPARATION (1960-2009). ON-GOING EXCAVATION AND TREATMENT OF C. 70,000 T OF HG-IMPACTED SOIL AND BUILDING RUBBLE CONTAINING HYDROCARBONS, WITH HG CONCENTRATIONS RANGING TO > 2,600 MG/KG AND LEACHATE TEST RESULTS OF UP TO 1.3 MG/L MERCURY. THE SITE IS CLOSE TO RESIDENTIAL HOUSING AND POTENTIAL AIR EMISSIONS ARE OF CONCERN TO THE LOCAL COMMUNITY.



Key learnings

- A combination of crushing, soil-washing, vacuum thermal desorption and stabilization was utilised to achieve cost-effective treatment.
- Coarser material (30 mm > 80 mm diameter) treated through soil washing.
- Finer material (< 30 mm) treated in a vacuum thermal desorption unit.
- Gradual heating in the vacuum thermal desorption unit allows recovery of high-purity Hg.
- The closed vacuum system ensures Hg emissions are well below regulatory limits.
- Stabilization of treated materials required for several co-contaminants, including As, Cd, and other metals.
- After stabilization, the treated material is re-used on site.
- Key project and design characteristics:
 - Project duration: 2010 – 2015 (planned).
 - Hg content of treated material: from 0.1 – 1 mg/kg with leach test results < 0.01 mg/l.
 - Treatment batch size: 8.4 m³.
 - Heating system: 1,800 kW/400°C thermal oil unit heated by natural gas.
 - Operating pressures: 10 to 800 mbar (absolute).

CASE STUDY 7: WASTE-WATER SETTLING POND, SWITZERLAND

SITE OPERATIONS DATING BACK TO THE LATE 19TH CENTURY INCLUDED THE ELECTROLYSIS OF SODIUM CHLORIDE SOLUTIONS USING HG ELECTRODES, AND THE SYNTHESIS OF AMINO-ANTHRAQUINONE USING AN HG-BASED CATALYST. A SITE ASSESSMENT, CONDUCTED FOLLOWING THE ESTABLISHMENT OF THE SWISS CONTAMINATED SITE ORDINANCE IN 1998, IDENTIFIED AN AREA IN THE VICINITY OF A FORMER WASTE WATER SETTLING POND AS A HIGH PRIORITY FOR FURTHER INVESTIGATION. THE SETTLING POND WAS BUILT IN 1932, AND UNTIL 1972, COLLECTED WASTE WATER FROM THE PRODUCTION FACILITY AND COMMUNITY PRIOR TO DISCHARGE INTO A NEARBY RIVER. SUBSEQUENT INVESTIGATIONS AND RISK ASSESSMENT IDENTIFIED POSSIBLE RISKS TO ENVIRONMENTAL RECEPTORS UTILISING THE HEAVILY-VEGETATED POND (E.G., AMPHIBIANS, DUCKS, SWANS AND OTHER BIRDS.) THE SELECTED REMEDIAL ACTION INCLUDED SLUDGE/SEDIMENT REMOVAL FROM THE POND BOTTOM FOLLOWED BY EXCAVATION OF UNSATURATED SOILS BENEATH THE POND.

Key learnings

- Total Hg concentrations of up to 200 mg/kg were measured in the pond sediments/sludge, with isolated hot spots up to 700 mg/kg Hg. Due to the low concentrations of Hg in site groundwater ($< 1 \mu\text{g/L}$), laboratory Hg speciation analyses were not conducted.
- Potential risks associated with groundwater down-gradient of the pond were related to organic co-contaminants and not Hg.
- The site characterisation (grid-based sampling) showed significant variability in the horizontal and vertical distribution of Hg within the pond. The highest concentrations were found within pond sediments/sludge and at the base of the dam supporting the pond.
- A risk-based remediation target value of $< 20 \text{ mg/kg}$ total Hg was initially established for the site, with the acceptance that complete decontamination of the site would not be possible, and that the site would remain in the Canton registry of contaminated sites.
- Down-gradient hydraulic containment was implemented during the removal action as a precautionary measure. However, Hg issues were not identified in groundwater during or after the remediation.
- A vacuum extraction technique applied under wet conditions was selected for the pond sediment/sludge rather than dry excavation under a tent. This technique had the advantage of avoiding dust generation and significant air emissions during sludge removal.
- The extracted sludge was dewatered through an extruder and the pressed soil cake (max concentration of 150 mg/kg Hg) transported to Germany for thermal desorption or incineration, based on the Hg concentrations.



Source: NICOLE member

- Hg concentrations in the generated filtrate ($30 \text{ m}^3/\text{hr}$) were below applicable criteria for discharge to the municipal sewage treatment plant.
- After removal of the pond sludge and sediment, it became apparent that previous sludge removal activities conducted in the 1970's had likely disturbed the low permeability layer beneath the pond and resulted in Hg migration deeper into soils beneath the pond. This prompted further soil excavation down to the average groundwater level. The additional remediation step resulted in an average total Hg concentration of $< 5 \text{ mg/kg}$, which was the revised threshold value after this remediation phase.



Source: NICOLE member

5. SITE MANAGEMENT TECHNIQUES

5.5 OTHER SOIL TREATMENT TECHNOLOGIES UNDER DEVELOPMENT

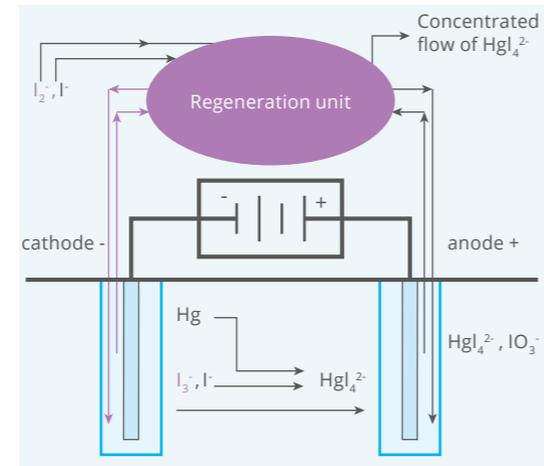
A number of other Hg remediation technologies are emerging for soils, although to date these have had limited commercial application or have not progressed beyond pilot stage. Some have significant technical hurdles to overcome prior to being readily available technologies. These include:

- In-situ electro-remediation;
- Bio-treatment (Fixed-Bed Bioreactors); and
- Phyto-extraction.

In-Situ Electro-Remediation

Electro-remediation involves the application of a low-intensity direct current across electrodes to drive migration of charged molecules to the opposite sign electrode. Electro-remediation is only effective on mobile contaminants. In most Hg-impacted soils, Hg is not mobile enough for the technology to be effective without the use of a mobilising agent. Promising results were shown at bench-scale using an iodine/iodide mobilising solution. A pilot test was built to evaluate the technology for the treatment of the unsaturated zone. At the start, the electro-osmotic flow that developed at the cathode was higher than expected, hence creating a risk of uncontrolled migration of mobilising solution. As a result, all partners in this project (technology provider, industrial operator, regulatory authority) decided to stop the pilot test. The control of this electro-osmotic flow is a major challenge to be solved for this technology.

Figure 6. In-Situ Electro-Remediation Schematic



Principle (patented EP 1 090 695 A1)

Bio-Treatment (Fixed-Bed Bioreactors)

Bio-treatment can be achieved using either an aerobic process which converts soluble ionic Hg (Hg^{2+}) to elemental Hg (Hg^0) for extraction/recovery, or a combined aerobic/anaerobic method which converts soluble ionic Hg to insoluble mineral phases. In both approaches, proprietary microbial cultures are used, and the effluent produced typically requires further treatment.

Phyto-Extraction

Phyto-extraction involves plants either naturally taking up chemicals into their biomass, or the same effect being chemically induced by mobilising agents. No plants have yet been identified which naturally hyper-accumulate Hg, although evidence exists of elemental Hg uptake from ambient air by plant leaves. Chelating agents (such as thiosulfate) have been shown to materially increase Hg mobilisation in soil solution, hence to increase

uptake by plants. Phyto-extraction is limited to the root zone of the particular plant being used and off-site disposal of Hg-impacted biomass is a major cost that needs to be factored into the design. The potential for Hg leaching below the plant root zone and the potential of bacterial reduction of ionic Hg to elemental Hg in the root zone need to be considered when contemplating phyto-extraction as a site management solution.

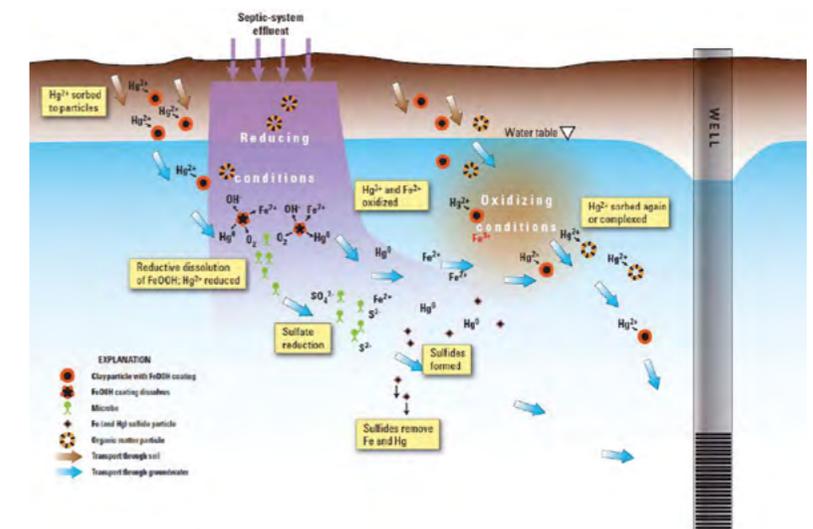
5.6 TECHNIQUES TO ADDRESS GROUNDWATER

Developing a robust CSM, by understanding the ambient and anthropogenic geochemistry, hydrogeological regime and current/future Hg speciation, is strongly advised prior to committing to implementation of groundwater remediation. Where remedial systems have been implemented to manage Hg-impacted groundwater, proven technologies include:

- Hydraulic Containment;
- Pump and Treat;
- Interception and amendment, permeable reactive barriers;
- Interception and capture, in-ground carbon walls (or other absorbents) in funnel and gate systems; and
- Containment using engineered in-ground barriers.

For hydraulic containment, pump and treat (via carbon absorption) and containment using engineered in-ground barriers, the technologies are well proven and much literature is present describing the merits of each approach.

This booklet is focussed on describing options that provide a variety of approaches which have a particular application with regard to Hg, such as the use of technologies designed to amend plume chemistry and capture Hg^{70,71,72}.

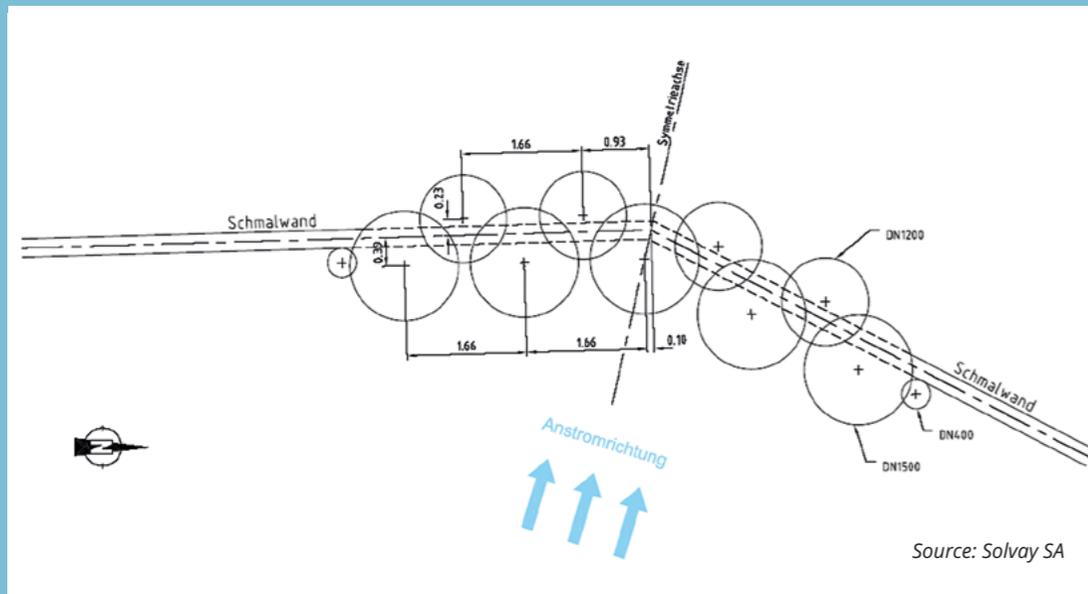


Mobilization of Hg from land to groundwater and biological transformation along flow paths in an unconsolidated sandy, acidic aquifer.

(Source: Occurrence and Mobility of Mercury in Groundwater⁷³. <http://dx.doi.org/10.5772/55487>)

CASE STUDY 8: FUNNEL AND GATE, AUSTRIA

FOLLOWING CESSATION OF OPERATIONS AND HOT SPOT REMOVAL (50 MG/KG SOIL TARGET), A FUNNEL AND GATE SYSTEM WAS CONSTRUCTED AT A CHLOR-ALKALI PLANT IN AUSTRIA. THE GATE WAS A MIXTURE OF GRAVEL AND ACTIVATED CARBON DESIGNED TO HAVE A LIFE-SPAN OF SEVERAL YEARS. THE RESIDUAL GROUNDWATER PLUME IS FUNNELLED TOWARDS AN ACTIVATED CARBON BOX IN THE GATE, AND HG IS REMOVED AS GROUNDWATER PASSES THROUGH. THE MAXIMUM LOADING WAS ESTIMATED AT 6 G/D HG FROM A RESIDUAL PLUME OF UP TO 50 µG/L. A SENSITIVE RECEPTOR IS LOCATED 350 M DOWN-GRADIENT OF THE SITE AND LONG-TERM MONITORING RESULTS SHOWED A STABILIZATION OF HG LEVELS DOWN-GRADIENT OF THE GATE BELOW THE 1µG/L TARGET.



Key learnings

- The system was built in two steps, with the funnel being built in 2001. This was initially operated by continuously pumping at 12.5m³/h for two years. This period was used to define the best material for the gate.
- The vibrating beam method was used to install the vertical barrier (funnel). A beam was vibrated down to the deepest point and then grout injected into the void created while withdrawing the beam. The final funnel characteristics are:
 - Total length 245 m
 - Depth 22-24 m-bgs
 - Thickness 0.06 m
 - Barrier starts at 0.6 m-bgs
 - Barrier ends at 2 m in the fine sands
 - Permeability 1x10-8 m/s



- A permanent gate was then built in 2004 by excavating 9 overlapping cylinders through the wall down to a depth of 15.5 m-bgs. Each column was then backfilled with a mixture of activated carbon and gravel from the base to up to 5.5 m-bgs (i.e. 0.5 m above mean ground water table).

- Renewal of the gate will be achieved by excavating the spent activated carbon and refilling with new carbon once the capacity has been reached. The final gate characteristics are:
 - Permeable gate volume 150 m³
 - Water residence time 205 minutes
 - Activated carbon 100 m³ (53 T)
 - Gravel 50 m³ (98 T)

5. SITE MANAGEMENT TECHNIQUES

5.7 OTHER GROUNDWATER TREATMENT TECHNOLOGIES UNDER DEVELOPMENT

There is on-going effort to develop effective treatment processes for dissolved Hg in groundwater. Current processes include absorptive systems and reactive systems. Absorbent systems include conventional activated carbon technologies. However, other absorbents are also being developed and offer potential advantages in certain circumstances. Absorbents may be based on natural products (e.g., immobilised algae, biochar) or may be synthetic chemicals (e.g., chelating agents, nanotechnologies). Reactive systems include technologies such as chemical reduction and stripping and the use of copper or brass shavings.

Immobilised Algae

Bio-Recovery Systems Inc. recently conducted a project as part of the US EPA's Superfund Innovative Technology Evaluation (SITE) Program to evaluate the ability of immobilised algae to adsorb Hg from impacted groundwater in laboratory studies and pilot-scale field tests. The algal biomass was incorporated in a permeable polymeric matrix within the treatment unit.

The product, AlgaSORB®, which was packed into adsorption columns made up of permeable polymeric matrix, reportedly exhibited excellent flow characteristics, and functioned as a "biological" ion exchange resin. Like ion-exchange resins, AlgaSORB® can be regenerated. A sequence of eleven laboratory tests demonstrated the ability of this product

to adsorb Hg from groundwater that contained high levels of total dissolved solids and hard water characteristics. However, use of a single AlgaSORB® preparation yielded non-repeatable results with samples collected at different times of the year⁵⁴.



Portable Effluent Treatment Equipment using AlgaSORB®.
Source: www.clu-in.org

The strategy of sequentially extracting the Hg from groundwater through two columns containing different preparations of AlgaSORB® was developed and proved successful in laboratory and pilot-scale field tests. Field test results indicate that AlgaSORB® could be economically competitive with ion exchange resins for removal of Hg, with the advantage that hardness and other dissolved solids do not appear to compete with heavy metals for binding capacity^{54,55}.

Biochar

A study conducted in 2013 at UMBC evaluated a range of biochars made from a number of agricultural residues, phragmites (beneficial use of invasive species in wetlands), and

hardwoods. In addition, some of the biochars were activated either physically or chemically to enhance their sorptive properties. Some of the biochars were impregnated with iron oxides to evaluate the enhancement of sorption of Hg and methyl-Hg.

The study showed that biochars were able to sorb organic contaminants, Hg and methyl-Hg, making them attractive alternatives to activated carbon for sites impacted with both organic and inorganic contaminants. Activated carbon products have a limited amount of sorption sites available for inorganic contaminants relative to biochars, and their performance typically drops with increasing Hg concentrations. The biochars, particularly those derived from poultry litter, were able to remove more Hg from solution at higher Hg concentrations compared to other carbons (>99% Hg removal in a study). It is possible that the high phosphate content of these poultry litter biochars is responsible for the enhanced Hg sorption⁵⁷.

In one laboratory-scale study of Hg-impacted sediments, 40 different substrates were charred to get the most optimal characteristics for absorbing Hg. Of these, a biochar called "Cowboy Charcoal", made from Red Oak from Kentucky, was narrowed down as the best. Mercury was present in the sediment as insoluble sulfides (metacinnabar) and also in soluble forms. The "Cowboy Charcoal" was able to remove considerable amounts of Hg from the water phase/sediment pore water. Adsorption/absorption sites remained available after treatment (the capacity was

not fully utilized), and the biochar retained the adsorbed Hg better than GAC (SediMite)⁵⁸. Based on the results of the laboratory testing, further pilot testing is planned.

More information regarding Biochar can be found at <http://www.biochar-international.org>.

Use of Chelating Agents

Chelating resins are commercially available and used for the removal of low-levels of Hg and soluble Hg salts from wastewaters such as brine and other industrial effluents, including from chlor-alkali processing facilities. Following treatment, the Hg is strongly bound to the resin's functional groups to form stable complexes. These properties are reportedly largely unaffected by high chloride or sulphate content in the water treated. Effluent solutions containing 2-20 mg/l Hg can be treated using resins such as Purolite® S-920 to reduce the concentration in solution to less than 0.005 ppm⁵⁹. Other chelating agents, such as Evonik Industries TMT 15® are also commonly used to remove heavy metals such as Hg from industrial waste waters, such as gas scrubber waters and other process waters⁶⁰.

A pilot study has been undertaken⁶¹ to examine the removal of low-levels of Hg from groundwater near a chlor-alkali plant using a synthetic chelating ligand. One commercially-available compound was found to be capable of reducing Hg concentrations to below detection limits (0.05 µg/l), with the added benefit of producing a stable precipitate.

5. SITE MANAGEMENT TECHNIQUES

Nanotechnology

Nanotechnology (Thiol SAMMS), developed by Pacific Northwest National Laboratory, comprises nano-porous ceramic substrate with a high surface area with layers of adsorptive plates with selective affinity for Hg. Testing shows Hg loading as high as 635 mg/l and sequential treatment yielded effluent < 0.1 mg/l⁶².

Chemical Reduction and Stripping

Field and laboratory tests have confirmed the use of chemical reduction and air stripping for treatment of water containing Hg²⁺. The process consists of dosing the water with low levels of stannous chloride (tin²⁺ chloride) to reduce the Hg to elemental Hg (Hg⁰). The Hg⁰ can then be removed from the water by air stripping. Reagent doses, with Sn to Hg ratios greater than about 5 to 25, showed nearly complete removal (~94%) and yielded final Hg concentrations of < 0.01 µg/L. The purge air can be treated with activated carbon as needed⁶³.

Use of Copper or Brass Shavings

The use of copper shavings to remove Hg from impacted groundwater by amalgamation has been investigated at an experimental level. Batch sorption experiments showed that 96 - 98 % of Hg²⁺ was removed within 2 hours. Column experiments were also performed with an Hg solution, which showed that no Hg breakthrough (> 0.5µg/l) could be detected after more than 2,300 percolated pore volumes. Copper was released from the shavings due to the amalgamation process and due to copper corrosion by oxidation, resulting in concentrations of mobilised copper of 0.2–0.6 mg/l. The authors suggest that given the efficient removal of Hg²⁺ from aqueous solutions, that copper shavings could be employed in a sequential system of Hg amalgamation followed by removal of mobilised copper using an ion exchanger (e.g. zeolites).

Brass (copper-zinc alloy) is being used in situ at pilot scale at a former wood treatment facility in order to treat an Hg plume by amalgamation⁶⁵.

6

BEST PRACTICE RECOMMENDATIONS

NICOLE PUTS FORWARD THE FOLLOWING BEST PRACTICE RECOMMENDATIONS, FIRSTLY FOR CHARACTERISATION AND RISK ASSESSMENT, AND THEN SITE MANAGEMENT.

NICOLE BEST PRACTICE RECOMMENDATIONS CHARACTERISATION AND RISK ASSESSMENT

1. Keep thorough historical records of industrial process and building structures, including infrastructure (foundations, networks). These are key elements of the Conceptual Site Model (CSM) and help to focus characterisation.
2. Sufficient characterisation is needed to build a robust CSM, set adequate reserves, negotiate the right clean-up goals and control project costs.
3. Select investigation/sampling techniques that avoid Hg migration and obtain representative data. Allow for full-time supervision by trained and experienced site engineers.
4. Understand Hg speciation and ambient/anthropogenic geochemistry, to quantify current and future Hg mobility/toxicity and potential risks.
5. Beware of “nugget effects”: use on-site measurements, increase sampling frequency, use statistical methods (e.g. 95 % UCL) for risk quantification.
6. Use direct measurement wherever possible (vs. relying on modelling) to characterise exposure media and migration pathways, so as to best quantify potential risks.
7. Make sure potential co-contamination is understood (e.g. dioxins, CVOCs).
8. Proactive management of Health & Safety risks needed during characterisation.

NICOLE BEST PRACTICE RECOMMENDATIONS REMEDIATION AND OTHER MANAGEMENT MEASURES

1. The management strategy should balance remediation with other management measures (e.g. deed restrictions) to mitigate risks and reduce long-term liability.
2. Negotiate appropriate and achievable clean-up goals. These should be risk-based, respect sustainable remediation principles and deliver Net Environmental Benefit.
3. Do not define clean-up thresholds for Total Hg, as these tend to be overly conservative. Instead, focus on mitigating Hg species driving risk and/or a mass removal approach.
4. Select the right remediation technique for the Conceptual Site Model, if needs be following appropriate feasibility testing (e.g. lab-scale tests, pilot trials).
5. Use qualified and experienced service providers (consultants, contractors).
6. During excavation and other ground disturbance, implement oversight by qualified personnel to optimise soil volumes and minimise the risk of downward Hg migration.
7. Given the high costs of off-site disposal, optimise soil volumes (e.g. careful segregation during excavation, sorting, washing).
8. Stringent health and safety management during remediation, including biological and air monitoring.

TWO KEY RESEARCH AREAS HIGHLIGHTED FOR CONSIDERATION:

1. Experimental work (laboratory, field) on the physic-chemical behaviour of Hg in the environment, so as to validate predictive models; and
2. Long term efficiency of in-situ stabilisation/solidification, including implementation of long-term monitoring programmes.

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