

Screening for Mercury at Suspected Contaminated Land Sites

Contaminated land. Land contaminated by previous industrial activities, past military uses and mining operations continue to be a source of concern to communities looking to redevelop brownfield sites, as local authorities struggle to evaluate the risk to health posed from these sites and formulate appropriate remediation plans. In addition to a long list of organic contaminants, such as chlorinated solvents, polyaromatic hydrocarbons (PAHs) and oil residues, soil at many former manufacturing sites have high levels of metals such as arsenic, lead, antimony, chromium, nickel and mercury, which impact drinking water quality.

“*In summary, a range of sampling and analytical methods can be used to assess mercury contamination at former industrial and mining sites.*”

Other routes by which these contaminants can affect the health of local residents may be less apparent, such as consumption of vegetables grown in contaminated soil, inhalation of airborne particles and hunting, so risk assessment has to take account not only of all the potential pathways for contaminants, but also the age and sex of likely receptors. Consequently, most regulatory agencies issue guidelines to assist investigators in evaluating contaminated land, such as the Department for Environment, Food and Rural Affairs (DEFRA) in England and Wales (Cole & Jeffries, 2009) or the Scottish Environmental Protection Agency (SEPA) in Scotland.

Mercury was used extensively in many industries, especially in chlor-alkali production, where it was used as an electrode in the production of Cl_2 and NaOH from brine. It was used in the gas industry for manometer and pressure measurements, in switches and thermostats, as well as thermometers. It is still widely used by artisanal miners to extract gold from ore. Mercury compounds are known to be highly toxic and were responsible for one of the most notorious environmental disasters at Minimata, Japan in the 1950's, where 2,265 victims suffered from often fatal neurological symptoms that were directly linked to the consumption of mercury tainted fish and shell food, later termed Minimata Disease. The source of Hg pollution was directly linked to water discharges from a factory operated by the Chisso Corporation, which manufactured acetaldehyde using mercury sulphate as a catalyst; mercury was discharged into Minimata Bay as a by-product. Mercury use in many industries has been greatly reduced through international agreements, with better control on sources and releases, although the single largest source of Hg^0 emissions is from coal-burning power stations.

Mercury is present in the environment in three main forms; elemental mercury (Hg^0) in the atmosphere, inorganic compounds such as the mineral cinnabar (HgS) in rocks and soils, and a range of organomercury compounds which are present in aquatic sediments and organisms. The toxicity of organic mercury compounds, such as methyl mercury (MeHg), is almost 100 times greater than their inorganic counterparts, so the form of Hg is crucial in assessing potential hazards. Low levels of inorganic mercury in soils and sediments can be converted into potentially more toxic levels through microbiological activity, if conditions are suitable. A further concern is that MeHg bioaccumulates in fish and through predation biomagnifies up the food chain, with methyl mercury accumulating in the tissue of many piscivore species to toxic levels. Mercury levels in some fish species can be 106 greater than Hg levels in river water (Leopold et al., 2010), with no obvious signs of ill effect. This creates a potential pollution linkage to communities downstream of contaminated sites that are dependent on fish as a major component of their diet. Many regions issue warnings advising pregnant women to limit consumption of certain fish such as because of the neurotoxicological effects of Hg on foetal development.

Sampling plans

Site investigation to determine the presence of toxic metals at a site involves the collection of soil samples from trenches, sediments from streams and water samples from boreholes and surface water and modelling the data to assess risk to potential receptors. Historical maps and aerial photographs are invaluable tools for identifying likely spots at the site where waste might have been dumped or chemical leaked, so a desk study of available published material is undertaken to formulate a detailed sampling plan. Analysis of aqueous samples by inductively coupled plasma-mass spectrometry (ICP-MS) is the most widely used method to simultaneously determine the concentrations of trace metals, with detection limits below $1 \mu\text{g L}^{-1}$ for most metals. However, as background Hg levels in surface water are typically in the range of $1 - 80 \text{ ng L}^{-1}$, ICP-MS is usually not sensitive enough to measure Hg in all but the most heavily contaminated environmental samples, although detection can be improved by using cold vapour generation prior to introduction into the instrument.

Other analytical techniques allow much lower detection levels for mercury analysis. The USEPA has approved Method 245.1 (USEPA, 1994) for the determination of mercury in water by cold vapour atomic fluorescence spectrometry (CVAFS), which has detection levels down to 0.5 ng L^{-1} under ideal conditions. Samples for CVAFS analysis should be collected in amber glass bottles, acidified and sealed with a Teflon® cap to minimise volatile Hg^0 loss and kept at 4°C until analysis.



Figure 1: Atomic fluorescence spectrometer (PS Analytical Ltd.)

Sequential chemical extractions (SCE) (Bacon & Davidson, 2008), using five or six steps of chemicals is often used to extract Hg from sediments as different inorganic species will be released by successively stronger extractants. Organic mercury compounds are removed by the potassium hydroxide extraction step, as shown in Table 1, and the results be used to estimate bioavailability based on the fractions that are likely to be dissolved in the digestive system.



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step	extractant	description	typical compounds removed
F1	DI water	water soluble	HgCl ₂
F2	pH 2 HCl/acetic acid	"stomach acid"	HgO, HgSO ₄
F3	1 N KOH	organo complexed	Hg humics, Hg ₂ Cl ₂ CH ₃ Hg
F4	12 N HNO ₃	strong complexed	mineral lattice, Hg ₂ Cl ₂
F5	Aqua regia	mercury sulphides	HgS, HgSe

Table 1: Sequential chemical extraction for determining Hg speciation (Bloom et al. 2003).

Sequential extractions are of limited value in determining organic mercury speciation and combinations of extraction, separation and detection instrumentation is usually employed for this purpose. Figure 2 shows the different combinations of Hg extraction/concentration, separation and detection components that can be coupled to provide the sensitivity needed to quantify mercury species.

Total mercury determinations, while useful, provides limited information of the form, and therefore potential toxicity of mercury present in soil and water. Coupling of separation techniques, such as high performance liquid chromatography (HPLC) with ICP-MS or AFS is widely used to separate methyl mercury species from inorganic mercury species and to quantify the amount present.

Pre-treatment & concentration	Separation	Detection
hydride generation	high performance liquid chromatography	ICP-AAS
cold vapour	gas chromatography	ICP-MS
distillation	capillary electrophoresis	AFS
solid phase extraction		GF-AAS

Figure 2: Hyphenated analytical methods used to separate and measure mercury species

In many studies, the determination of methyl mercury, ethyl mercury and inorganic mercury is adequate to access the bioavailability of mercury at a contaminated site and can be accomplished by selective extraction. Extraction of methyl mercury and ethyl mercury by dichloromethane (DCM) solvent has been successfully used in combination with HPLC-CV-AFS to measure methyl mercury in Hg-contaminated sediments (Chen, 2012) with detection limits around 200 ng l⁻¹ for MeHg reported.

Soil Screening

Soils metal levels are normally determined by extraction using acid followed by ICP-MS or ICP-AES and compared to published soil guideline values. Elemental mercury, which may be present at many sites, is highly volatile, so care must be taken to preserve soil samples such as freezing. Soil extractions are a time consuming and expensive method and are also limited by the detection levels of the instruments. Field portable X-ray fluorescence (FPXRF) is being increasingly utilised for in-situ screening of soil, with hand-held instruments available from Bruker GmbH, Thermo-scientific (Niton) and Oxford Instruments, among others. As the analysis time using FPXRF is a few minutes or less, hundreds of measurements can be made during a site investigation. Analysis takes less than a minute, with result immediately available to investigators, allowing the sampling plan to be modified to target anomalous zones. Although measurements can be made with little or no sample preparation, repeatability is greatly improved if the samples are sieved, dried and homogenised. Levels of detection are typically around 5 – 30 ppm for intermediate atomic weight metals and as low as 2 ppm for total mercury. However, it should be noted that at Minimata Bay, mercury levels in sediment rarely exceeded 1 ppm (Kudo & Miyahara, 1991), so FPXRF cannot be used as the sole soil screening method.

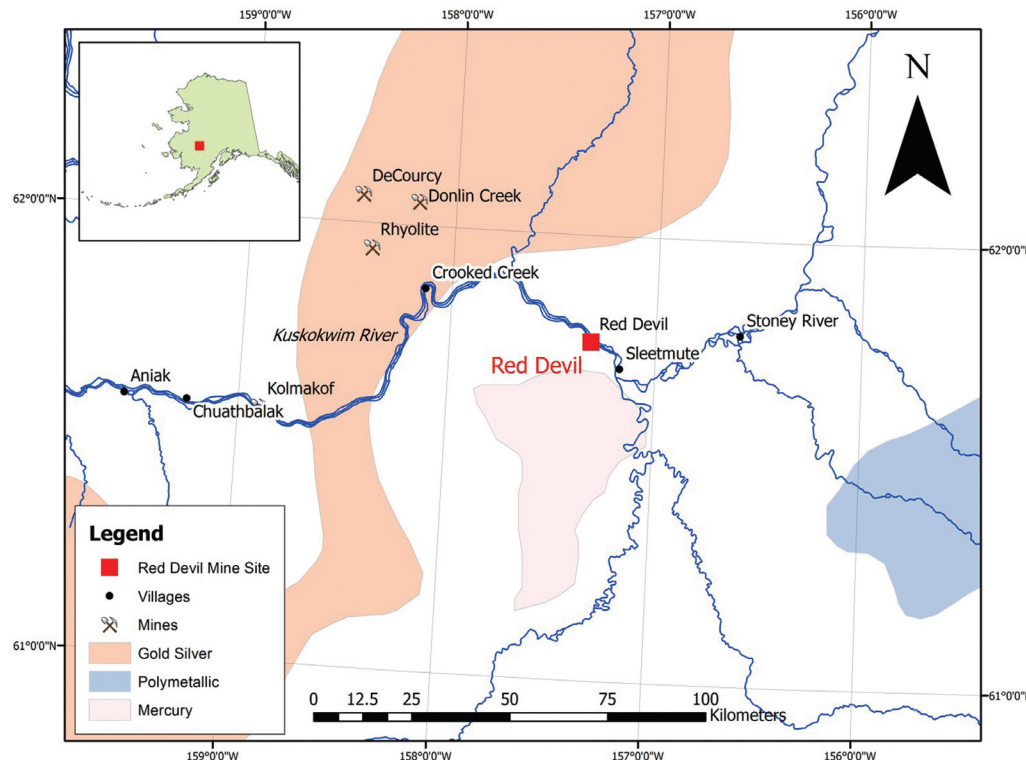


Figure 3: Map of the Kuskokwim River showing Red Devil

Case study : Red Devil Mine, Alaska

The challenges of screening a contaminated site are best illustrated by examining a case study. The state of Alaska has a well-characterised mercury mineralisation belt that was mined for most of the 20th century (Gray et al., 1998), of which the most productive mine was Red Devil in the Kuskokwim region of southwest Alaska (Figure 3), which operated from 1937 until 1971, after which it was abandoned. Over 1,224 tonnes of Hg were produced at the site during its operational life. Despite successive remediation efforts, the Red Devil mine site remains heavily contaminated by waste tailings from mining and ore processing and is believed to be a point source for mercury entering the Kuskokwim River.



Figure 4: Drilling a monitoring well at Red Devil. (Photo credit Keith Torrance)

Hg is present at Red Devil as the mineral cinnabar, which is found in quartz veins within a Cretaceous greywacke sequence, in association with the mineral stibnite (Sb₂S₃). Liquid mercury was extracted from cinnabar ore at the mine site using a simple furnace/retort to roast the ore and condense Hg vapour sublimated from the ore; at least three generations of retorts operated at Red Devil. Other metals were not recovered from the ore, so waste calcines from the furnace have elevated levels of Hg, As and Sb, with the potential to pollute the environment.

As part of a remedial investigation in 2011, soil samples were collected and water sampled at Red Devil by a contractor working on behalf of the Bureau of Land Management (BLM). The development of a detailed sampling plan is important if the goals of the site investigation are to be met and the possibility of undiscovered contamination excluded. As the site is remote with no road connections, equipment and personnel had to be flown in and samples preserved for weeks before they could be sent to the laboratory for analysis. Water samples were collected from a series of newly installed monitoring wells and Red Devil Creek, which bisects the site, and analysed by ICP-MS for elements of concern and AFS for total mercury.

FPXRF was used to screen soil inaccessible areas of the site that may have been used to dump tailings, delineate sluiceways and locate any 'hot spots' for future investigation. Sub-surface soil samples were collected from the drill cuttings and by split spoon recovery and selectively extracted to measure methyl mercury and total mercury (Ecology & Environmental, Inc., 2012). Samples of spruce, alder and blueberry were also collected and methyl mercury

extracted and measured to assess possible pathways through consumption of vegetation by game animals.

Despite the considerable body of analytical data collected at Red Devil it is extremely difficult to model mercury fluxes from the site, in part because there is no baseline data from before mining in the region Cinnabar and even liquid mercury was noted by early gold prospectors panning streams in the region, so there clearly was a natural Hg flux from the mineralisation. The main transportation mechanism by which mercury is transported into the Kuskokwim River is believed to be erosion of the tailings, with subsequent methylation by bacteria in the organic-rich river sediments. Consequently, analytical investigations have focused on measurement of methyl mercury in fish tissue sampled at different points on the river. However extraction of methyl mercury from tissue is more difficult than from soils and yields must be quantified using certified reference materials.

In summary, a range of sampling and analytical methods can be used to assess mercury contamination at former industrial and mining sites. Analysis of mercury in soils and water at such sites is complicated by sub-ppb detection levels in instrumentation needed to quantify mercury species and the requirement to properly preserve samples to avoid loss of volatile Hg⁰. The choice of analytical techniques should reflect expected Hg levels at the site and include speciation to allow a proper assessment of potential toxicity to be made. However, for results to be meaningful, robust quality assurance protocols must be followed and verified by concurrent extraction and analysis of certified reference materials

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