NICOLE

Network for Industrially Contaminated Land in Europe

Mercury Contaminated land management – state of the art

NICOLE Mercury Working Group Paper

Context

Mercury is a natural element formed primarily through hydrothermal processes. Its occurrence is rare, but major ore bodies have been exploited in Europe since antiquity. The Almaden ore district in Spain is the world's largest ore body and is responsible for one third of the historic global production of mercury. The most common ore form of mercury is cinnabar (HgS). In some ore districts, significant proportions of liquid metallic mercury are present as well. Volcanic activity is the major natural source of mercury release to the atmosphere. In addition to mining of natural ores, mercury arises as a by-product from gas cleaning and from the refining of copper and zinc ores. Although in the European contaminated land management arena mercury may not have necessarily received significant attention, a series of governmental policies and legislative acts [1,2] restrict the use of mercury in industry, and are likely to lead to the closure (and possible redevelopment) of some industrial operations.

The United Nation Environmental Program (UNEP), an intergovernmental negotiating committee, is preparing a global treaty that will be legally binding for the signing parties concerning the use of mercury. The objective is to *"protect human health and the global environment from the release of mercury and its compounds by minimizing and, where feasible, ultimately eliminating, global, anthropogenic mercury releases into the air, water and land, in line with the overall goal of the UNEP Global Mercury Partnership and in accordance with Decision 25/5 of the Governing Council of UNEP"*.

Most of the sites with activities impacted by the new and/or pending legislation will have to be investigated, and contamination management measures may subsequently be required at these properties. This concerns not only chlor-alkali plants using the mercury cathode process (Hg°), which are the major user of mercury in Europe, but also other industrial activities, such as wood impregnation ($HgCl_2$), battery manufacturing & recycling, and a variety of other manufacturing activities (thermometers, electrical switches, processes using mercury based catalysts, oil & natural gas production).

A critical mass was reached within the membership of the NICOLE network to initiate a technical working group on mercury. The aim of the group was, through networking, sharing experience and organizing a one day workshop [3], to get a snap shot of the current industry practices and on-going development of information on the various associated topics.

Scope

The scope of this paper is to summarize the work of the working group and communicate its conclusions.

Conclusion of the Mercury Working Group

Mercury exhibits physical and chemical properties (liquid metal, surface tension, vapor pressure) which make it unique and which make the characterization of mercury contamination at industrial sites a challenge. Its distribution, transport and migration are unlike that for other metals found at industrially contaminated sites. Characterization, fate & transport modeling and management of mercury contaminated sites are challenging due to mercury's unique behavior in the environment.

Characterization

Characterization of mercury contamination at industrial sites poses some major issues for classical investigation methodologies, these are:

- Large spatial heterogeneity created by a 'nugget effect' when droplets of the metallic form (liquid) are present in soil. This effect means that the evaluation of the total load of mercury is very difficult to quantify;
- Questions around the behavior of metallic mercury in soil: does it behave like an organic DNAPL? Does liquid metallic mercury behave differently in the unsaturated and saturated zones?;
- Mercury phase and speciation, meaning the potential for mercury compounds to be present at the site in different geological environments and different forms.

Field observation is important and attention should be paid to possible bias due to field work. The 'nugget effect' requires adaptation of standard sampling strategies and means that large and/or composite samples are preferred over small discrete samples which would likely bias sampling results. The presence of different phases of mercury (liquid or gas) requires focused assessment. Mercury vapor in the vadose zone has been investigated with good results, and investigation in this manner presents the advantage of averaging the concentration which means that the impact of the heterogeneity of the mercury distribution is reduced.

As an alternative or in addition to the collection of soil samples, the measurement of adsorbed ionic mercury in the soil can be done in the field using portable instruments (e.g. XRF, portable cold vapor analyzer, possibly equipped with a pyrolitic oven for soil/water analyses), with the added advantage that this enables on-going adjustment of the sampling strategy in a reflective manner. In addition, work is underway to adapt a MIP probe to determine mercury concentrations, and early results from this show promise.

Experimental work will be necessary to improve our understanding of the behavior of metallic mercury in the subsoil.

Speciation of mercury is not currently standard procedure for many commercial laboratories in Europe.

Laboratory determination of the mercury species provides a powerful tool to allow development of the Conceptual Site Model and hence an appropriate assessment of the risks posed by the mercury contamination. Consideration of the speciation and the interpretation of these results needs to be undertaken utilizing the correct framework.

Contaminant fate & Transport and risk assessment

Standard risk assessment procedures can be used for assessing the impact of mercury contamination, but developing an understanding of the hydrochemical regime (pH and redox) is extremely important as it plays a role in the mobilization, seepage and accumulation of different mercury species. As for any metal, an understanding of the chemical speciation is important for human health and environmental risk assessment, not least because exposure pathways can vary depending upon the mercury species present and the site specific conditions (e.g. liquid metallic mercury sewer systems).

Assessment of the vapor phase provides a direct measure of the main pathway of exposure to mercury vapor from the subsoil.

Methyl-mercury is a sensitive issue as it is known to bio-accumulate in the aquatic food web creating potentially both an environmental as well as a human health risk. The process of mercury methylation is mainly the result of biological processes in anaerobic sediments. It is a very dynamic process as de-methylation is also biologically driven, and coupled to the reduction of ionic mercury to metallic mercury. In the terrestrial food web, methyl-mercury bio-accumulation has not been demonstrated to be the major risk for terrestrial wildlife [4].

Risk control & Remediation

Classical remedial techniques such as containment excavation and speciation control to less toxic forms can easily be applied to mercury contamination.

Some in situ technique have been tested without success, for example:

- Electro-remediation requires a mobilizing agent, the drawback of the technology is to ensure the capture of all mobilized mercury by the electric field
- Phyto-extraction requires to mobilize mercury in the pore water because no plant have been identified that can significantly take up mercury via its root system. It has been confirmed by lab experiments [5]. Therefore, just as for electro-remediation, mobilization of mercury is necessary to improve significantly the extraction yield. If applied in-situ the risk of migration of mercury outside the root zone is real. The second disadvantage is the production of a large biomass that will have to be treated as a waste. A third disadvantage is that often the residual concentration after mobilization rarely does reach the set fixed remedial target value.

Ex-situ techniques like soil washing have been applied to mercury contaminated soil, yielding to significant reduction of concentrations. In some cases, residual concentrations were low enough to allow reuse of the sandy soil fraction, whilst in other cases they remained above the fixed target value.

The development of extraction techniques may be impaired by the risk of not reaching the target value and having to rely on excavation and land filling as a fall back scenario. In this case, a sound approach should be taken to allow the risk evaluation of the residual mercury contamination before triggering the fallback scenario.

Other in-situ techniques have been applied with success and/or are being adapted specifically to mercury, e.g. in situ stabilization [6]. The challenge is to develop formulations that will act on both the mobility and the speciation (reduction of toxicity) and be stable for the long term in the local condition of the site. In these cases, no concentration reduction is obtained but a reduction of risk is achieved due to reduction in the toxicity/mobility of the contaminant.

Management considerations

Though mercury exhibits a unique combination of physical and chemical properties among the metals, the management principles for mercury contaminated land are not different from those for other contaminants. These are:

- Risk Based Land Management [7]
- Sustainable contaminated land management [8]
- Net Environmental Benefit Analysis [9] (for application to impacted environmental receptors outside the industrial perimeter)

The difficulty with mercury is to acquire the relevant data to identify the level of toxicity (linked to speciation), and the relevant pathways and receptors in order to build a robust site conceptual model.

Those approaches enable companies and society to prioritize sites based on the risk posed in order to allocate resources in the most cost efficient way considering the environmental benefit gained and cost of any action.

References

1. *'Regulation on banning mercury export … and the safe storage of metallic mercury'*

   Download pdf (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:304:0075:0079:EN:PDF).

2. UNEP decision 25/5 on the development of a global legally binding instrument on mercury.

   See: UNEP (http://www.unep.org/hazardoussubstances/Mercury/Negotiations/tabid/3320/Default.aspx).

3. *NICOLE Mercury Workshop, Dec. 4th, 2012*

   Download pdf (http://www.nicole.org/uploadedfiles/nicole-brussels-december2012.pdf).

4. Gnamus, A. & M. Horvat (1999). *Mercury in the terrestrial food web of the Idrija mining area. Mercury Contaminated Sites.* (Eds. Ebinghaus, R. et al.; Springer.)

5. Caille, Nathalie (Mai 2002). *Mobilité et phytodisponibilité du mercure dans des dépôts de sédiments de curage*. Thèse de doctorat Institut National Polytechnique de Lorraine.

6. *NICOLE – Mercury Technical Workshop (2012).*

   Download pdf (http://www.nicole.org/uploadedfiles/nicole-brussels-december2012.pdf).

7. *Clarinet/NICOLE – Joint statement.*

   Download pdf (http://www.commonforum.eu/Documents/DOC/Clarinet/clarinet_nicole_jointstatement.pdf).

8. *NICOLE SR – Final report*

   Download pdf (http://www.nicole.org/uploadedfiles/wg-sustainableremediation-finalreport.pdf).

9. *NICOLE – Mercury Technical Workshop Environ*

   Download pdf (http://www.nicole.org/uploadedfiles/nicole-brussels-december2012.pdf).