Maneuvering the Maze of Heavy Metal Cleanup Standards – a Site-Specific Approach

by

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Abstract

Heavy metals are common contaminants of concern at brownfields and other sites where industrial activities have taken place. If the concentrations of heavy metals in the soil exceed regulatory limits, they can represent a severe restriction to development. For a regulatory agency to grant approval for such heavy metals to remain in the ground, it is necessary to demonstrate that human and ecological exposure pathways are not present. In Pennsylvania, two general exposure pathways are often considered, direct contact and soil-to-groundwater, the latter often representing a lower (more conservative) allowable total heavy metal soil concentration as part of the Statewide Health Standards.

Total heavy metal concentrations commonly include non-bioavailable forms and can therefore be overly conservative when used to evaluate human and environmental risk. Soluble fractions of heavy metals in soil are usually considered to be more biologically relevant and the degree of risk they present relates to both toxicity and mobility. Among the properties governing the environmental fate of heavy metal contaminants, the soil/water partitioning coefficient (Kd) is perhaps the most significant. The Pennsylvania Statewide Health Standards for heavy metals in soil were derived on the basis of risk-based calculations considering Kd values to be constants. In reality, Kd values for a specific metal depend on many factors (e.g., speciation of the metal, pH, soil type, presence of organic compounds, initial concentration of soluble metal, etc…) and are highly site-specific.

This paper presents a process whereby site-specific parameters can be derived and used in fate and transport calculations. An example of this process is provided for lead, cadmium and selenium in soils as part of the remediation of an industrial site in accordance with Pennsylvania’s site-specific standard.

Introduction

Heavy metal contamination of soil at industrial sites poses a serious environmental concern. Assuming that it is practical to either remove or isolate the most heavily contaminated soils such that the hazard from direct contact is eliminated, a serious condition can still exist if there is a potential threat to ground water. Common sources of contamination of heavy metals include emissions from steel plants, mine refuse and industrial sites, all of which are well-represented in western Pennsylvania and are associated with brownfields development. Of the 2,369 sites remediated under Pennsylvania’s Land Recycling Program (Act 2) by January 2007, 28% involved the cleanup of inorganics, in particular lead, which is listed for about two thirds of the sites with inorganics.

This review focuses on three metals encountered at an industrial site in Indiana County, PA: lead (Pb), cadmium (Cd) and selenium (Se). The numerical standard (Medium Specific Concentration – MSC) for these metals in soils in Pennsylvania in terms of direct contact and soil-to-groundwater is provided in 25PA Code CH 250, Administration of the Land Recycling program (Act 2) in Appendix A, Table 4. The most conservative of these

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MSCs are often those for the soil-to-groundwater pathway where the site is underlain by a used, freshwater aquifer. For the contaminants in this study, the soil to groundwater pathway MSCs are 450 mg/kg Pb; 38 mg/kg Cd; and 26 mg/kg Se.

Pennsylvania Act 2 allows for remediation of sites that do not meet Statewide Health standards, as long as it can be demonstrated that the sites do not represent a significant risk to human health or the environment. This might be achieved by means of institutional controls or by otherwise demonstrating that risks are acceptable. A key component to a risk assessment is a fate and transport analysis of the contaminants of concern. If it is possible to demonstrate that there are no current or probable future exposure pathways, the site can qualify for remediation under the site-specific standard under Act 2.

Eliminating exposure pathways is not a simple process when heavy metals are considered. Heterogeneities in chemical or physical properties of subsurface media complicate our ability to make adequate predictions of contaminant mobility. Metals are especially difficult to characterize. Whereas organic contaminants are defined by specific compounds with specific properties, metals can be present as a wide range of compounds with an equally wide range of properties. For example, a high concentration of copper in soil does not necessarily make the soil hazardous. Native copper has been found to be stable in the soils of the Upper Peninsula of Michigan for thousands of years, whereas copper sulfate commonly found in some pesticides is a highly mobile contaminant that has been the subject of extensive research (Edwards, 2006).

As can be inferred from the title of Pennsylvania’s site-specific attainment standard, fulfilling the requirements of this standard requires obtaining a substantial amount of site-specific data. The following reviews factors important to conduct representative fate and transport analyses that provide the type of information needed to make the analysis site-specific.

**Fate and transport considerations**

Current risk assessment methodologies consider numerous potential exposure pathways when evaluating the risks posed by environmental contaminants. With the soil-to-groundwater pathway scenario, the concerns are direct exposure by aquatic biota and human exposures occurring through ingestion of contaminated drinking water. Understanding the potential for these exposures requires careful consideration of the environmental soil/water partitioning behavior of the metals of concern.

Contaminant migration via leachate seepage is a porous-medium contaminant transport problem. Leaching is defined as interphase transfer of contaminants from the solid phase to the pore water surrounding the solids and the subsequent transport of these contaminants by pore water seepage. Thus, leaching is interphase mass transfer coupled with porous-media fluid mechanics. Interphase mass transfer is a complicated interaction of many elementary processes and factors affecting these processes. Quantification of these processes, interactions, and other factors affecting these processes is not presently possible. Instead, a lumped parameter, the partitioning coefficient, is used to describe the distribution of contaminant between aqueous and solid phases. This term is defined as follows:

\[ K_d = \frac{q}{C} \text{ or } q = K_d C \]

where \( K_d \) = equilibrium distribution coefficient in units of liters per kilogram (l/kg), \( q \) = contaminant concentration in the solid phase at equilibrium, mg/kg, and \( C \) = contaminant concentration in the aqueous phase.
at equilibrium in units of milligrams per liter (mg/l). Values of $K_d$ for heavy metals are provided in PA Code 250 Appendix A Table 5B that are the same as those provided by the USEPA in their *Soil Screening Guidance* (USEPA, 1996a) for soils with a pH of 6.8. The USEPA (1996b) details the assumptions they followed in the derivation of $K_d$ values for metals:

1. There is no contaminant loss due to volatilization or degradation.
2. Adsorption is linear with concentration.
3. The system is at equilibrium with respect to adsorption.
4. Adsorption is reversible.

It is this last assumption that is most critical in applying a specific $K_d$ value to a fate and transport analysis. To assume that the adsorption is reversible implies that the metal is in a soluble form in the soil, which is frequently not the case, as noted above with the example for copper, where the reaction would not be reversible for native copper. Other important factors in deriving $K_d$ values include pH, soil type, presence of organic compounds, and initial concentration of soluble metal (USEPA, 1999a,b; Frisch et al., 2003; Chapman and Wang, 2000; Chapman et al., 2003).

The USEPA has continued to conduct research into the development of $K_d$ values that are appropriate to specific site conditions (Allison and Allison, 2005). These researchers conducted a survey of approximately 245 articles and reports from which a total of 1170 individual $K_d$ values were obtained either directly or calculated from reported media concentrations. The variability of reported $K_d$ values is exemplified by the results reported by Allison and Allison (2005) for cadmium, lead and selenium (Table 1).

**TABLE 1 – RANGE OF $K_d$ VALUES FROM ALLISON AND ALLISON (2005) COMPARED WITH PENNSYLVANIA STATEWIDE HEALTH STANDARD (SHS)**

<table>
<thead>
<tr>
<th>Metal</th>
<th>$K_d$ values (l/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low</td>
</tr>
<tr>
<td>cadmium</td>
<td>1</td>
</tr>
<tr>
<td>lead</td>
<td>5</td>
</tr>
<tr>
<td>selenium (IV)</td>
<td>1</td>
</tr>
<tr>
<td>selenium (VI)</td>
<td>0</td>
</tr>
</tbody>
</table>

* $K_d$ values in PA SHS only indicate selenium, without distinguishing state

Some of the reasons for the variability in reported test results in the case of cadmium and lead are provided in another USEPA study published by Loux et al. (2005), who develop relationships for estimating $K_d$ accounting for variations in pH, sand content of the soil, and organic content. The results reported by Allison and Allison (2005) show that the SHS $K_d$ values are generally conservative when compared to published results, but it should also be noted that they were derived from a starting point where the metals were already in solution.

$K_d$ values are typically calculated by means of leaching contaminated water through clean soil, a procedure that requires the contaminants to be in a soluble form where the reactions are reversible. This is appropriate if the problem is to determine the effectiveness of a clay landfill liner in containing leachate, but it may be overly conservative if the problem is to determine the concentration of leachate generated from contaminated soil. This discrepancy is well documented by the US Army Corps of Engineers (USACE).
The USACE has undertaken considerable research in the subject of estimating the mobility of heavy metals in soils due to the issue they face of assessing the environmental impact of dredged sediment (Brannon et al., 1989, 1990, 1994; Myers et al., 1991; Schroeder et al., 2003). They note that the USEPA determinations of $K_d$ values are based on leaching contaminated water through clean soils, not clean water through contaminated soils. This allows for the assumption of a reversible reaction to be valid, but ignores the situation where contaminants may be resistant to leaching because of their chemical form (speciation). These researchers define the general form of the $q$ versus $C$ relationship as follows (Brannon et al., 1994):

\[ q = K_d C + q_r \]

where $q_r$ is the soil contaminant concentration resistant to leaching. These researchers conclude that assigning $K_d$ values without considering the chemistry of the heavy metal results in inaccurate predictions of mass transfer.

This observation is supported by several other recent studies (Frisch et al., 2003; Chapman et al., 2003; Åkerblom, 2006;), who conclude that it is not possible to understand the mobility of heavy metals without understanding speciation of the metals. These researchers point out that it is the soluble fractions of heavy metals in soil that are more biologically relevant than the total heavy metal concentration. In particular, Chapman et al. (2003) note that the common practice of removing soil with contamination from metals has developed largely because of the historical poor understanding of fate processes in soils, as it is still too often assumed that metals bioavailability in the environment is similar to that determined in laboratory toxicity tests using soluble metal salts. These researchers document that bioavailability in the environment is generally lower, sometimes much lower, not only because environmental exposures do not involve solely soluble metal salts, but also due to many other factors such as complexation; competition with environmental ligands; sorption onto soils and sediments; precipitation in anoxic environments in the presence of sulfides, and coprecipitation.

Case history of heavy metals cleanup under Pennsylvania Act 2 site specific standard

Cadmium, lead and selenium were detected at concentrations exceeding the Pennsylvania SHS for direct contact at non-residential sites (for cadmium and lead) and for the soil-to-groundwater pathway standard (for cadmium, lead, and selenium). Cadmium used at the plant was in the form of a powder comprised of elemental metal and/or cadmium sulfide. The selenium was also used in an elemental form. Neither the chemistry of the lead nor a mechanism for its release to the site soils could be determined, so lead was conservatively assumed to be in a leachable form in the soil. The soils exceeding the direct contact standard were remediated on the basis of removal and institutional controls, but the bigger problem was what to do with the remaining soil that exceeded the soil-to-groundwater pathway standard. If all of the soil contaminated with heavy metals was excavated and removed, not only would the remediation be very expensive, but it is possible that the integrity of the building foundations could be compromised. The best solution would be to remediate the site under Pennsylvania’s site-specific standards such that the metals could remain in place.

The Act 2 site-specific standard requires a “rigorous scientific evaluation of a remedy to provide a protective cleanup standard unique to that site.” This implies that it is necessary to conduct a comprehensive characterization of soil and groundwater conditions and that there is a good understanding of the fate and transport of the contaminants of concern. This information then needs to be incorporated in a risk assessment to
demonstrate that the post-remediation site risks meet the human health and environmental protection goals specified in Pennsylvania regulations.

To achieve the requirements of the Act 2 site-specific standard, the following program was followed:

- **Site characterization**: Site conditions were characterized by analyses of 192 soil samples (not including an additional 32 attainment samples to demonstrate post-remediation compliance) and advancement of 15 soil borings, 7 of which were completed as monitoring wells.

- **Fate and transport analysis – vadose zone**: A conceptual model was developed and contamination migration via leachate seepage was calculated. Calculations were based on the characteristics of site soils and soil water conditions, as well as site-specific soil-water partitioning of the metals of concern.

- **Fate and transport analysis – saturated zone**: A conceptual model was also developed where contamination could be associated with saturated soils. In this case, potential for migration was calculated on the assumption that the metals of concern would be in solution and that the reasonably conservative $K_d$ values published as part of the SHSs would be applicable.

- **Preparation of a Cleanup Plan**: This plan primarily involved constructing controls to potential soil erosion while allowing for the contaminated soil to remain in place.

The most significant part of this approach was in the definition of site-specific partitioning characteristics of the metals of concern within the vadose zone.

There are several types of tests that can derive $K_d$ values. A good discussion of the possible types is presented in USEPA (1999a) where five general methods used to measure $K_d$ values are presented: laboratory batch method, in-situ batch method, laboratory flow-through (or column) method, field modeling method, and $K_{oc}$ method. Each method has advantages and disadvantages, but what was important for this situation was that the $K_d$ values be as representative as practical of site field conditions. To achieve this, the testing was designed to simulate the infiltration of clean water through contaminated soil.

**Distribution of total cadmium in shallow soils at the plant site.** This distribution was determined on the basis of 192 soil samples. At this location the cadmium was known to be in the forms of native metal and sulfide, which are both of very low solubility.
Testing consisted of following the procedures for TCLP analysis, but substituting deionized water and actual ground water taken from the site, rather than using acetic acid (pH = 2.9) as would normally be used in the TCLP test. This procedure is similar to the Sequential Batch Leaching Test recommended by the USCOE (Brannon et al., 1994).

The leaching tests indicate that neither the cadmium nor selenium is in a form that is leachable to either neutral deionized water or actual ground water. The apparent $K_d$ values for cadmium and selenium based on this testing are $>5.3 \times 10^3$ and $>3.2 \times 10^4$, respectively. The values are considered to be apparent as USCOE testing has shown that leaching tests frequently show that the $K_d$ values are not constant as leaching progresses. The most soluble portion of a metal in soil is the first to leach out, yielding a $K_d$ value that is lower for the beginning of the leaching process than at the end. The USCOE testing procedure requires the recirculation of the leachate through several leaching cycles. Our procedures used only one cycle, which is conservative in that additional cycles of leaching that might have mobilized the remaining less soluble forms of the metals, could have shown higher (less conservative) $K_d$ values, but not lower. These apparent $K_d$ values are appropriate for estimating the concentration of leachate derived from the passage of clean water through contaminated soil. They are not appropriate for estimating the passage of contaminated ground water through clean soil. In this latter situation, the best estimate of the behavior of the dissolved metal would be to assume $K_d$ values consistent with those derived by the USEPA (1996) and listed in Table 1 as the SHS.

The TCLP and SPLP testing of the soils that were removed as part of the initial site remediation also provide evidence as to the immobility of the cadmium and selenium in the soil. The aggressive TCLP testing for selenium would lead to the derivation of $K_d$ values on the order of $10^3$ to $10^5$. The TCLP testing will leach out cadmium from the soil, but the SPLP testing with a less aggressive acid solution would still yield $K_d$ values on the order of $10^3$. Although these tests are not appropriate for defining representative $K_d$ values, they still demonstrate that the application of the SHS $K_d$ values tabulated in Table 1 would be very conservative. Based on the SHS values of $K_d$ provided in Table 1, it would be expected that selenium is the most mobile of the heavy metals encountered at the site. The site-specific leaching tests indicate that it is actually the least mobile under site conditions. For lead, the soil chemistry and source of contamination was unknown, as it was released at the site prior the ownership responsible for the management of cadmium and selenium. For this reason, the $K_d$ value of $8.9 \times 10^2$ published in Table 5B in Appendix A of PA Code 250 was used in the fate and transport analyses.

Three computer codes were used to model the contaminant fate and transport in the soil and ground water. In the vadose zone, the hydrologic modeling for the soil profile was conducted with the Hydrologic Evaluation of Landfill Performance model (HELP) published by the USCOE (Schroeder et al., 1997). Contaminant transport in the vadose zone was calculated using the Hydrologic Evaluation of Leachate Quality (HELPQ) computer
code, developed by the USCOE Waterways Experiment Station Environmental Laboratory (Aziz and Schroeder, 1998). These programs were selected, because they offered the possibility of including site-specific precipitation, as well as site-specific soil properties into the model. Contaminant transport in the saturated zone was modeled using a Microsoft® Excel spreadsheet, entitled Quick_Domenico.xls, recommended in the Act 2 Technical Guidance Manual (PADEP, 1997 – upgraded 2002) that references Domenico (1987) as its technical basis.

The results of the contaminant transport modeling for cadmium, lead and selenium with worst case parameters using the HELPQ program indicate none of these metals has the potential for reaching the ground water in 30 years. The greatest amount of contaminant transport is postulated to occur with lead, where the assumption has been made that the maximum total concentration of lead is in soluble form, and even in this case the maximum predicted transport is about three feet. The cadmium is predicted to penetrate less than two inches through the buffer zone and the analysis indicates that the selenium migrates less than one inch. Based on the HELPQ modeling and as supported by sampling and analyses of ground water, it is concluded that that the metals do not need to be removed to protect ground water resources. This is due to the relative insolubility of the lead and the occurrence of the cadmium and selenium in similarly insoluble forms.

The plant was constructed on fill over drained wetlands and these soils were also where lead and cadmium were detected. In the case of the cadmium, the groundwater in the zone of soil contamination contained dissolved cadmium to a degree consistent what would be expected to be equilibrium conditions based on the laboratory-calculated K_d value. Nevertheless, the modeling of cadmium transport in the saturated zone required different assumptions for equilibrium partitioning than were utilized to derive the maximum potential ground water contamination from soil contamination. The leaching tests predicted how much contamination would be leached by clean water through contaminated soil, but not interphase transfer by contaminated water moving through uncontaminated soil. It is reasonable to assume that the migration of contaminated water through clean soil will be associated with reversible chemical reactions, the main assumption followed by the USEPA (1996a,b) in their derivation of K_d values. The SHA partitioning coefficient K_d for cadmium of 75 references a pH of 6.9 (USEPA, 1996a). The USEPA (1996a) indicates the K_d value at a pH of 6.2 (the pH measured from a monitoring well in the zone of saturated contaminated soil) to be 42. Accordingly, a K_d value of 42 was utilized for the Quick_Domenico.xls analysis. As the maximum observed contamination in the ground water was consistent with what would be estimated for the worst case given the results of the leaching tests, this concentration was assumed to be the source concentration for the modeling of cadmium transport in the saturated zone. The result of the analysis with these worst case assumptions indicates that, over 30 years, the cadmium will not migrate more than four feet from the edge of the source. A similarly conservative analysis was conducted for lead with the result that lead will not move more than about one foot from the zone of contaminated soil.

The result of the fate and transport modeling was that the potential for migration to surface water where an exposure pathway could be present is negligible. Based on sediment and surface water sampling and testing, contamination had not migrated into the surface water regime. Prior to remediation, evidence of impacts to surface water or stream sediments were not encountered. The remedial activities provide assurance that no exposure pathways will develop in the future. The remediation of this site under the site-specific standard was approved by the PADEP.
Discussion

The transport of metals in soil is a complicated process dependent on many site-specific factors: speciation of the metals, pH, soil type, presence of organic compounds, initial concentration of soluble metal, etc. In particular, the speciation (chemical form) of a metals, which relates directly to its solubility and bioavailability, is often overlooked, as it is common practice to assume that metals are in the form of soluble metal salts, which is frequently, if not usually, not the case. Most regulatory standards relate to total metals in the soil, which can significantly overestimate the risk from metals in soil. Some researchers have postulated that the common practice of removing soils contaminated with metals is because the insolvency of many metal compounds is not considered when conducting risk assessments.

In the case history presented, the forms of the cadmium and selenium (native metal and sulfide) were known because of the manufacturing processes involved at the site. In most cases it is not easy to determine the speciation of metals when they are present in the mg/kg range in soil, although X-ray diffraction studies can sometimes be useful. The critical process in evaluating if speciation is significant is to conduct leaching tests that simulate site-specific conditions to calculate soil-water partitioning coefficients ($K_d$ values). If the derived values are much higher than published values, it will be apparent that non-soluble or low-solubility forms of the metal are present. The procedures for the Sequential Batch Leaching Test recommended by the USCOE (Brannon et al., 1994) can be considered for the development of site-specific $K_d$ values. Once site-specific $K_d$ values have been derived, the fate and transport analyses also need to be based on actual site conditions. For the case history presented, the HELP and HELPQ programs were used for the vadose zone modeling because they offer the possibility of easily calculating infiltration based on site-specific meteorological and surface conditions. Other modeling programs could also have been used.

Metals in soil can represent a severe restriction to brownfields redevelopment if they exceed regulatory limits for allowable total concentrations. If the heavy metals are to remain in the ground, it is necessary to demonstrate that human and ecological exposure pathways are not significant. Because the transport of metals in soil is such a complicated process, site-specific conditions need to be considered to the maximum degree practical if exposure pathways are to be eliminated. A key component to this process is to adequately address soil-water partitioning with site-specific tests.

REFERENCES


