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Project Summary

Factors Affecting Trace Metal Mobility in Subsurface Soils

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Laboratory and field investigations were conducted to study factors affecting the mobility of metals in soils.The project focused on subsoils associated with waste disposal sites and examined a wide range of conditions that might be present influencing movement of metals.

Field and laboratory work demonstrated acidic wastes associated with a battery recycling operation has combined with the relatively poor metal retention properties of the soils in the area to transport excess lead to the shallow groundwater zone in a southeastern Louisiana location. Conversely, field and laboratory data indicate a soil with a higher clay content and a near neutral to slightly alkaline pH can effectively immobilize high levels of metals such as now-closed disposal pits used for metals plating and other waste at an Oklahoma Air Force base.

The study showed important interactions between soil types, metals, metal concentrations, and the presence of additional non-metallic waste materials (co-wastes) on the movement of metals in subsoils. Disregarding any of these factors when evaluating the potential for metals leaching at a contaminated site could result in large errors in predicting metal mobility and the potential for groundwater contamination.

The most significant new information from this project pertains to the effects of co-wastes, when present, on facilitating the movement of trace and toxic metals in subsoils. The findings of this project lead to the recommendation that more research should be done to: (1) identify the important characteristics of various types of co-wastes that facilitate metal mobility, and (2) quantify these effects to aid in development of models predicting metal mobility in subsoils. The particular metals present, the amounts of metals present, and soil properties must also be considered as all of these parameters interact in affecting metal mobility in subsoils.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Background

The transport of metals to groundwater below hazardous waste sites is of considerable environmental concern. The movement of a particular metal is determined by the amount and form of the metal, the soil's chemical and physical properties, and the composition of the soil or waste solution with which the metal is associated. The soil properties affecting metal retention/release and transport include bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, type and amount of metaloxides present, and type and amount of clay minerals (Fuller and Warrick, 1985). Soils with a wide range of these properties were selected for this study except that all of the subsoil materials had typically low levels of organic matter. Soil organic matter, at levels commonly found in surface soils and sediments, is one of the primary immobilizing processes for trace and toxic metals (Gerritse and van Driel, 1984; Levi-Minzi et al, 1976). Subsoils, usually beginning 15 to 30 cm beneath the surface, generally contain so little naturally-occurring organic matter that it becomes important to focus on other metal retention processes in the region between surface soils and groundwater.

The greater the concentration of a specific pollutant in the soil, the more likely it is to move through the soil. When the concentration of a metal exceeds the capacity of the soil to retain it, migration may take place as if the soil were an inert, porous medium (Fuller, 1980).

Solution composition will also greatly affect metal retention and movement. Doner (1978) reported that the mobility of Ni, Cu, and Cd through soil columns was 1.1 to 4 times greater in Cl^- solutions than in ClO_4^- solutions, with the greater effect seen for Cd. Perchlorate was reported to not complex metals. In most of the cases studied by Benjamin and Leckie (1982), addition of Cl^- or SO_4^{2-} reduced Cd retention indicating that chloro- and sulfato- complexes are retained less strongly by the soil than are uncomplexed Cd ions. Garcia-Miragaya and Page (1976) found that Cd retention decreased in the order (same ionic strength): $Cl_4^- > SO_4^{2-} > Cl^-$. Brown (1979) stated that the formation of complexes of Pb with various anions such as Cl^-, F^-, CO_3^{2-}, HCO_3^-, and OH^- increased the concentration of Pb in natural waters by preventing Pb from taking part in other chemical reactions, primarily adsorption, which would lower the solution concentration.

Knox and Jones (1979) reported that all of three sanitary landfill leachates they tested were able to complex Cd to some extent, although their ability to do so varied, and in some cases might well have been insufficient to greatly affect metal retention. The reaction between Cd and leachate appeared to be mononuclear and predominately the result of a 1:1 complex formation. Although fatty acids were the most important complex-forming fraction in one leachate studied, other organic compounds, such as fulvic acid, were important in the other two leachates. Thus, the degree of metal immobilization or transport depends upon interaction between soil properties, amount of metals present, and the properties of the leachate phase with which the metals are associated.

An aerobic environment increases the solubility and mobility of metals (Fuller, 1980; Bates, 1980), or decreases the solubility of metals (Page and Pratt, 1975), depending on the absence or presence of sulfides and other redox-active components in the system (Gambrell, et al. 1980; Khalid et al., 1981). The adsorption and coprecipitation of trace and toxicmetals with colloidal hydrous oxides is an important process in decreasing metal availability in some soils. The oxides and hydroxides are favored by an increase in pH and/or redox potential. When hydrous Fe and Mn oxides are reduced, the trace and toxic metals which are coprecipitated with or retained by the oxides may be released (Thibodeaux, 1979). The formation of insoluble metal sulfide precipitates limits the bioavailability of most metals in some strongly reduced soils and sediments. In general, where sulfides are not present, as in most subsoils, a moderately low pH and redox potential environment favors the relatively bioavailable soluble and exchangeable chemical forms of metals while higher pH and oxidation levels favor sparingly soluble, oxidized compounds. Cadmium, however, has been found to show the opposite redox effects in sediments (Gambrell, et al. 1976). In surface soils and sediments, oxidizing, weakly acid conditions greatly increases levels of soluble and weakly acid conditions greatly increases levels of soluble and exchangeable Cd.

There are a number of reviews and reports on factors affecting the mobility and plant availability of trace and toxic metals. Much of this work has focused on topsoils or sediments containing an appreciable amount of naturally occurring organic matter compared to subsoils. Soil humic material is known to be very effective in immobilizing most trace and toxic metals. Since subsoils contain much less organic matter and are the primary transport media if metals contamination of groundwater is to occur, research efforts should be directed toward processes regulating metal mobility in subsoils.

The objectives of this project were as follows:

(1) To identify soil physical and chemical properties regulating the mobility of metals in subsurface soil materials. This research focused on subsoils between the contaminated soil at or near the surface and the groundwater. Much has been published on the mobility and biological availability of metals in surface soils and sediment Factors affecting the mobility of meta from waste disposal sites in subsoils h received comparatively little attention.

(2) To show for a number of ke metals the important interaction between metal concentrations, was mixtures, and soil properties in reg lating the mobility of metals. It is we documented that all metals do n respond identically to mobilizatio immobilization processes in soil. I addition to soil properties and th particular metals present, there are tw other important factors that may influenc the mobility of metals in subsoils: (1) th concentrations of metals present, and (the presence of other types of waste that may influence the mobility of metal These two factors have particul relevance to waste sites presenting threat to groundwater and wer considered in planning this study. Th interaction between the four factor mentioned above were studied in th context of hazardous waste disposal site which represent the greatest potenti threat to groundwater contamination b metals.

In a hazardous waste dump or landfil a variety of types of waste may b present that become mixed with metal at or beneath the site. Mixtures of metal and other wastes may interact t influence the mobilization of metals. Th presence of toxic metals with acidi wastes, for example, would greatl enhance the leaching of metals beneat the initial disposal zone towar groundwater. This is a set o circumstances that has not bee thoroughly addressed in the toxic metal studies associated with sludge amended soils or dredged materials a very acidic conditions are very rarel encountered in these situations. Als certain organic wastes in higl concentration may affect the mobility c metals. It is likely there are man locations where waste mixtures ar present that may enhance or hav already enhanced the leaching of metal to groundwater. The concept of facilitate transport of metals in waste mixtures ha not yet received the research attention i deserves. This project was designed t begin to examine this topic.

The greatest potential threat fo groundwater contamination by toxi metals comes from the many illegal poorly planned, and/or poorly manage hazardous waste disposal sites in th country. Many of these were establishe and used prior to the knowledge we now have on groundwater contamination and the better regulatory restrictions of recent years. It is not unreasonable to expect a combination of coarse-textured subsurface soils, high concentrations of metals, and the presence of co-wastes that tend to mobilize metals at a substantial number of these sites.

Procedure

Field and laboratory studies were conducted to examine factors affecting the mobility of metals in subsoils. The experimental approaches for these studies are summarized below.

Field Studies

The objectives of the field studies were to determine the distribution of forms of trace and toxic metal contaminants in the subsoil at sites with known or suspected potential for groundwater contamination. Soil cores were taken to a depth generally between 2 and 3 meters at the sites with a hydraulically-driven 4.75-cm stainless steel coring tube. The plan was to obtain duplicate cores within the disposal zone and two additional pairs of cores over increasing distances from the disposal ozone where possible. The cores were sectioned with depth in the field, stored in plastic bottles, and then returned to the lab for analysis.

The field studies were planned to be coordinated with laboratory studies in terms of the soil materials and the contaminants present. Assistance in locating and accessing contaminated field sites was obtained from the USEPA, U.S. Air Force, the Louisiana Department of Environmental Quality (DEQ), and the Louisiana Department of Transportation and Development (DOTD). We were seeking five sites with known metal contamination problems.

Though considerable effort was expended in identifying the sites, securing authorization for access to the sites, sampling, and analyzing samples, this effort was only partially successful because clear indication of high metals contamination was not apparent in core samples from several of the locations. Two of the most promising sites in Louisiana were unavailable at the last minute, and alternative sites were selected.

Laboratory Studies

Three laboratory studies were conducted to examine factors affecting metals movement in subsoils. These included batch and column transport studies. The first batch study focused on retention of a number of metals (Cd, Ni, Pb, and Zn) in many soil types with and without the presence of a simulated co-waste. The term co-waste refers to a non-metallic waste material that may be present at a disposal site, possibly facilitating the mobility of metals. Calculations of adsorption coefficients and regression analyses were used to examine the effects of specific soil properties and the presence of a leechate on metal retention. Because of the importance of soil redox potential on the environmental chemistry of metals, a second batch study was done with Cd and Pb and various co-wastes in fewer soil materials, but under different purge gases simulating aerobic and anoxic conditions in the subsoil materials. The column transport study included two soil materials receiving two levels each of Pb and Cd associated with four leaching solutions.

Results and Discussion

Field Studies

Of the field sites studied, a lead-acid battery reprocessing location yielded the most information in terms of metals contamination which has apparently moved to shallow groundwater. A waste disposal pit for metals and other materials at another Air Force base may have also contributed to shallow groundwater contamination by metals. The data collected at an arsenic dipping vat, a metal waste disposal pit at another Air Force base in OK, and an oil reprocessing site in Louisiana did not indicate significant metals transport was occurring in the subsoils associated with these sites.

A brief summary of the results from the field study sites is given below.

Kolin Arsenic Dipping Vat

It is acknowledged that As (arsenic) is not a metal. But, for simplicity in this report where the focus of the project is mentioned, the terms trace metals and toxic metals are used and intended to include As.

This was the site of a concrete-lined dipping vat used to treat livestock to remove parasites. A shallow groundwater sample taken from very near the pit contained about 0.3 mg/l As or, for comparison purposes, this was about six times USEPA drinking water quality criteria. Levels exceeding 500 µg/g total As in the soil were found to a depth of about 0.5 meters in cores taken from very near the vat. Five of six samples above the 0.5 meter depth contained 180 µg/g As or higher. However, beneath 1.5 meters, levels dropped to near background. The high total levels near the surface supported elevated levels of water and acid-extractable As. These forms dropped to near background levels beneath about 1.5 meters.

Maximum As levels in the shallow subsoil vs. deeper subsoil suggested that most of the As associated with the pit may be retained strongly by the soil at this site such that leaching beneath at least a couple of meters may have been negligible. However, it should be acknowledged that the history of use of this cattle-dipping vat is not known and the first sampling occurred about three decades after its use was discontinued. The possibility of transformations between different species of As with different mobilities and the presence of a crack in the concrete liner of the pit complicated evaluating the data obtained at this site. Therefore, it is possible that considerable As may have been transported from the site during the intervening years for which there is no current evidence.

Combustion, Inc.

Combustion Inc. is a site where waste oil was stored in pits for later reprocessing. The now-closed facility is a Superfund site. Cores taken to 2 meters depth at the edge of an oil pond particularly recommended to us by DEQ personnel, as well as additional cores taken in the area, did not indicate elevated metal concentrations over levels typically found in uncontaminated soils. At this time, we do not know if additional exhaustive sampling would have indicated very localized areas of metal contamination at the site, or whether DEQ was basing their belief of metals contamination at this site on unreliable information.

Tinker Air Force Base, Waste Pit #2 and Waste Pit #1

According to Air Force personnel and maps provided us, our Waste Pit #2, "A" core samples were collected within the old waste disposal pit (now covered and not discernible from the surrounding landscape). Neither these samples nor two additional pairs of core samples taken downslope from the disposal pits showed concentrations of any metals measured above typical soil background levels.

At this site, reliable information is available that high levels of metals are associated with the site. This information comes from personnel familiar with the operations of the site years ago and much more recent metal survey work done at the site. Though a geologist working with us believed we were in the pit based on examining the core material collected, we can only surmise now that our cores missed the actual disposal pit, possibly penetrating an adjacent zone disturbed for some other purpose. Nevertheless, the lack of metals from deep cores obviously very close to the actual pit and additional downslope cores indicates the subsurface soil at this site does very effectively immobilize high concentrations of metals. The laboratory work with control soil from the site confirms this conclusion. Similarily, high concentrations of metals were not found at another waste disposal site sampled at Tinker Air Force Base.

Robins Air Force Base

As for Tinker Air Force Base, maps and information from personnel familiar with the former waste disposal operations at this base were made available to us. Though covered with soil when disposal operations ceased, visual confirmation of the disposal pits was possible at this site.

Beneath the cap or cover soil placed on the pits, the core samples were saturated with a black, oily liquid from organic wastes also dumped at the site. This necessitated special precautions working with this possible hazardous, volatile organic waste, and complicated sample processing using conventional methods of characterizing the form of metals present in soil materials. Thus, a complete chemical characterization of the site was not completed in time for this report.

Many samples from several cores at this site were highly contaminated with Cd, Cr, Cu, Ni, Pb, and Zn. In addition, cores from an adjacent area between the disposal pits and the surrounding swamp were also saturated with the same oily liquid as the pit samples, and also contained some of the highest levels of metals. Clearly, this is a site with a high potential for metals movement through subsoils, possibly facilitated by high levels of organic waste present. If information that our Core E samples were taken away from the disposal area is correct, then the data indicate substantial movement of several metals has occurred in the shallow groundwater.

Pontchatoula Battery

The study site at Pontchatoula Battery was the former location of a pile of old automobile and marine batteries awaiting reprocessing to reclaim the Pb. The pile was reported to be 100 meters X 30 meters X 10 meters high at one time. The battery cases were not stacked upright and apparently cracked in many cases such that substantial quantities of concentrated sulfuric acid containing Pb spilled from the pile onto the soil. Surface soil samples contained several thousand µg/g Pb and another zone of excess Pb concentrations was found at the surface of the shallow groundwater just over a meter beneath the surface. Elevated Pb in the shallow groundwater zone at a depth of over 2 meters in what was believed to be a control area (several hundred meters away from the battery storage site) suggested Pb transport in groundwater may be occurring at this location.

This is an example of a worst case situation for metals mobility. The surface and subsurface soil at the site is coarse textured containing relatively low levels of clay and hydrous iron oxides that would normally be effective in immobilizing Pb. An important additional circumstance is the presence of large quantities of spilled, strong acid which acidified the soil to the shallow groundwater. This apparently facilitated transport of this metal through the soil.

Laboratory Studies

Most work with metal mobility and bioavailability has been done with surface soils containing an appreciable organic matter content compared to subsurface soils which are the transport media for metals between waste disposal sites and groundwater. Data were presented illustrating the difference between surface and subsurface soils on metal retention capacity. More importantly, and pertaining to the focus of this project, the laboratory studies clearly demonstrated that subsoils differing in physical and chemical properties will show substantial differences in their ability to immobilize trace and toxic metals. Sandy soils and weakly acid soils are much less effective in retaining metals than soils near neutral to alkaline in pH and containing high levels of clay.

The amount of metals present in the soil was shown to be an important factor in determining mobility. At higher concentrations that may be associated with waste disposal sites, many soils become less effective in immobilizing metals. Apparently, the immobilization processes in soils are overwhelmed. However, as indicated in the previo paragraph, some soils showed the abil to effectively immobilize very hi concentrations of metals.

Though this project focused on subs materials, the preceding two paragrap summarize findings that one mig expect based on previous work w surface soils. The paragraph bel briefly introduces a significant, relative new research topic.

A subject that has received minin research attention related to met mobility in soils is facilitated transport other waste materials that may present. The likely role of facilitat transport was evident at two of the fie sites studied. Both batch equilibrati and column leaching studi demonstrated the presence of oth waste materials in addition to metals concern can significantly enhan mobility of metals. The presence a effects of such co-wastes are importa factors that have been overlooked t often in the past when evaluating t potential for metals movement a groundwater contamination. The c wastes studied included a synthe municipal leachate, a simulated acid metals waste, and a synthetic oil fie waste. Column leaching studies clea demonstrated complex formati between both Cd and Pb with differe components of the synthetic municip landfill leachate since two distin concentration peaks occurred with time column eluents.

Another topic that has received litt research attention is the influence subsoil redox potential conditions metal mobility. One of the project's bat equilibrium retention studies included th parameter. Under the conditions of th study, the data suggested soil oxidati status may have some influence on met retention, but the effect was less than t other variables studied in this proje (different metals, metal concentration soils, and co-wastes present).

Conclusions and Recommendations

Field Studies

Kolin As Dipping Vat

Our data suggested that As associat with this old cattle dipping vat may strongly retained by the surroundi subsoil such that leaching beneath couple of meters has been negligib However, definite conclusions at this si are not possible because a chemic history of the site is not available (the vat was last used decades prior to any sampling at the site) and because transformations between several species of As with different mobilities may have occurred complicating determination of what may have happened over the years. Also, a crack in the concrete walls of the below-ground vat may have released As directly into the subsoil zones where samples were obtained making an evaluation of the data difficult. There was some indication that iron oxides in the subsoils tended to retain the As.

Combustion Inc.

Contrary to the information provided us, metals wastes do not appear to be a problem at this site based on our limited sampling.

Pontchatoula Battery

Lead, usually one of the least mobile of the common toxic elements in soils, had moved vertically to shallow groundwater at a former battery recycling plant. Subsequent lateral movement in the groundwater is also indicated. At this site, Pb movement was facilitated by the combined presence of sandy subsoils and a co-waste consisting of large quantities of spilled sulfuric acid.

Tinker AFB

Field sampling indicated metals were not moving appreciably in subsoils from closed waste disposal pits examined at Tinker Air Force Base. Soil properties at this site apparently result in effective immobilization. Laboratory studies with this soil supported the conclusions that metals are strongly retained in the soil at this site relative to other sites and soil materials examined.

Robins AFB

Assuming disposal zone boundaries were correctly delineated on maps provided us, high concentrations of several metals have moved laterally in shallow groundwater from a closed disposal site toward an adjacent swampy area. High levels of organic wastes may have facilitated metals movement at this site.

Laboratory Studies

The laboratory studies demonstrated:

1. Subsoils are generally less effective in immobilizing metals compared to surface soils and sediments.

2. The metal-immobilizing capacity of subsoils increases with pH, clay content, cation exchange capacity, and hydrous oxide content of the subsoil. Several of these factors are related in soils such that in general, sandy soils offer a high potential for metal mobility compared to finer textured soils.

3. Metals tend to be more mobile in soils as their concentration increases. This is likely due to high levels exceeding the capacity of various immobilizing processes.

4. One of the important aspects of this study was the demonstration that the presence of co-wastes containing complexing anions, competing cations, or high acid contents tend to facilitate metal movement in soil. In particular, a synthetic municipal landfill leachate studied resulted in substantially less retention of metals by most of the soil materials studied.

5. Results of short-term laboratory studies suggested oxidized subsoils tend to be more effective in immobilizing metals than anoxic subsoils, but the differences found in this preliminary study were relatively small.

6. There are important interactions affecting metal mobility between: (1) the kinds of metals present, (2) the amounts of metals present, (3) soil properties, and (4) the presence of co-wastes. For example, whether or not the presence of a particular co-waste will have no effect, a moderate effect, or a very large effect on the mobility of metals can depend on the properties of the soil material.

Complimentary Findings of Field and Laboratory Studies

Though a quantitative relationship between field and lab results was not attempted, the laboratory data supported the findings of the field studies. Using the same or very similar subsoil materials, the lab studies demonstrated the effective metal immobilizing characteristics of the subsoil at the Tinker AFB site where field sampling indicated metal movement is apparently not a problem.

In contrast, lab studies demonstrated coarse-textured subsoils permitted leaching of Pb, normally considered a relatively immobile toxic metal. The additional presence of other simulated wastes substantially facilitated release and transport of Pb and other metals.This helped explain shallow groundwater contamination by Pb at an old battery recycling plant and the apparent movement of Pb and other metals at another Air Force base disposal site.

A major finding of this work representing a relatively new research topic was the demonstration that several types of non-metallic wastes can greatly facilitate the movement of metals in subsoils.

Recommendations

The findings of this project lead to the recommendation that the presence of waste materials other than metals at disposal sites must be considered in evaluating the potential for metals contamination of groundwater. Additional research should be done on: (1) identifying the important components of various types of co-waste that facilitate metal mobility in soils, and, (2) quantifying these effects to aid in model development. Also, the interaction between subsoil properties, kinds and amounts of metals present, and kinds and amounts of co-wastes present should receive more research attention in order to develop models that will adequately predict metals movement under the range of conditions associated with waste disposal sites.

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The complete report, entitled "Factors Affecting Trace Metal Mobility in Subsurface Soils," (Order No. PB 88-224 829/AS; Cost: $19.95, subject to change) will be available only from:
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