



Project Summary

Development of Land Disposal Decisions for Metals Using MINTEQ Sensitivity Analyses

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A metal speciation modeling approach was developed for evaluating potential mobilities of arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, silver and thallium in ground waters under conditions reflecting leachate contamination from a failed land disposal facility. A modified version of metal speciation model MINTEQ was used in combination with a set of generic ground-water specifications and an E_h /pH uncertainty window to determine metal solubility limitations. Metal speciation results were interpreted in combination with an infinite-source, steady-state advective dispersion model used to estimate dilution during transport to a down-gradient exposure point.

The ten metals were divided into "mobile" and "relatively immobile" groups. The mobile group included arsenic, barium, cadmium, lead, nickel and thallium. At least one E_h /pH combination within the uncertainty window was found for which each of mobile metals was dissolved up to concentrations sufficient to exceed health-based thresholds at the hypothetical down-gradient exposure point. The relatively immobile group included chromium, mercury, selenium and silver. These four metals had limited solubilities at all E_h /pH combinations within the uncertainty window. After allowing for dispersion, predicted concentrations at the down-gradient exposure point were below the drinking water standards. Chromium, mercury and selenium were, however, more soluble under conditions more oxic than those reflected by the uncertainty window. Ad-

ditional sensitivity tests were performed to establish the E_h range above which the respective solubilities were predicted to increase significantly. The order of dissolution with increasing E_h was selenium > mercury >> chromium.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, 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).

Background

The U.S. Environmental Protection Agency often has the responsibility for dealing with pollutants in situations where the specific environment available for interaction with the pollutant at each individual site is unknown. In these cases, the decision process must involve a generic component. The full report outlines a generic approach for evaluating the speciation and transport of metals in ground-water environments. The primary emphasis was on the simultaneous solution of metal speciation equations that determine dissolved phase metals concentrations.

Speciation and transport of arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, silver, and thallium in ground waters are considered in an example setting designed to mimic the behavior of the leachate from a failed land disposal site. The procedures used are designed to be compatible with recently proposed methods for treating organic leachates. Expected variations in site-specific chemical backgrounds relative to the presumed

generic ground-water chemical environment were accommodated using an E_H/pH uncertainty window approach. The uncertainty window was developed from statistical data on existing wells around the country.

Potential transport of equilibrium-dissolved-phase metal species resulting from solution of the speciation equilibria are estimated using a back-calculation screening procedure. Simply stated, the goal of the screening procedure was to establish health-based concentration thresholds for dissolved metal species that would be applicable to extracts of raw waste and that were assured of being protective of human health and the environment at a down-gradient exposure point (possible drinking water source). Health-based concentration thresholds (C_{ADI}) applicable to the point of exposure served as the starting point. These were apportioned such that exposure to other sources (surface water, air) were taken into account. Elaboration of the detailed conceptual approach used in establishing the C_{ADI} 's was outlined in the *Federal Register*, 40 CFR, Part 260, January 14, 1986. The C_{ADI} 's were used in concert with a steady-state advective-dispersion model and the metal speciation model (MINTEQ) results to back-calculation allowable concentrations in leachates from the landfill. Leachate concentrations were assumed to be mimicked by pollutant concentrations observed in extracts of the raw waste material.

The primary emphasis of this work was on evaluating the impact of metal speciation equilibria on transport of metals in a generically defined ground-water environment.

Methods

A schematic representation of the plume from a failed land disposal unit is shown in Figure 1. Metals in the disposal unit leachates are presumed to equilibrate geochemically with the saturated zone solution instantaneously at the point of contact. Dissolved metals concentrations in the resulting mixture would be subject to reduction by precipitation of solid phases as well as dilution and dispersion. Dilution due to dispersion was estimated using the model represented in Equation 1 in conjunction with a Gaussian boundary condition. This model also was used to estimate transport of organic leachates, and it was designed to account for

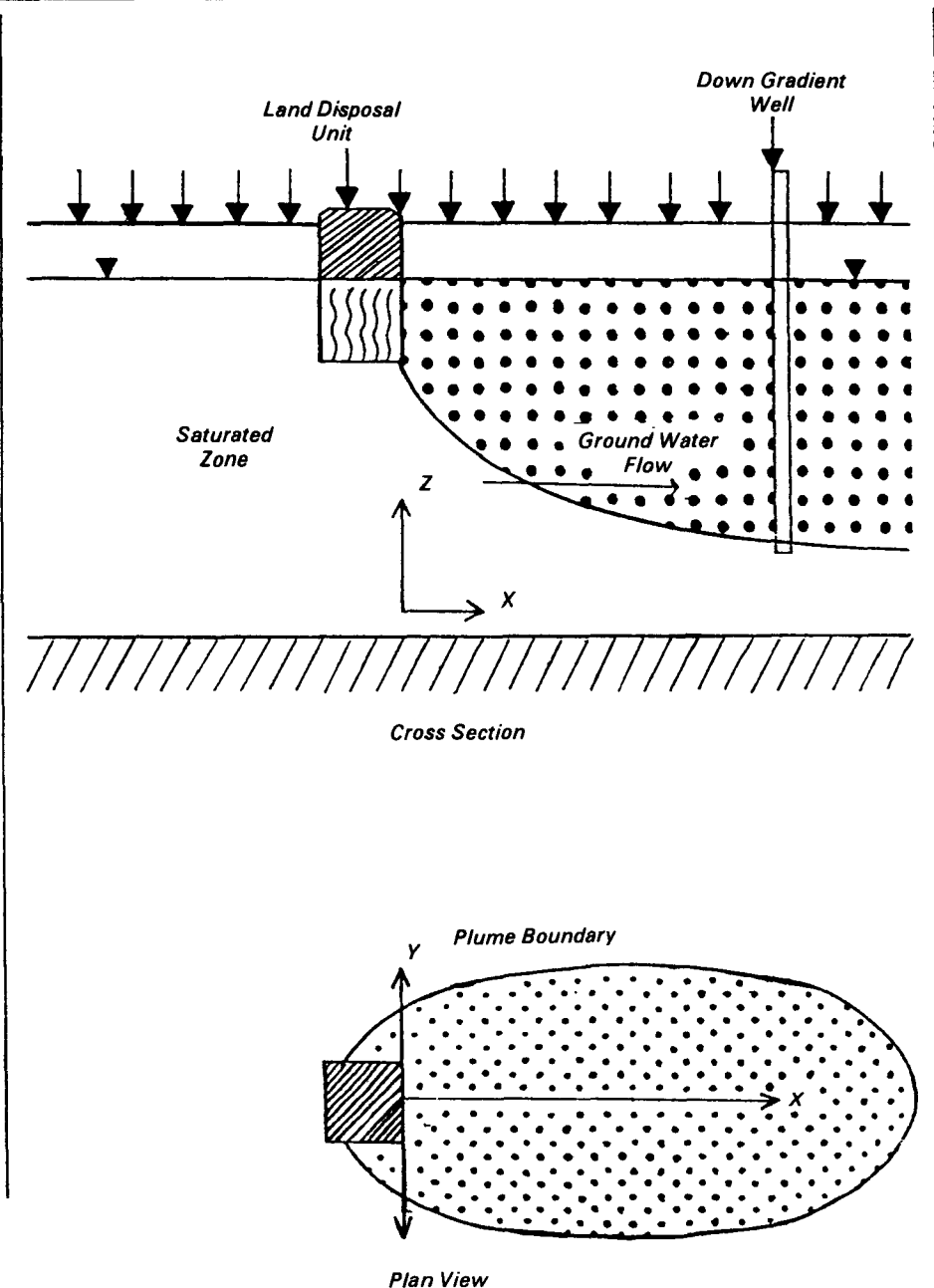


Figure 1. Schematic representation of plume from a failed waste disposal unit.

chemical-specific decay rates and velocity retardation due to sorption consistent with several assumptions regarding chemical behavior of the wastes and characteristics of the transport medium.

$$D_{xx} \frac{\partial^2 c}{\partial x^2} + D_{yy} \frac{\partial^2 c}{\partial y^2} + D_{zz} \frac{\partial^2 c}{\partial z^2} - \frac{V}{R_f} \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} + \lambda c + \frac{Ic}{R_f} \quad (1)$$

where:

x, y, z = spatial coordinates in the longitudinal, lateral, and vertical directions, respectively (m)

c = dissolved concentration of chemical (mg/l)

D_{xx}, D_{yy}, D_{zz} = retarded dispersion coefficients in the $x, y,$

and z direction, respectively (m^2/yr)

V = groundwater seepage velocity assumed to be in the x direction (m/yr)

R_f = retardation factor (dimensionless)

t = elapsed time (yr)

λ = effective first order decay constant (yr^{-1})

I = dilution rate due to net recharge (yr^{-1})

The retardation factor, R_f , and the effective decay constant, λ , are defined as follows:

$$R_f = 1 + \frac{\rho_b K_d}{\theta} \quad (2)$$

and,

$$\lambda = \frac{\lambda_1 \theta + \lambda_2 \rho_b K_d}{\theta + \rho_b K_d}$$

where:

ρ_b = bulk density of the porous medium (g/cm^3)

K_d = distribution coefficient (cm^3/g)

θ = volumetric water content (cm^3/cm^3)

λ_1 = decay constant for dissolved phase (yr^{-1})

λ_2 = decay constant for sorbed phase (yr^{-1})

Because the behaviors of individual waste constituents are highly dependent on the chemical properties of the compounds as well as on the input variables relating to the transport environment, selection of "reasonable worst case" values would involve considerable uncertainty. To avoid this ambiguity, a Fortran computer code, EPASMOD-P, was developed for the dispersion model that allowed monte carlo simulation of the input parameter distributions. Back-calculated concentration values were determined for a large number of randomly selected combinations of the input variables (typically 5000). Results could then be expressed as distributions of back-calculated dispersion factors keyed to relative probabilities of occurrence. These dilution factors combined with results of the metal speciation modeling procedures described herein formed the basis for back-calculating allowable leachate concentrations. The dispersion model is described in more detail in the *Federal Register*, CFR 40, Part 260, January 14, 1986.

Two additional constraints on the dispersion model were employed in applying it to the transport of metals. The

degradation parameter was set to zero ($\lambda = 0$) in accordance with the assumption that metals are conservative. This also negated the consideration of sorption for metals because the retardation effect would not change the concentration of a conservative pollutant ultimately arriving at the down-gradient exposure point.

The geochemical model MINTEQ is a third generation equilibrium model that uses the equilibrium constant approach to solving the chemical equilibrium problem. Its use in this work required several modifications and additions. Thermodynamic data for chromium, mercury, thallium, and selenium were not present in the original data base and had to be added. Also, because the original model would not handle more than 20 input components, the code was modified for matrix expansion up to 50 components. Numeric underflows, which caused the program to abort occasionally when individual component concentrations became very low ($\approx 10^{-30}$ mol/l), were eliminated by modifying the program to set the con-

centration to a lower limit of 10^{-30} whenever this level was reached. This allowed the executions to continue.

Because chemical properties of ground waters underlying existing and future waste disposal sites were not known, generic specifications were substituted. These were derived from large volumes of well data extracted from the EPA STORET data retrieval system. Because of the undue influence of extreme values on the means, the medians for each variable were selected for use. These are tabulated in Table 1. All speciation model runs were performed in the chemical environment indicated, with the exception of the E_h and pH.

Clearly, a single set of generic chemical specifications could not be derived that would accurately reflect conditions existing at all waste sites. To accommodate uncertainties associated with the generic specifications, an uncertainty window encompassing several combinations of E_h and pH values was defined. The window spanned the range of E_h and pH variations one standard deviation (σ) either side of the median

Table 1. Median Ground-Water Chemical Specifications

Component	Mean	Analytical Concentrations (mg/l)	
		Stand. Dev.	Median
Arsenic	.021	.174	.010
Barium	.235	.251	.200
Cadmium	.030	.207	.005
Chromium	.044	.121	.200
Lead	.035	.078	.010
Mercury	.0006	.0008	.0005
Selenium	.007	.008	.005
Silver	.019	.030	.010
Thallium	.068	.037	.010
Aluminum	1.134	2.620	.200
Calcium	79.000	118.478	48.000
Iron	2.780	7.365	.200
Magnesium	51.240	134.840	14.000
Manganese	.242	.615	.040
Potassium	5.670	11.390	2.900
Sodium	182.610	642.780	22.000
Bicarbonate	189.730	111.000	190.000
Bromide	3.400	12.800	.300
Carbonate	22.300	30.037	0
Chloride	161.470	778.530	15.000
Nitrate	2.660	5.100	1.000
Phosphate	1.450	5.210	.090
Sulfate	153.810	347.350	25.000
Sulfide	.471	1.334	.200
Organic carbon	12.762	15.603	7.2
Temperature ($^{\circ}C$)	14.403	5.287	14
pH	6.621	1.285	6.8
E_h (mv)	-10.535	155.786	-50

values obtained from the STORET data. The resulting window is illustrated by the small rectangle in Figure 2. Shifts in metal speciation equilibria possible within the window were mapped by initiating MINTEQ model calculations using nine different E_h /pH combinations selected from within the window. The nine combinations were formed by combining each of three E_h values with each of three pH values. The three values of each variable consisted of the median value, the median value plus σ

and the median value minus σ . The E_h /pH combinations used to represent each region of the uncertainty window are illustrated in Figure 3.

The E_h /pH combination that resulted in the maximum dissolved phase metal concentration in a series of pilot model runs was defined as the worst case. This worst case combination was then used in a final series of model runs to map the input/output dependence of equilibrium dissolved metal concentration as a function of the analytical input

concentration. Input concentrations of each metal over the range of 1 to 10,000 times the current or proposed drinking water standards (DWS) were investigated.

Because of the complex nature of the speciation mixtures investigated, formation of a large number of solids was possible. For simplicity, only those solids that were known to supersaturate and that contained one of the test metals or a key anion known to interact strongly in terms of potential solid formation were considered. To arrive at the final solids list, a series of "solution chemistry only" model runs was performed with no solids selected. In these systems, all ten metals were added to the generic matrix simultaneously at input concentrations of 100 times DWS. The log saturation index listings from the MINTEQ outputs were consulted and a master list of potential solids selected. This list was screened for solids that contained one or more of the test metals or key anions. Solids that did not meet these criteria were eliminated. The final list of solids retained for each metal is given in Table 2.

Possible interactions with organic ligands were treated by adding six model ligands (acetate, tartrate, glycine, salicylate, glutamate, and phthalate) to the generic matrix on an equal molar basis. Final concentrations were adjusted such that the total organic carbon concentration corresponded to the median value of 7.2 mg/l obtained from the STORET well data.

Results

Table 3 indicates the input/output concentration relationships for all ten metals using worst case E_h /pH combinations. Added increments of six of the test metals, including arsenic, barium, cadmium, lead, nickel and thallium, remained almost entirely in solution and were categorized as mobile. Because no significant solid phases formed, concentrations of these metals would be influenced primarily by dilution due to dispersion while moving to the down-gradient exposure point. Assuming aquifer physical characteristics corresponding to the 90% probability level and a down-gradient distance of 500 feet, the dispersion model predicted that raw leachates of these metals would be reduced by a factor of about 22 at the exposure point.

The other four metals were more strongly influenced by formation of solid phases. The worst case conditions

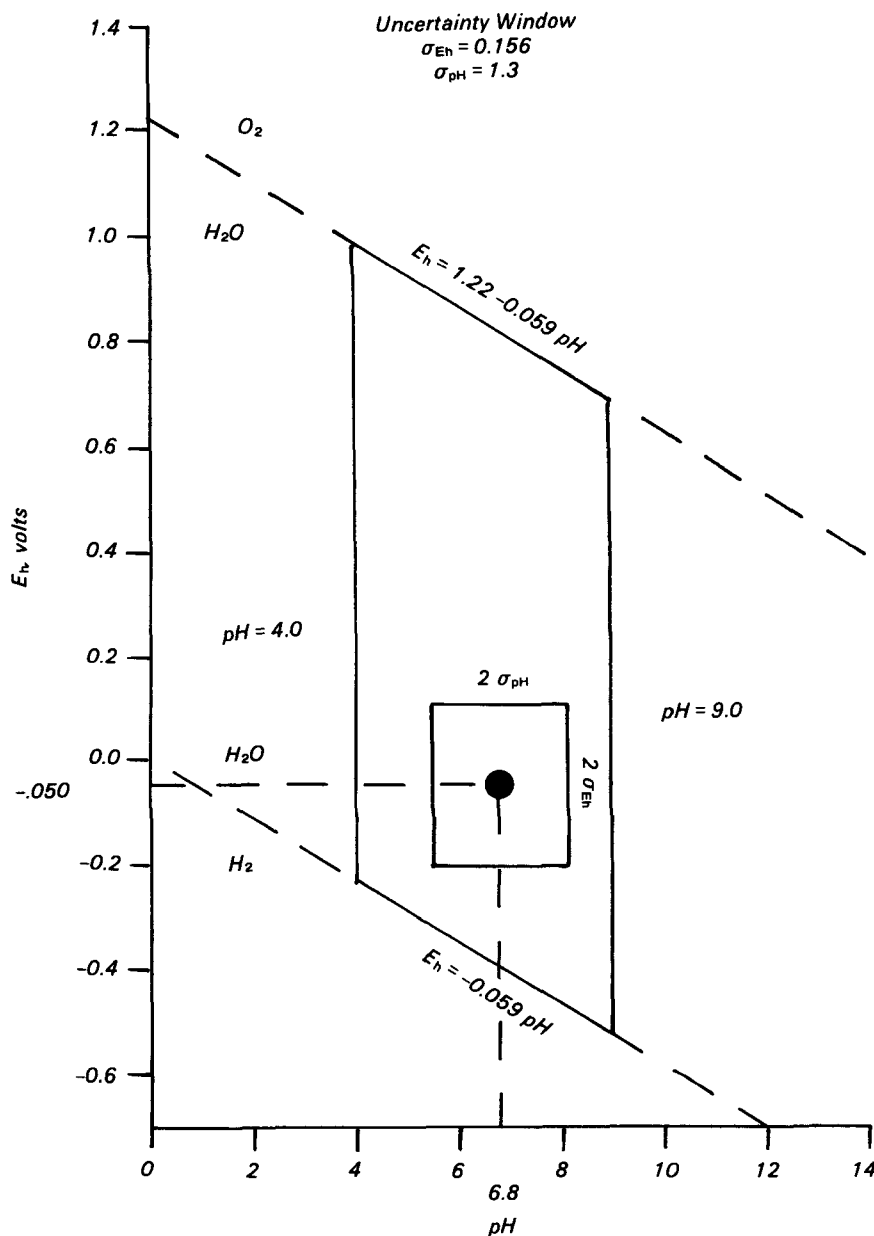


Figure 2. Uncertainty window relative to possible environmental conditions.

for chromium were at low pH (5.5) and high E_h (106 mv) and the solubility was limited (0.08 mg/l) by formation of the Cr_2O_3 solid. Additional tests at E_h levels above the E_h window (Figure 4) indicated dissolved chromium concentrations increased substantially above 700 mv. Values this high are however, ap-

parently, unlikely to be based upon the STORET data base.

Predicted dissolved mercury levels were limited to 0.024 mg/l by the formation of $Hg^0(l)$ at the highest E_h available from the uncertainty window. The transition to $Hg(II)$ ion began to occur at about 300 mv (Figure 5). Above this

level mercury was much more soluble and would be expected to stay in solution at concentrations high enough to exceed the DWS even after dilution due to dispersion.

Selenium solubility was very sensitive to E_h and increased substantially at E_h levels just above the upper limit (106 mv) of the uncertainty window (Figure 6). At $E_h = 106$ mv and pH = 8.1, dissolved selenium concentrations were limited to about 0.34 mg/l by the formation of Ag_2Se and an amorphous Se allotrope. At slightly higher E_h 's the Se(IV) and Se(VI) species began to dominate and the added selenium dissolved completely so that only dilution due to dispersion would reduce leachate concentrations.

Silver solubility was limited by the formation of Ag_2S at low E_h and by the chloride and bromide solids under more oxic conditions. It would not be expected to migrate significantly under any circumstances unless a strong complexing agent such as ammonia or cyanide ion also was present. Neither of these were considered in the present analyses.

Conclusions

Of the ten metals investigated, only chromium, mercury, selenium and silver were found to have solubility constraints sufficiently stringent to critically limit their transport in typical groundwater situations. Chromium, mercury and selenium solubilities were, however, quite sensitive to E_h and increased substantially above the original uncer-

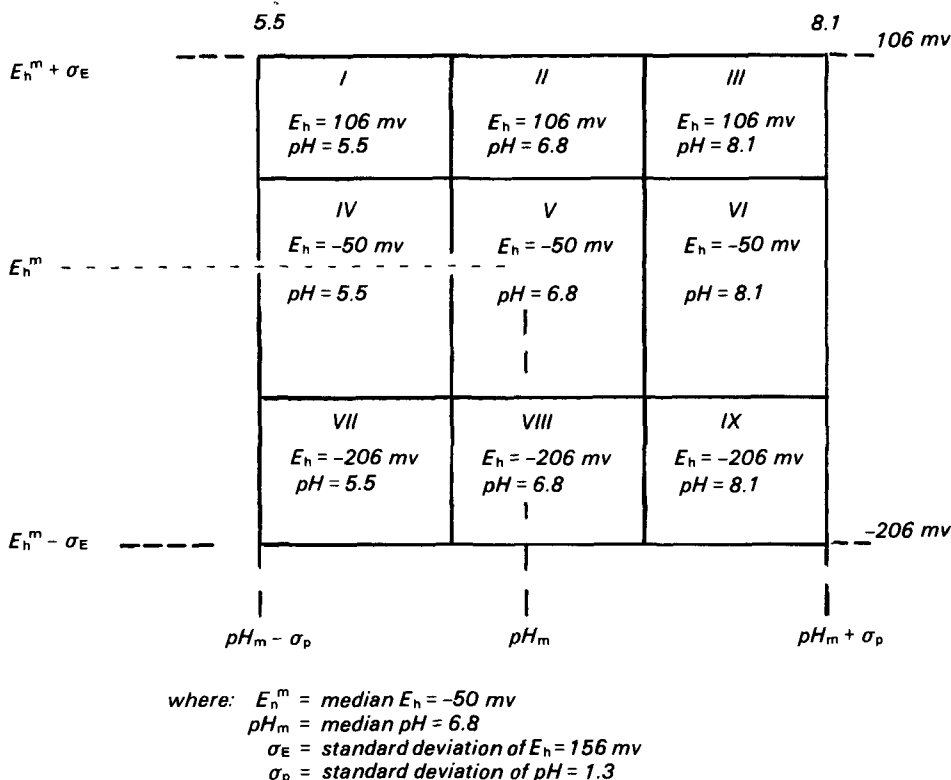


Figure 3. E_h , pH uncertainty window.

Table 2. Selected Solids List

As	Ba	Cd	Cr	Pb	Metal	Hg	Ni	Se	Ag	Tl
Orpiment	Barite	Otavite	$FeCr_2O_4$	Clypyromorph		$Hg(l)$	Millerite	Se, hex. blk.	Ag_2Se	Tl_2S
Realgar	$Ba_3(AsO_4)_2$	CdSe	$MgCr_2O_4$	Hypopyromorph		Cinnabar	NiSe	Se (A)	Acanthite	
$Ba_3(AsO_4)_2$	Witherite	Greenockite	Cr_2O_3	Plumbogummite		Metacinnabarite	$Ni(OH)_2$	Ferroselite	Ag^0	
			$Cr(OH)_3(A)$	$Pb_3(PO_4)_2$				Ag_2Se		
			$Cr(OH)_3(C)$	Clausthalite				CdSe		
				Galena				FeSe		
				Cerrusite				NiSe		
				Hydcerrusite				Tl_2Se		
				$Pb(OH)_2$						

Table 3. Worst Case MINTEQ Output Concentrations Compared to Total Metal Input Concentrations (mg/l)

	pH, Eh mv	DWS + back Input/ Output	25 DWS Input/ Output	50 DWS Input/ Output	100 DWS Input/ Output	10,000 DWS Input/ Output
Arsenic	8.1, 106	0.060 3.58×10^{-7}	1.25 1.18	2.50 2.43	5.00 4.93	500 500
Barium	6.8, -206	1.70 1.70	37.5 37.5	75.0 75.0	150 150	15,000 13,967
Cadmium	6.8, 106	0.010 0.010	0.125 0.120	0.250 0.250	0.500 0.500	50.0 50.0
Chromium	5.5, 106	0.140 0.00513	3.00 0.079	6.00 0.079	12.00 0.079	1,200.0 0.079
Lead	5.5, 106	0.030 1.25×10^{-6}	0.500 0.398	1.00 0.887	2.00 1.67	200 199.7
Mercury	8.1, 106	0.0035 0.0018	0.0750 0.0243	0.1500 0.0243	0.300 0.0243	30.0 0.0243
Nickel	5.5, 106	0.160 0.160	3.750 3.748	7.500 7.497	15.00 14.97	1,500 1,500
Selenium	8.1, 106	0.050 0.046	1.13 0.0808	2.25 0.0808	4.50 0.0808	450 0.0805
Silver	6.8, -206 (Undeter- minant)	0.100 $\approx 9 \times 10^{-7}$	2.25 $\approx 9 \times 10^{-7}$	4.50 $\approx 9 \times 10^{-7}$	9.00 $\approx 9 \times 10^{-7}$	900 $\approx 9 \times 10^{-7}$
Thallium	6.8, -026	0.059 0.059	0.480 0.480	0.960 0.950	1.92 1.29	192 81.3

tainty window. Considering the wide variability of reported groundwater E_h values, the ambiguity of interpreting E_h data and the strong evidence for lack of redox equilibrium in many ground-water systems, the expected mobilities of these three metals remain very uncertain. Better understanding of ground-water redox processes is a critical need for future progress in predicting subsurface geochemical phenomena.

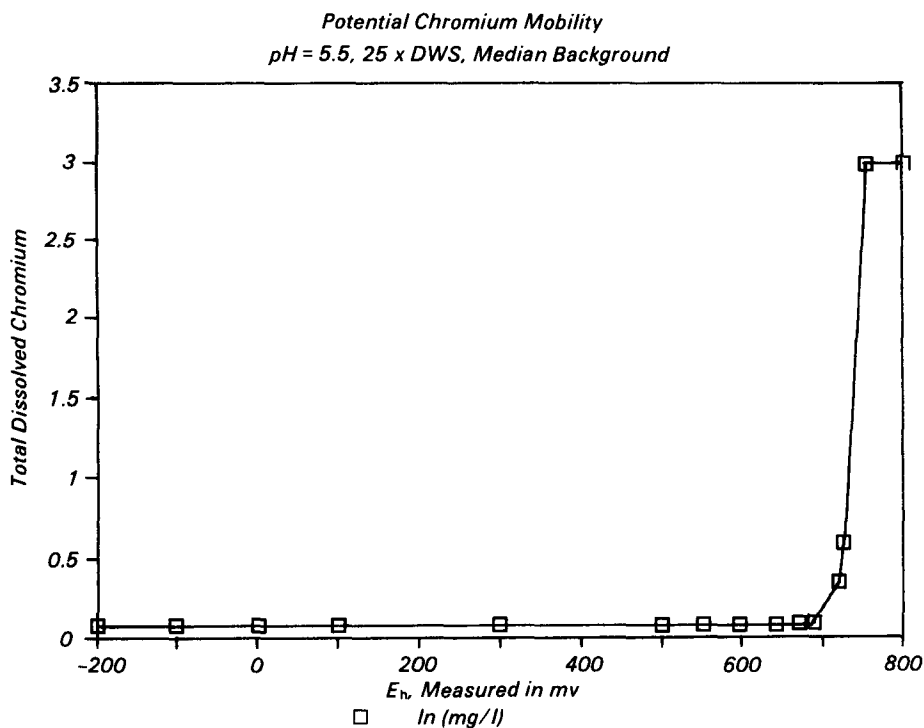


Figure 4. Sensitivity of dissolved chromium concentration to E_h at pH = 5.5.

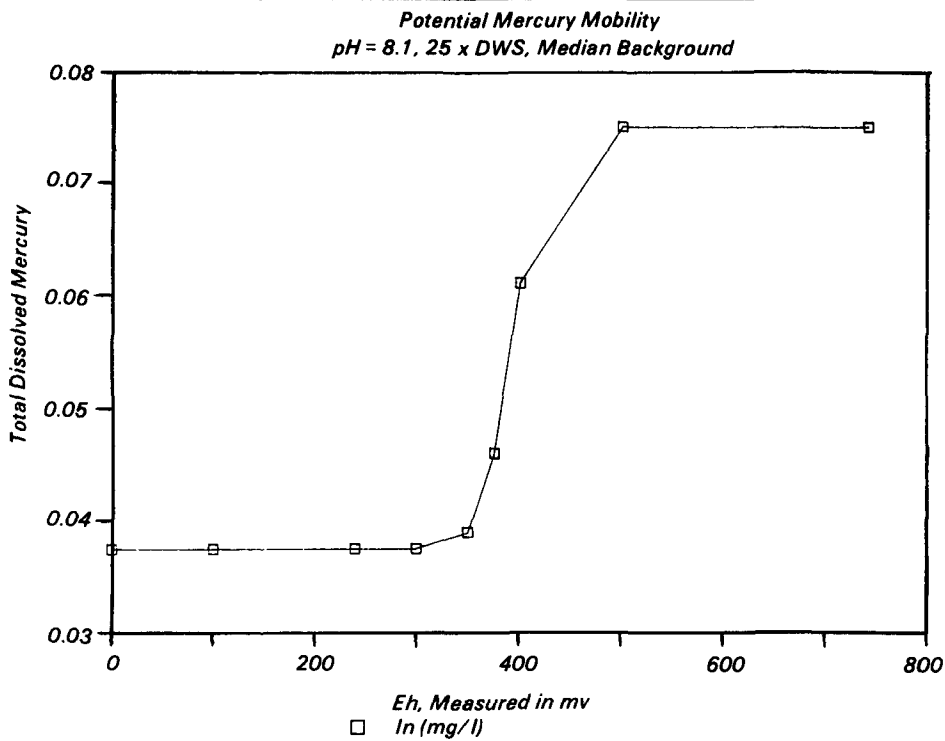


Figure 5. Sensitivity of dissolved mercury concentration to E_h at pH = 8.1.

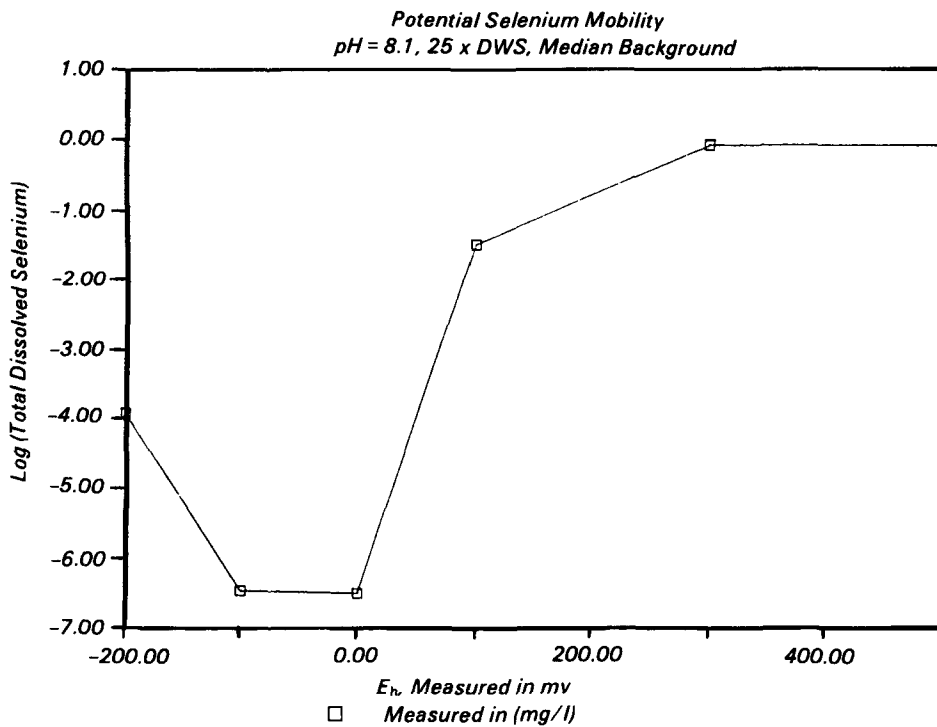


Figure 6. Sensitivity of dissolved selenium concentration to E_h at pH = 8.1.

The EPA authors D. S. Brown (also the EPA Project Officer, see below), R. E. Carlton, and L. A. Mulkey are with the Environmental Research Laboratory, Athens, GA 30613.

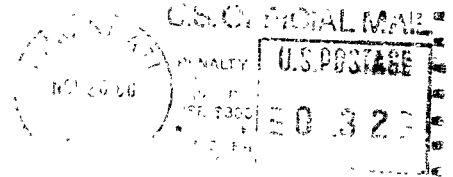
The complete report, entitled "Development of Land Disposal Decisions for Metals Using MINTEQ Sensitivity Analyses," (Order No. PB 86-233 186/AS; Cost: \$11.95, subject to change) will be available only from:

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