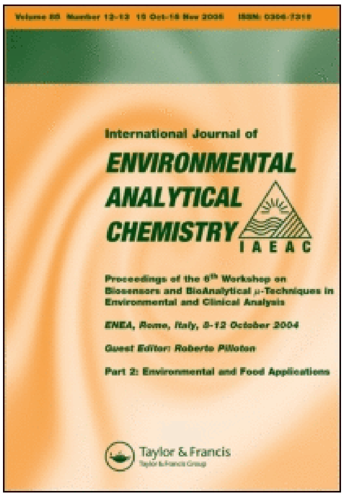

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Acquisition and Analysis of Groundwater/Aquifer Samples: Current Technology and the Trade Off Between Quality Assurance and Practical Considerations

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ACQUISITION AND ANALYSIS OF GROUNDWATER/AQUIFER SAMPLES: CURRENT TECHNOLOGY AND THE TRADE OFF BETWEEN QUALITY ASSURANCE AND PRACTICAL CONSIDERATIONS

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As part of its mission to protect groundwater quality, the U.S. Environmental Protection Agency regulates the land disposal of solid wastes. Mathematical models such as MINTEQA1, a thermodynamic equilibrium model for metal speciation, are used to predict the concentrations of harmful pollutant species at potential exposure points, and thus determine the requirements for waste treatment and disposal. The Environmental Research Laboratory, Athens, GA, is engaged in a bench-scale testing project for the attenuation processes currently in MINTEQA1.

In the migration of a high organic carbon content landfill leachate through the subsurface environment, the mobility of inorganic contaminants can be seriously influenced by oxidation-reduction, complexation, precipitation and adsorption processes. These processes in turn depend on the dissolved major (and minor) element composition, dissolved gas content, degree of equilibrium and the nature of the aquifer surfaces exposed to groundwater. ERL-Athens has been collecting groundwater, acquifer material and municipal landfill leachate samples from various locations within the continental United States. These samples have been characterized in terms of elemental composition, pH, Eh, dissolved gases and solid phase analyses (Specific Surface Area, CEC, extractable amorphous components, identifiable crystalline components, etc.). Batch distribution behavior studies have been performed with these samples with 14 potential metals and metalloids of concern to the EPA. Of more interest to the analytical chemist, however, are the manifold sampling, analytical and interpretative problems encountered: (1) What are the major sources of error in terms of the necessary expertise and equipment for sample acquisition? (2) Can samples be collected in an unperturbed manner and what is the best way to collect them? (3) How meaningful are field pH, Eh, dissolved oxygen, and alkalinitiy measurements? How stable are these values? (4) Are current commonly available experimental procedures sufficient for modeling attenuation processes? These and other problems persisting at the state-of-the-art will be discussed, as well as trade-offs necessary to achieve adequate quality with reasonable cost.

KEY WORDS: Sampling, groundwater, leachate, metal compounds, geochemical speciation, transport, distribution coefficients, adsorption constants, database, model prediction, quality assurance.

INTRODUCTION

The United States Environmental Protection Agency (USEPA) is presently engaged in the development and validation of the MINTEQ[1-3] family of geochemical speciation models for use as prospective screening tools[4-5] in predicting the fate and mobility of 14 inorganic contaminants (Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn) in the sub-surface environment. A joint research effort between the USEPA Office of Solid Waste and the USEPA Environmental Research Laboratory, Athens, GA (ERL-Athens) has focused on four major areas of effort: (1) collecting aquifer material, groundwater and leachate samples from municipal landfills located within the continental United States for the purposes of developing an experimental database of regional sub-surface properties as they pertain to geochemical speciation modeling, (2) incorporating thermodynamically-based models of adsorptive processes into the MINTEQ geochemical speciation model, (3) testing MINTEQ model predictions against laboratory inorganic contaminant distribution behavior and (4) coupling the thermodynamically-based geochemical speciation model with a metals transport code. This paper summarizes the information gained while working toward the first three objectives.

The distribution coefficient (K_D) provides a historical framework for linking experimentally-obtained concentrations of soluble and particulate-phase-associated metal contaminants with predictions using fundamental process models. The experimentally determined partition coefficient is:

$$K_D = \frac{[\mathrm{Me}]_{\mathrm{solid}}}{[\mathrm{Me}]_{\mathrm{water}}} \tag{1}$$

The distribution coefficient (K_D) is defined as the ratio of the concentration of a metal associated with a particulate phase to that of the metal in the aqueous phase.

For modeling purposes, the terms in the numerator and denominator of expression 1 must be further resolved into a testable collection of individual contributors. Specifically, the individual contributors currently being examined at ERL-Athens include:

$$[\mathrm{Me}]_{\mathrm{water}} = [\mathrm{Me}]_{\mathrm{free}} + \mathrm{SUM}\,[\mathrm{Me}]_{\mathrm{inorg.\ complex}} + \mathrm{SUM}\,[\mathrm{Me}]_{\mathrm{org.\ complex}} \tag{2}$$

$$[\mathrm{Me}]_{\mathrm{solid}} = [\mathrm{Me}]_{\mathrm{ads,\ Fe}} + [\mathrm{Me}]_{\mathrm{ads,\ Mn}} + [\mathrm{Me}]_{\mathrm{ads,\ OC}} + \mathrm{SUM}\,[\mathrm{Me}]_{\mathrm{ppt}} \tag{3}$$

The individual terms describing the aqueous phase speciation of the metal contaminant (expression 2) include the free metal ion concentration ($[\mathrm{Me}]_{\mathrm{free}}$) and a summation of inorganic complexed species ($\mathrm{SUM}\,[\mathrm{Me}]_{\mathrm{inorg.\ complex}}$). Both terms are included and/or are believed to have adequate representation in the current implementation of MINTEQA2. The last term in Eq. (2), the summation of organic complexed species ($\mathrm{SUM}\,[\mathrm{Me}]_{\mathrm{org.\ complex}}$), may contain contributions from anthropogenic organic complexing agents and/or from dissolved natural organic matter.[6] Because groundwaters (and aquifer material) typically possess a fairly low natural organic matter content, aqueous phase contributions from this source currently have a relatively low research priority.

In expression 3, the terms $[Me]_{ads,Fe}$ and $[Me]_{ads,Mn}$ represent the solid phase concentrations of the metal contaminant due to adsorption on amorphous iron and manganese oxides. The present work includes the generation of a database of intrinsic adsorption constants to permit modeling these terms.[7-8] The term $[Me]_{ads,OC}$ represents the concentration of contaminant metal associated with the particulate organic carbon. As noted previously, this term is the subject of current long term research efforts at ERL-Athens.[6] The last term in expression 3, SUM $[Me]_{ppt}$, represents a summation of all the precipitation reactions leading to an increased solid phase concentration of a metal contaminant. At present, MINTEQ contains a database of constants describing these precipitation terms; more recent evidence suggests they may require modification (e.g., because of "solid solutions", solubility product sensitivity to the amorphic properties of the solid phase, corrections to insoluble sulfide mineral solubility products, etc.).

Testing the chemical equilibrium approach for predicting the behavior of ionizable inorganic contaminants in the sub-surface environment requires experimental determinations for a suite of chemical parameters that are not commonly performed. Specifically, the measurement of only the distribution behavior of an inorganic contaminant provides no insight into the distribution mechanism. The fundamental water chemistry and the properties of the immobilizing solids must also be known. Unfortunately, there are at present finite limits on the ability to experimentally characterize these parameters.

Collecting a sample from the subsurface region can lead to alterations in temperature, pressure, dissolved gas composition, and perhaps solid phase stability. Although the groundwater pH can be measured to within a reasonable degree of accuracy, the estimation (and interpretation) of Eh (redox potential) values in natural waters is subject to considerable difficulty.[9-11] At a more fundamental level, the experimental determination of a "dissolved" constituent, being operationally defined, is not entirely unambiguous, nor is it clear that the mechanism by which a contaminant is removed from solution will ever be easily determined. Collecting a groundwater sample from the subsurface region cannot be performed without considerable uncertainty as to its "representativeness".[12-14] Drilling into the sub-surface region may lead to the generation of abraded drilling fines or the introduction of foreign particulates;[12] quantitative removal of either the particulates or their effects, at best, is subject to uncertainty. The present modeling effort is based on an assumption of thermodynamic equilibrium; under what circumstances is this a reasonable assumption? How correct is the current understanding of adsorption theory; is it reasonable to apply models derived from pure phase, low solids concentration studies to mixed phase, high solids concentration systems?

The present work was designed to provide a database to test the application of theoretical distribution models to sub-surface environments; lack of agreement between model predictions and experimental data should provide direction for model improvement (assuming the experimental data are accurate). The validity of this assumption is the subject of this paper.

PROCEDURES

During the period August 1987 through April 1988, personnel from ERL-Athens and an OSW sub-contractor visited six Subtitle D (municipal) landfills located in the continental United States 8/87, Custer, Wisconsin; 9/87, Goshen, Oregon; 9/87, Quincy, Florida; 2/88, Pennsauken, New Jersey; 3/88, southeastern Texas; and 4/88, Salt Lake City, Utah).[15–17] Aquifer material, groundwater and leachate samples were obtained from each site and chemical characterization analyses were performed in the field (temperature, dissolved oxygen, pH, Eh, conductivity and alkalinity), at sub-contract laboratories (organic C, inorganic C, organic N, nitrate, nitrite, ammonia, cyanide, sulfate, sulfide, suspended solids, COD, Cl, Br, and F) and at the ERL-Athens (common inorganic ions, Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn).

Field analyses at the first three sites were performed on groundwater and leachate samples collected using bailer-type samplers. Groundwater samples at all sites were collected from up-gradient pre-existing monitoring wells. Wells were purged for 3 to 5 well casing volumes and until chemical parameters were stablized to within 10 percent on consecutive volumes. Conductivity, pH and Eh measurement at the second and third sites were performed using portable equipment and calibration was performed in the field (pH using 4, 7, and 10 buffers;[18] Eh using Light's solution;[19] conductivity using a standard KCl solution).[18] Dissolved oxygen was measured using a Yellow Springs Instrument model 57 dissolved oxygen meter pre-calibrated using "air" calibration. Measured values were obtained using a probe placed in the well casing. Alkalinity in the field was performed titrimetrically with an indicator endpoint detector. Field analyses were duplicated upon sample arrival at ERL-Athens. (Laboratory alkalinity measurements were performed by titration to pH 4.5).[18]

Based on observations and results of analyses at the first three sites, attempts were made to improve procedures and quality of data for the last three sites. Field analyses at the last three sites were performed using a Yellow Springs Instrument Model 3560 water quality monitoring system with an in-line flow-through chamber. Eh,[20] pH, temperature, and conductivity probes were calibrated in accordance with manufacturer's instructions. Purging, monitoring, and sample collection of groundwater samples were performed using a bladder pump with a pneumatic controller. Dissolved oxygen was determined using the YSI model 57 in the well casing. Modified Winklers[18] were used to check DO probe performance. Field alkalinity measurements were performed titrimetrically using a pH electrode for a pH 4.5 endpoint detector. (Leachate samples had substantial color and hence, interfered with color indicator endpoint detectors.)

At all six sites, duplicate total and dissolved samples (for metals analysis) were collected in the field. Dissolved samples were obtained using a nitrogen-pressure, stainless-steel filtration apparatus. Filtration was performed using a 0.4-micrometer, acid-washed Nucleopore membrane filter with a glass fiber pre-filter. Total and dissolved groundwater, leachate and field blank samples were placed in acid-washed HDLP bottles, acidified to 0.5% HNO_3, placed in coolers with

Table 1 Analytical methods with representative detection limits for analyses performed by subcontract laboratories and ERL-Athens during the course of this study. Dissolved parameters estimated using samples pre-treated via nitrogen pressure filtration through a 0.4 micrometer membrane filter

Contract laboratory analyses					*ICP analyses (ERL-Athens)*			
Analyte	*SW-846 (21)*	*Std. methods (18)*	*MCAWW (22)*	*DL (mg/L)*	*Analyte*	*DL (mg/L)*[a]	*Analyte*	*DL (mg/L)*[a]
DOC & TOC	9060			0.5	Al	0.0216	As	0.219
DIC & TIC	9060			0.5	Ca	0.0006	Ba	0.0003
DON & TON		420A		2.0	Co	0.0222	Be	0.0006
COD		508C		5.0	Fe	0.0249	Cd	0.024
TSS		209C		1.0	K	0.2916	Cr	0.0237
Oil & grease	9070			1.0	Li	0.0057	Cu	0.0051
VOA's	8240				Mg	0.0018	Hg	0.0246
DOC & TOC	9060			0.10	Mn	0.0027	Ni	0.0636
DIC & TIC	9060			0.10	Mo	0.0327	Pb	0.307
DON & TON			351.2t	0.1	Na	0.012	Sb	0.110
COD			410.2	3	P	0.305	Se	0.330
TSS		209C		1.0	Si	0.051	Tl	0.293
SO4		9038		1.0	Sr	0.0003	Zn	0.009
Cl	9252			1.0	Ti	0.0027		
Br		429		0.10	V	0.018		
F		429		0.10	Zr	0.0054		
NO2		418F		0.01				
NO3		418F		0.01				
NH3		417E		0.05				
S=	9030			1.00				
CN-A[b] analyzed according to EPA's				10.0				
CN-T[b] CLP (contract lab program)				10.0				

[a] Detection limit calculated via the method in reference 23.

[b] Cyanide amenable to chlorination.

[c] Total cyanide.

refrigerants, and shipped to the appropriate laboratory using overnight package services. Several liters of "raw" (unacidified) groundwater and leachate samples also were shipped under refrigeration. All samples in the laboratory were stored at 4 °C.

Table 1 lists the laboratory analyses and analytical procedures (with detection limits) performed on groundwater and leachate samples during the course of the study. This list of analyses was developed in an attempt to acquire a reasonably complete set of data for describing groundwater and leachate contaminant content, major element chemistry, complexation capacity, and oxidation-reduction chemistry. Metals analyses (the last four columns in Table 1) were performed at ERL-Athens using a Perkin Elmer Plasma II inductively coupled plasma emission spectrometer.[17]

Aquifer material samples from the Wisconsin and Florida sites were collected from the inside of a split spoon sampler driven into the saturated zone. The consistancy of the aquifer material at the Oregon site made it nearly impossible to remove the sediment from the split spoon sampler; hence, samples from this site were collected from the vanes of the hollow stem auger as it proceeded through the saturated zone. Aquifer materials were collected at the New Jersey, Texas, and Utah sites using an acid-washed mylar tube liner inside of a split spoon sampler. (Tubes were sealed with caps and refrigerated immediately upon collection).

The majority of the aquifer material characterizations were performed at extramural laboratories. Briefly, air drier sediments were analyzed for: (1) specific surface area (N_2 BET analysis), (2) cation exchange capacity (ammonium acetate), (3) organic and inorganic carbon content (oxidation followed by infra-red detection of CO_2), (4) identifiable crystalline phases (powder X-ray diffraction, EDAX), and (5) extractable amorphous iron and manganese (hot hydroxylamine hydrochloride).

RESULTS

Table 2 compares unfiltered groundwater chemical analyses obtained from the present study with statistical analyses derived from the STORET database.[24] The Eh values given in Table 2 were derived from a summation (Macalady, unpublished results) of the carefully scrutinized database generated by Lindberg (1983)[25] and Lindberg and Runnells (1984).[9] In comparison with the other five sites, the Utah groundwater is in contact with the Great Salt Lake and hence the mean values for Na, K, Cl and SO_4 tend to be skewed. In general, the ranges of analyses from the present study tend to agree with those obtained from the STORET database. Most mean values for the present study are higher, possibly because arithmetic means were calculated by ignoring all values less than the detection limit. An analytical detection limit can be instrument- and sample-dependent; therefore, inclusion of older datasets by assuming zero concentration for all measured values less than the detection limit may significantly underestimate the true value.

Tables 3 and 4 display a summary of the average municipal (Subtitle D) leachate composition calculated from literature values and from the present study. Mean values for both the present study and the literature data were obtained by excluding all values less than the detection limit. In comparison with the present study, a much larger range of values is observed with the literature data (especially with respect to the 14 inorganic contaminants of concern). It is possible that literature-reported values may have been derived from sites where excessive concentrations of problem elements were identified; with the present study, permission to collect samples was requird from site operators—hence the analysis of leachate samples must be evaluated accordingly. In addition, all sites visited had leachate collection systems and were relatively modern. Because leachate composition is known to be a function of the composition of the waste, land-fill geometry and environment, and the age of the landfill,[26–27] variations may be expected. With these data, the large variations between mean and median values, as is evident in Table 3, the assumption of a normal parameter distribution may be inappropriate.

Six general trends were common to all sites. (1) Leachate Eh values (particularly when collected from leachate sumps rather than a leachate collection pond) tend

Table 2 Comparison of unfiltered groundwater chemical analyses from the STORET database with results obtained during the present study

STORET[a]					*Present 6 sites*		
Element	*Range (mg/L)*	*Mean (mg/L)*	*Std. dev.*	*Total n*	*Range (mg/L)*	*Mean*[e] *(mg/L)*	*n<DL (n=6)*
Ag	0–0.050	0.017	0.014	2839			6
As	0–0.100	0.01	0.0125	4384			6
Ba	0–0.700	0.177	0.142	5524	0.016–0.380	0.136	0
Cd	0–0.100	0.007	0.014	5150			6
Cr	0–0.100	0.021	0.023	6278			6
Cu	0–0.250	0.039	0.046	7931			6
Ni	0–0.100	0.024	0.288	2882			6
Pb	0–0.100	0.018	0.024	6730			6
Tl	0.0008–0.007	0.0023	0.0024	6			6
Zn	0–2.00	0.195	0.319	12226		0.108	5
Al	0–0.100	0.06	0.038	440	0.271-2.00	1.34	3
Ca	0–0.990	72.4	89.8	12549	8.71-128	47.3	0
Fe	0–10.0	1.11	1.91	19541	0.141-100	20.5	1
K	0–98.2	4.9	7.33	7014	0.800–175	36.6	1
Mg	0–1000	33.8	82.6	11141	0.615–37.4	17.4	0
Mn	0–0.700	0.115	0.147	11078	0.018–4.48	0.967	1
Na	0–1000	53.4	117	16281	2.12–4020	700	0
Si	0.30–48.5	10.1	6.45	757	4.91-17.0	11.5	0
Sr	0.005–8.07	0.276	0.89	339	0.026–1.46	0.415	0
NO3	0–10.0	1.95	2.24	15844	0.024–11.8	3.97	1
SO4	0–1000	96.9	171	21607	0.53–1910	333	0
Cl	0–1000	59.4	129	40590	3.34–5180	898	0
F	0–10.0	0.55	0.855	12369	0.359–8.53	2.52	2
pH[b]	3.00–10.0	6.65	1.16	24550	5.94–7.81	6.84	0
pH[c]	3.00–10.0	6.83	1.11	34965	6.26–7.96	7.04	0
Eh[d]	0–352	190	170	681	−46–+375	126	0
Temp.	3.00–30.0	14.4	5.09	16641	9.8–20.5	15.2	0
Spec. cond.	(uS/cm)				45–17050	3240	0
Alk.	(mg CaCO(3)/L)				0–460	332	1
O2	(mg/L)				0.2–8.7	3.6	0
TIC	(mg/L)				12.7–114	76.3	0
DIC	(mg/L)				11–109	73.7	0
TOC	(mg/L)				0.6–7.16	3.8	1
TSS	(mg/L)				1–73	30.7	0
COD	(mg/L)				6–38	18.3	0

[a] STORET analysis, by Pope-Reid Assoc. 1985 (24).

[b] pH measured in field.

[c] pH measured in the laboratory.

[d] Macalady from (9, 25).

[e] Mean values estimated by excluding all measurements less than the DL.

Table 3 Average subtitle D unfiltered leachate composition, calculated from the literature (17)

Element	*Range*		*Mean*[a]	*Median*[a]	*Std. Dev.*	*n < DL*	*Total n*
	Min.	*Max.*					
Ag						8	8
As	0.001	4.6	1.13	0.012	1.92	7	15
Ba	0.09	1.1	0.41	0.28	0.326	0	8
Be							
Cd	0.0008	17	0.956	0.012	3.61	27	48
Cr	0.001	18	1.24	0.15	3.79	18	39
Cu	0.003	9.9	1.20	0.175	2.51	21	49
Hg	0.0003	0.87	0.090	0.005	0.194	7	28
Ni	0.01	13	0.758	0.155	2.31	0	30
Pb	0.01	5	0.849	0.4	1.18	14	43
Sb				0.26		5	6
Se	0.001	14	0.945	0.012	3.37	13	29
Tl	0.55	0.81	0.637	0.55	0.123	3	6
Zn	0.01	1000	38.0	0.935	143	3	53
Al	0.075	700	73.2	0.36	200	6	17
Ca	5	7200	707	215	1210	0	75
Fe	0.08	5500	448	50	986	3	81
K	0.3	2300	390	214	504	0	51
Li						6	6
Mg	2.6	15 600	798	130	2810	0	67
Mn	0.01	1400	56.5	1.53	243	0	32
Na	3	7700	630	344	1050	0	70
P	0.04	130	13.2	2	26.8	4	47
S	15	180	71.6	35.5	66.1	0	6
Si	7.8	41	22	19.6	11.7	0	8
Sr	0.83	3.2	1.79	1.7	0.815	0	6
Ti	0.022	0.094				4	6
V				0.085		5	6
Zr				0.041		5	6
TOC	16	28 000	4270	940	6940	1	38
DOC	130	30 000	5780	945	10 900	0	6
TON	0.08	1000	167	23	292	1	24
COD	31.1	750 000	28 200	4530	98 300	0	58
TSS	8.9	26 500	1260	204	4960	0	27
NO_2+NO_3	0.03	1300	47.2	0.555	218	5	55
NH_3	0.04	1110	276	126	338	3	45
SO_4	1	1826	258	47	406	1	69
Cl	1	3480	686	300	869	1	73
F	0.1	2	0.582	0.3	0.713	2	7
pH	3.7	8.5	6.42	6.3	1.08	0	59
Eh	−180	−60	−132	−155	51.7	0	3
Spec. cond.	129	16 800	5340	3380	4430	0	33
Alkalinity·	21.6	20 850	3090	1300	4150	1	42

[a]Value calculated omitting all values less than detection limit.

Table 4 Average unfiltered leachate composition from the present study

Element	Range		Mean[a]	Median[a]	Std. Dev.	$n < DL (n = 6)$
	Min.	Max.				
Ag						6
As						6
Ba	0.188	0.67	0.48	0.509	0.186	0
Be						6
Cd						6
Cr			0.096			5
Cu			0.088			5
Hg						6
Ni						6
Pb						6
Sb						6
Se						6
Tl						6
Zn	0.045	7.91	1.68	0.121	3.12	1
Al	0.091	4.19	1.59	0.638	1.58	1
Ca	102	419	227	197	115	0
Fe	1.46	128	36.6	14.2	43.6	0
K	54.5	491	277	276	137	0
Li	0.010	0.855	0.163	0.027	0.310	0
Mg	46	262	146	132	79.5	0
Mn	0.323	4.88	1.45	0.631	1.60	0
Na	223	2850	1160	729	957	0
P	1.33	11.8	4.72	2.96	3.94	1
S	5.3	201	44.5	14.7	70.2	0
Si	11.8	43	20.7	18.1	10.5	0
Sr	0.583	1.76	1.23	1.21	0.428	0
Ti	0.027	0.085	0.056	0.057	0.021	2
V						6
Zr	0.014	0.05				4
TOC	125	12.40	474	357	373	0
DOC	95	1280	468	361	388	0
TIC	15	32.3	22.1	20.5	6.73	0
DIC	250	1700	761	665	468	0
TON	2	300	67.8	25	105	0
DON	7.4	280	85.9	28.2	113	2
COD	464	3680	1530	1150	1100	0
TSS	14	2010	418	99	715	0
$NO_2 + NO_3$	0.136	2.2	0.749	0.50	0.758	1
NH_3	42.9	328	172	145	112	0
SO_4	5	182	63.1	32.7	69.8	2
S=	0.03	49.2	10.8	0.58	17.9	0
Cl	7.18	3140	1390	860	1270	0
Br	3.23	14.9	6.32	4.9	3.94	0
F	0.46	18.9	8.00	9.56	6.94	1
pH	6.55	8.26	7.16	7.03	0.536	0
Eh	−185	+182	−88.5	−131	+126	0
Spec. Cond.	1610	15600	7800	5930	5040	0
Alkalinity	1100	4800	2600	2630	1170	0
Temperature	15	32.3	22.1	20.5	6.73	0
D.O.	0.15	7.8	1.78	0.7	2.71	0

[a] Values calculated omitting all values less then detection limit.

to be significantly lower than those measured in groundwater; lower Eh values also tend to be associated with lower measured dissolved oxygen concentrations and elevated concentrations of dissolved iron and manganese. Elevated concentrations of organic carbon and reduced nitrogen and sulfur species also tend to be associated with lower measured Eh values. (2) Leachate temperature, conductivity and (with the exception of the Utah site) dissolved alkaline earth (Na, K, Ca, Mg, Sr, and Ba) and halide (Cl, Br, and F) element concentrations tend to greatly exceed the values observed in groundwater. (3) With both leachate and groundwater samples, alkaline earth and halide elements tend to pass through the 0.4-μm filter. (4) The elements Al, Si, Ti, Zn, and Zr tend to be removed by filtration (presumably through association with particulate matter via adsorption, precipitation or as background solid phases). (5) With both groundeater and leachate samples, inorganic and organic carbon tended to pass through the 0.4-μm filter. (6) Ba and Zn were the only elements of concern that were routinely detected in either total groundwater or leachate samples.

In terms of quality control/quality assurance, nearly undetectable levels of chromium and nickel were reported in filtered leachate samples at the Wisconsin, Oregon and Florida sites. This was observed despite the fact that these elements were not detected in the total samples. The most likely explanation for this phenomenon is that these elements leached from the stainless steel pressure filtration apparatus; filtration of leachate samples often required a several-hour contact period with the filtration apparatus. These observations were not repeated with the groundwater samples—very possibly due to the relatively short contact period with the apparatus and/or a less aggressive aqueous medium.

Table 5 illustrates a potentially significant difficulty encountered during the study. At all sites, leachate samples were collected using bailers or a Kemmerer type sampler. Table 5 contains the data obtained for three unfiltered leachate samples obtained at the Utah site. These samples were collected sequentially, yet the analytical results are significantly different. The more soluble elements (such as Na, K, and Li) are relatively consistent in concentration, but elements expected to be associated with the particulate phases (Ca, Si, and Fe) are highly variable.

From these data, is it clear that care must be exercised in the interpretation of the analytical data concerning leachate properties. Specifically, leachate sumps may exhibit stratification from density gradients due to variations in temperature, dissolved salt, or suspended solids content.

Figure 1 illustrates this problem from a different perspective. The profiles in Figure 1 display the operational nature of the measurement of "dissolved" elements in an Oregon leachate sample. For a baseline estimate of dissolved concentrations in solution, raw leachate samples were acidified and then centrifuged at room temperature for 46 minutes at 10000 RCF. This centrifugation procedure is designed to remove particulates of a density equal to or greater than 2.5 g/cm^3 and with a radius greater than 0.05 micrometers. The second column represents the ratio (to the preceding measured values) of the elemental concentrations where acidification is performed only on the supernatant solution after centrifugation. The third column depicts elemental concentration ratios where separation is achieved using more conventional 0.4-μm filtration (nitrogen pres-

Table 5 Comparison of ICP analytical results for three leachate grab samples from the Utah site

Element (mg/L)	*Sample ID number*		
	SU-ULE-006	*SU-ULE-007*	*SU-ULE-008*
Ag	<DL	<DL	<DL
Al	4.22	0.461	7.88
As	<DL	<DL	<DL
Ba	0.667	0.555	0.75
Be	<DL	<DL	<DL
Ca	149	92.4	191
Cd	<DL	<DL	<DL
Co	<DL	<DL	<DL
Cr	<DL	<DL	<DL
Cu	<DL	<DL	<DL
Fe	16.7	5.46	25.4
Hg	<DL	<DL	<DL
K	192	186	211
Li	0.894	0.779	0.893
Mg	151	126	170
Mn	0.543	0.314	0.739
Mo	<DL	<DL	<DL
Na	2880	2800	2870
Ni	<DL	<DL	<DL
P	6.44	4.95	6.95
Pb	<DL	<DL	<DL
S	413	111	78.1
Sb	<DL	<DL	<DL
Se	<DL	<DL	<DL
Si	45	29.4	54.6
Sr	1.79	1.5	1.95
Ti	0.113	0.056	0.13
Tl	<DL	<DL	<DL
V	<DL	<DL	<DL
Zn	0.18	0.096	0.311
Zr	0.045	0.055	0.053

sure). The last column illustrates results obtained using nitrogen pressure ultrafiltration (10000 molecular weight cut off).

These results support the contention that, with leachate samples, the estimate of "dissolved" concentration will depend not only on the separation procedure, but also on the distribution behavior of the element being measured. For example, potassium concentrations are relatively insensitive to separations procedure. Zinc is more likely to be associated with particulate matter, so its observed concentrations display less dependency on separation efficiency. Particulate matrix elements (Mn, P, Fe, and Al) likely exist in a size continuum ranging from dissolved ions and polynuclear species to discernable particulates. These data suggest that both total and filtered samples should be collected for modeling purposes.

Figures 2 and 3 illustrate some difficulties encountered in obtaining estimates of

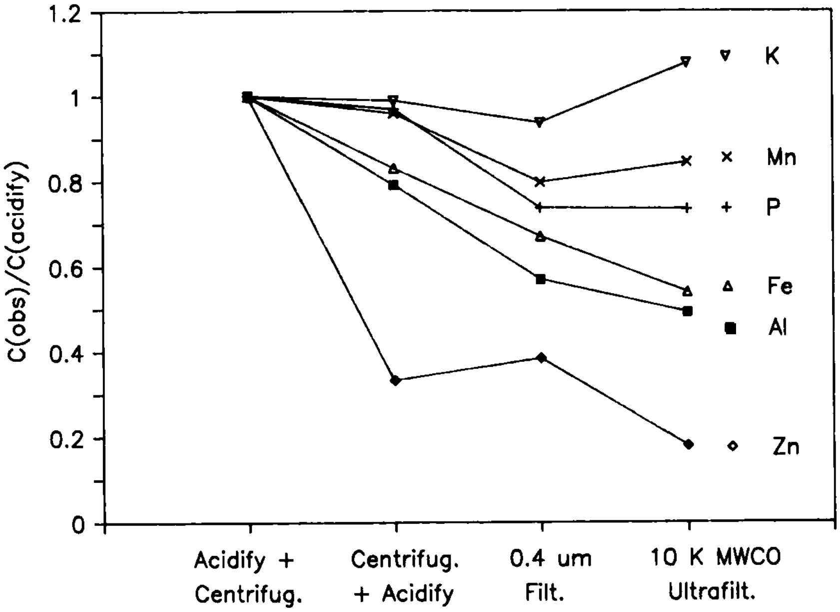

Figure 1 Relative concentrations of selected elements in an Oregon leachate sample as a function of particulate phase separation procedure.

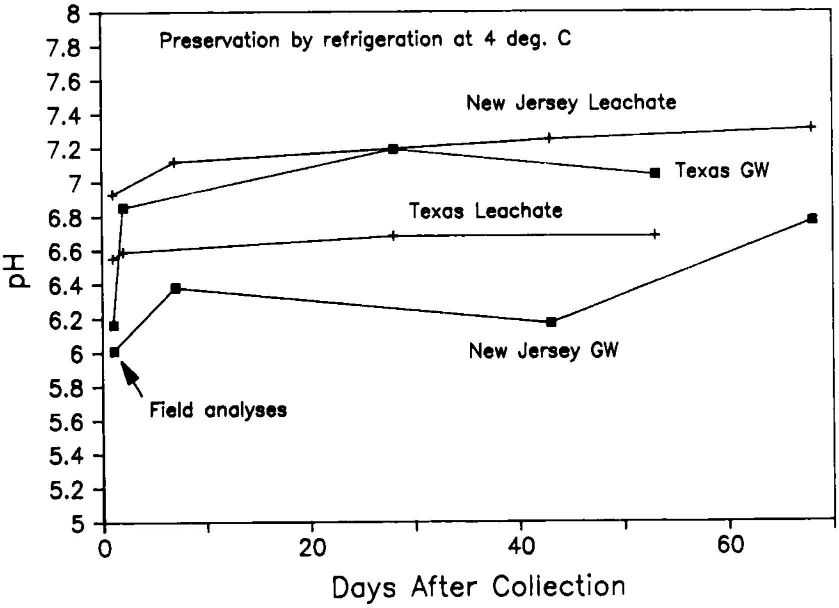

Figure 2 pH values for New Jersey and Texas groundwater and leachate samples as a function of storage time. Initial groundwater pH values were determined using an in-line monitor (field analyses).

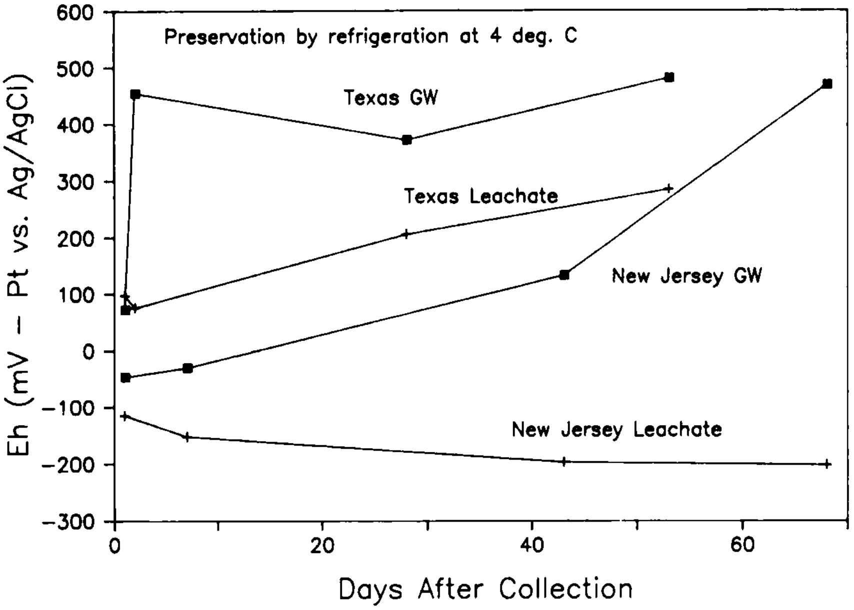

Figure 3 Eh values for New Jersey and Texas groundwater and leachate samples as a function of storage time. Initial groundwater Eh values were determined using an in-line monitor.

groundwater and leachate pH and Eh values. Figure 2 depicts measured pH values as a function of storage time for New Jersey and Texas groundwater and leachate samples. Figure 3 demonstrates similar behavior with respect to measured Eh (relative to a Ag/AgCl reference electrode). The removal of groundwater and leachate samples from their source environment will likely result in exposing samples to conditions of altered temperature, pressure, and partial pressures of dissolved gases. As a first approximation, diminishing the partial pressures of dissolved gases such as CO_2 and H_2S when the samples are raised to the surface can lead to an immediate evolution of these gases. Because the loss of either of these gases results in the consumption of aqueous hydrogen ions, an accompanying increase in measured pH also can be expected. This same phenomenon is also likely responsible for the disparity between field and laboratory pH values given in Table 2.

The instability of measured Eh values can result from two processes: (1) under oxidizing conditions, Eh measurements derived from a Pt electrode can be pertubed by a pH-sensitive platinum oxide coating, and (2) contamination from atmospheric gases at the time of collection and/or long term diffusion of atmospheric oxygen through the walls of the storage vessel can lead to altered Eh conditions. pH and Eh values for modeling *in situ* groundwater systems should be obtained in the field using in-line monitoring equipment. Because both pH and Eh values are master variables under examination with the current version of MINTEQ, variations in these values are inherently considered in the modeling of both field and laboratory data.

Table 6 summarizes the Wisconsin aquifer material characteristics measured

Table 6 Summary of solid phase characteristics of Wisconsin aquifer material

Porosity (% void space)[a]	33.1
Solids + H_2O Density (g/cm 3)[a]	2.07
Solids Density (g/cm 3)[a]	2.6
Specific Surface Area (m 2/g—BET-N2)[b]	0.38, 0.46
Carbon Content (percent)[c]	
Total	0.34
Organic	0.17
Inorganic	0.17
Size Distribution[d]	
% Sand (2.0–0.050 mm)	99.3
% Silt (0.050–0.002 mm)	0.6
% Clay (< 0.002 mm)	0.1
Texture[d]	sandy

Identifiable Phases[d]

Sand—vermiculite and/or mica, feldspars quartz, dolomite, olivine, and calcite

Silt—all of above plus hematite and boehmite

Clay—kaolinite, boehmite, potash feldspars, plagioclase, calcite, dolomite and apatite.

Major Element Extraction Results

	0.5% Ammonia	*0.5% HNO(3)*	*Amorph.*[e] *(Jenne)*	*Total*[e] *(HF)*
	ug/g			
Fe	<DL	81	806	6390
Mn	<DL	16.5	101	113
Al	2.07	27.7	73.1	19 800
Si	16.1	31	88.4	396 000
Ca	16.3	6660	35 500	32 500[f]
Mg	0.46	3000	19 300	19 500[f]

Cation Exch. Cap. (c mol/kg − 1)[d]	7.1
Exchange Acidity	0.0
Exchange Cations	
Al	0.0
Ca	6.5
Mg	1.1
Na	0.05
K	0.04

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[a] Analyses performed at ERL-Athens, 28.31-mL saturated sediment oven dried at 105 °C.

[b] Analyses courtesy of Dr Donald Macalady, Colorado School of Mines.

[c] Analyses performed by Dr Michael Perdue and Mr Steve Serkiz, Georgia Institute of Technology.

[d] Analyses performed by Dr Kim Tan, Mr John Rems, and Mr Didiek Goenadi, University of Georgia.

[e] Analyses performed by Dr E. A. Jenne, Battelle Laboratories, Pacific Northwest.[28]

[f] Ca and Mg total analyses performed at ERL-Athens, these numbers are preliminary.

during the study. The results represent a compendium of more conventional characterization procedures. This aquifier material consists primarily of sand and has a high hydraulic conductivity. The relatively low organic carbon content, specific surface area and cation exchange capacity is typical of a sandy aquifer. The crystalline phases, identified by powder X-ray diffraction, were obtained in order to test MINTEQ predictions using major element groundwater composition values. The data concerning the extractive elemental composition of the aquifer material are designed for comparison of extraction procedures that may reflect the amorphic adsorptive phases of the material. The ammonia and nitric acid extractions were performed by adding 30 mL of 0.5% reagent to 5 g of groundwater-saturated aquifer material. The amorphous iron and manganese values were obtained by Dr E. A. Jenne (Battelle Laboratories, Pacific Northwest);[28] total analyses were performed by ERL-Athens after HF digestion by Dr Jenne.

DISCUSSION

Site Selection and Sample Acquisition

Several potentially significant problems were encountered and dealt with during the course of this study. During the original planning stage for this project, it was decided that an ERL-Athens field representative would be present at all sample collection efforts. Because there is no definitive established protocol for collecting representative groundwater, aquifer material and leachate samples[13] the presence of a field representative, i.e.., someone who is going to use the data, is invaluable not only for making decisions in the field, but also for interpreting field data. In particular, there may be a significant divergence between what is desired and what is possible during a well drilling session. Commercially available drilling crews are typically not knowledgeable about the QA/QC aspects of chemical analyses.

A decision to restrict collection efforts to sites with available monitoring wells addressed a major potential limitation in any sample collection effort. Specifically, the drilling of a well (particularly if drilling fluids are required—as at the Wisconsin site) will almost certainly alter the properties of the groundwater in the immediate vicinity of the borehole. The quality of groundwater samples collected from a newly drilled well is almost certainly suspect. The alternatives include either proper well development followed by a long (and expensive—since two sessions may be required) equilibration period (permitting the natural movement of the groundwater to sweep away many of the effects of drilling) or use of the present procedure—collection of groundwater samples from pre-existing wells after purging. The limitation with the latter approach includes the assumption that the pre-existing well was properly installed and developed and has not been contaminated by subsequent sampling efforts. Collection of aquifer material samples from newly drilled wells using a split spoon sampler with liners minimizes contact with atmospheric gases and permits paring of suspect portions of the solid sample.

The filtration of groundwater and leachate samples is subject to a number of problems. Because anaerobic groundwater or leachate samples may contain elevated levels of dissolved ferrous iron, samples should either be filtered using nitrogen pressure filtration or better yet, using in-line filtration as the sample is pumped from the well. Recent recommendations[13] suggest using acid-washed, monopore-size membrane filters; the pore size should be the smallest that is practical. Our experiences suggest that although groundwater samples may be easily filtered, leachate samples immediately clog the filter. Very real practical problems arise from filtering leachate: (1) volumes of sample are so difficult to obtain that discarding the initial sample through the filter (as can be done with groundwater) is not practical; (2) filtration may require 3 to 4 hours for a relatively small volume of filtrate; and (3) in our effort, the nominal filter pore size was 0.4 micrometers; the effective pore size (after clogging) was unknown. This last problem cannot be solved by changing filters because clogging is nearly instantaneous.

The collection of groundwater samples from a properly installed and developed well should be performed using in-line monitoring equipment.[12–13] Practical difficulties arise in that recent recommendations[13] include: (1) the installation of an inflatable packer immediately above the well screen (in order to minimize contact with water exposed to atmospheric gases in the well casing); (2) the use of a slow, gentle purging to avoid resuspension of sediments in the bottom of the casing and suspension of fine particulates not ordinarily present in the groundwater outside of the casing (it has been proposed that the groundwater velocity at the screen should not exceed ten times the normal groundwater velocity—Gschwend, 1988);[13] (3) teflon or PVC casings should be used; (4) proper well development should be performed; and (5) all well material should be permitted to equilibrate with groundwater chemical constituents (Rees, 1988).[13] Difficulties with these recommendations include: (1) the expenses associated with a multiple-term sampling project if lengthy equilibration is required; (2) the expenses associated with fielding a crew for an extended purging period (purge periods in excess of 8 hours may be required); and (3) although a slow purge and collection rate may minimize resuspension of particulates, diffusion of atmospheric gases (particularly oxygen) through the sample tubing will be enhanced.[14] Sampling equipment is currently being designed at ERL-Athens to address many of the above problems.

Analyses

In view of the above difficulties, the analysis of dissolved oxygen should be considered suspect. Specifically, with any of the current collection procedures, the possibility of sample contamination from atmospheric oxygen cannot be entirely dismissed. Even with an in-line monitoring system, teflon tubing is notoriously susceptible to diffusion of gases through the tubing wall. From the data presented previously, there does appear to be, at least, a qualitative relationship among Eh, dissolved oxygen, oxidized nitrogen and sulfur species, and decreased iron and manganese content; ordinal relationships do tend to exist.

With few exceptions, the analysis of field blanks did not indicate major problems during this study. The exceptions included possible contamination of field rinse (reserve osmosis) water that was stored in glass containers. Reverse osmosis water contained low levels of major cations (Ca, K, and Na) and relatively high silica levels.

The equipment used for installing wells and collecting samples many impose a finite limit on the ability to perform speciation analyses on dissolved elements. For example, an unsuccessful attempt was made to determine Fe(II)/Fe(III) ratios in samples collected at the first three sites (using bailers). The use of in-line samplers at the last three sites may have alleviated this problem. With newly drilled wells, the hollow stem auger typically was coated with a fine patina of iron oxide; this layer, it is hoped, was scraped from the auger prior to entering the saturated zone. With pre-existing wells, mineral deposits on the well casing can be dislodged by

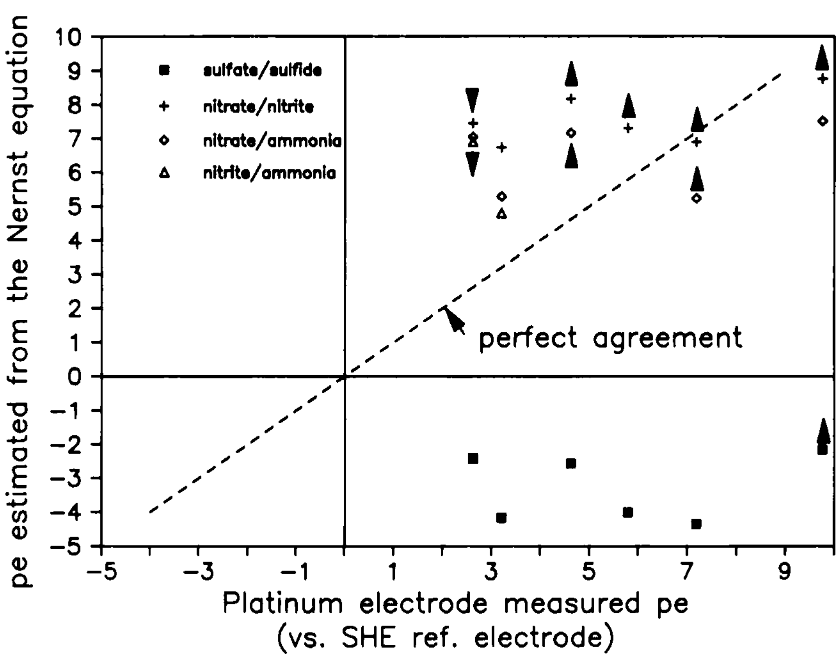

Figure 4 Comparison of platinum electrode derived pe values with estimates obtained from Nernstian couples.

the intrusion of the sampling apparatus. For trace level analyses, it may be necessary to install dedicated wells with permanent *in situ* positive pressure pumps.

Current commonly available well drilling and sample collection apparatuses are ill suited for monitoring trace metal contaminant content. It is probable that even with substantial improvements in sample acquisition equipment, the presumption(s) that: (1) dilution of introduced contaminants by groundwater, (2) equilibration of well equipment, and/or freshly abraded surfaces with groundwater, or (3) natural groundwater transport processes minimize the impact of well drilling fines, drilling fluid and/or equipment/gravel pack contamination will always lend a degree of uncertainty to the confidence in the analytical results obtained.

A comparison of leachate analyses with groundwater composition (Tables 2 and 3) illustrates the following general trends: (1) leachates tend to have lower measured Eh and dissolved oxygen values, and (2) leachates tend to have elevated temperatures, conductivities, organic carbon, Na, Cl, K, Br, F and alkalinity contents. Many of these parameters are believed to be relatively conservative and may possibly be of use as tracers for field leachate migration studies.

Groundwater Eh Determination

Figure 4 compares measured groundwater platinum electrode (pe) values (pe = Eh/59 at 25 °C [Eh is in millivolts]; adjusted upward by 3.33 pe units for comparison of values relative to the standard hydrogen electrode—SHE) with values calculated from four Nernstian relationships provided by Stumm and

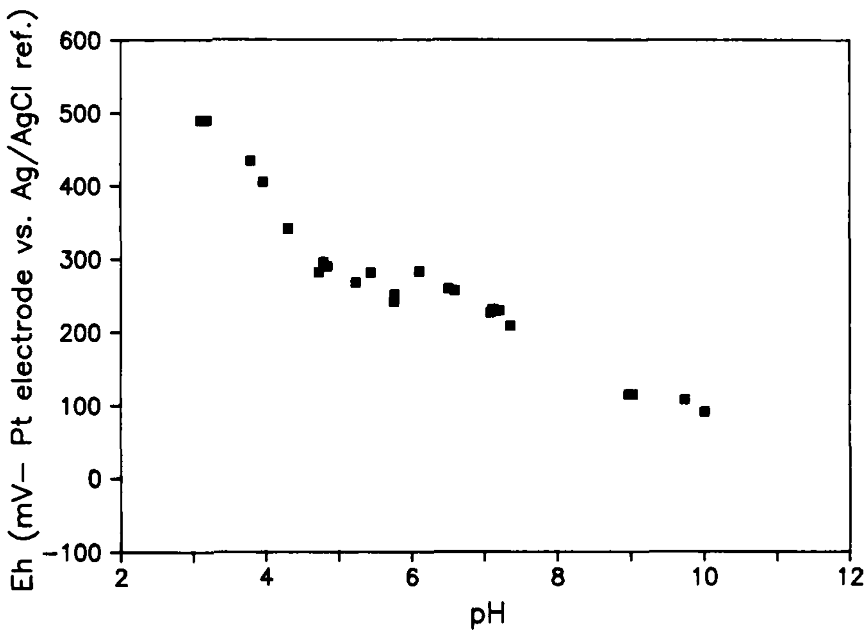

Figure 5 Platinum electrode measured Eh values as a function of pH observed during contaminant distribution studies using Wisconsin aquifer material and groundwater.

Morgan (1981).[29] The computation of pe values was performed using raw concentrations only; revised values containing activity coefficient corrections are likely to be comparable to those illustrated in the figure. Arrows adjacent to individual data points indicate that one of the species in the couple was below the analytical detection limit. (These values, therefore, represent maxima or minima depending on whether the reduced or oxidized species respectively was below the detection limit).

The dashed line in Figure 4 represents perfect agreement between the two estimates of pe. Clearly, from these data, the Pt-electrode-derived estimates are poor predictors of estimates derived from Nernstian couples. This finding is in accord with previous reports.[9,10,25]

It is clear that the redox potential will be a master variable in any modeling effort. Experimentally-derived Pt electrode estimates, however, may not be representative of the desired thermodynamic quantity. Figure 5 illustrates results obtained during a pH-dependent distribution behavior study using an oxic Wisconsin aquifer material, and groundwater, spiked elements and measured volumes of added standard acid or base. In addition to the rather prominant correlation between pH and Eh given in Figure 5, ICP analyses suggested a strong correlation between measures Eh and soluble cationic iron species dissolved from the aquifer material. High dissolved iron concentrations at elevated pH values, presumably due to formation of $Fe(OH)_4^-$, appeared to be unrelated to measured Eh values. The processes to which the Eh electrode was responding in this study are not really known. Preliminary work in which the electrode was polished with an aluminum oxide slurry before and after both calibration with Light's solution and in groundwater did not appear to lead to significant differences. This suggests that easily removable coatings were not perturbing the electrode. Macalady[6] suggests that observing agreement between Pt and waxy impregnated graphite electrode measurements lends credibility to measured Eh values because these electrodes may presumably suffer from complementary sources of error.

Contaminant Solubility Controls in the Sub-Surface Environment

The question of solubility limitations may at first appear to be inappropriate in a paper of this nature. Monitoring the subsurface environment, however, is a resource intensive endeavor. For practical considerations, the limits to the quantity and quality of the necessary analytical data can be estimated only after the questions being addressed have been defined. From another perspective, a mechanistic predictive model, by definition, requires a database of analytical results where the limits of acceptable precision and accuracy are imposed by the mechanisms incorporated in the model.

There appear to be at least two main schools of thought concerning the processes controlling the solubility of ionizable inorganic trace contaminants in natural waters: (1) adsorptive (surface) processes and (2) precipitation/co-precipitation/solid solution processes. Conceptually, this distinction may be artificial; adsorption experiments often display fast and slow mechanisms (a slow mechanism can be interpreted as resulting from diffusion into the three dimensional matrix) and precipitation studies often require empirically-developed procedures to obtain the desired crystalline phase (additionally, solubility products and precipitation kinetics are often sensitive to surface areas and solution properties). At present, these processes are modeled in a computationally distinct manner. Further complicating the issue is the fact that it is very difficult to determine the processes by which trace contaminants are removed from solution. We suggest that indirect evidence can be discerned from distribution behavior as a function of pH.

Figure 6 illustrates the results obtained from 48-hour, batch, "competitive", pH-dependent distribution behavior studies of metal/metalloid contaminants using Wisconsin aquifer material (a high sand content, low cation exchange capacity sediment). This study was conducted under aerobic conditions with centrifuge tubes containing simultaneous spikes of 12 elements (As, Ba, Be, Cd, Cr, Cu, Ni, Pb, Sb, Se, Tl, and Zn) with initial elemental concentrations of approximately 3.1 mg/L and a solids concentration of approximately 80 g/L.[30]

Figure 6 illustrates tendencies that were common to all six aquifer material samples: (1) removal of cationic species from solution was decreased at low pH values, and (2) at most pH values, affinity sequences for the solid phase were in the following general order:

$$\mathrm{Pb} > \mathrm{Cu} > \mathrm{Be} > \mathrm{Zn} > \mathrm{Cd},\ \mathrm{Ni} > \mathrm{Ba},\ \mathrm{Tl}.$$

This sequence is consistent with sequences observed [not including all elements] in

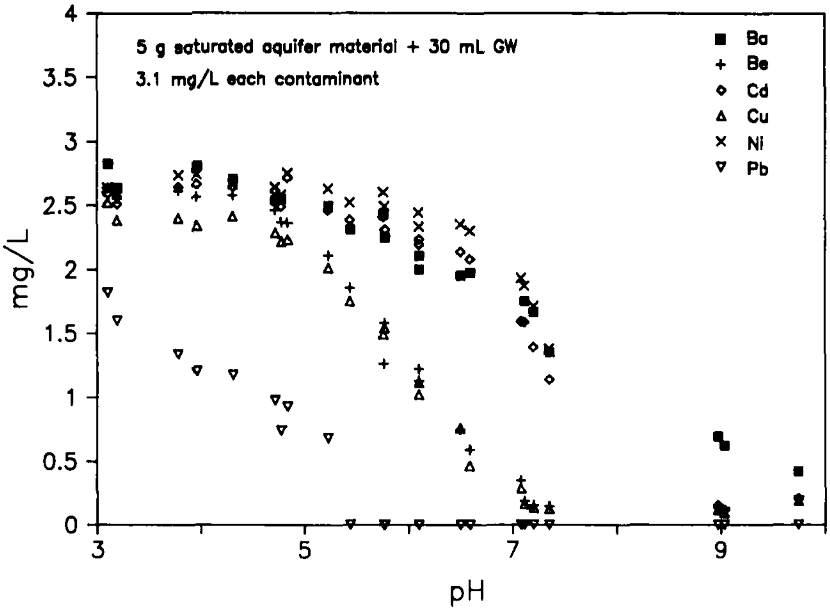

Figure 6 pH dependence of partitioning of cationic metallic contaminants on Wisconsin aquifer material.

the literature for the adsorption of trace cationic metallic contaminants on amorphous iron oxides.[7-8]

Anionic contaminants (As, Cr, Sb, and Se) displayed a lesser pH sensitivity under the experimental conditions of the study. They tended to display behavior more consistent with literature results obtained using clay phases as the substrate.[31]

A preliminary comparison of these laboratory data with MINTEQ simulations (using the amorphic iron values listed in Table 6) indicates that, although many elements displayed ion activity products of the same magnitude as limiting precipitate solubility products (indicating a proclivity to precipitate), the overall behavior of the cationic species tended to display pH-dependent distribution behavior more consistent with adsorptive processes.

CONCLUSIONS

Questions concerning the potential fate and mobility of inorganic contaminants in the sub-surface environment suffer from all the ambiguities associated with contaminant partitioning in surface waters as well as a significant sub-set resulting from the difficulties in sampling this environment. At present, the ability to collect groundwater and aquifer material samples representative of true conditions is confounded by a variety of processes including: (1) generation of potentially contaminating drilling fines, (2) potential contamination and/or adsorption by particulates suspended in drilling fluids, (3) potential resuspension of non-representative solids in the casing and/or gravel pack, (4) potential dissolved and particulate phase instability due to altered temperature, pressure and gas phase partial pressure composition, (5) potential oxygenation of groundwater samples from the sampling effort, and (6) potential carry-over contamination from multiple sampling efforts.

In contrast to anthropogenic organic contaminants, all inorganic species are present in the background at some level. A major difficulty arises, however, in that confidence in the understanding of the geochemical behavior of these elements will require a substantiating database of analytical data (for model validation). Because the majority of these elements can be expected to be present at low ppb or ppt concentrations, sampling problems further exacerbate the analytical difficulties.

At present, uncertainties in the processes controlling contaminant mobility (i.e., distribution among soluble, colloidal and/or mobile particulate phases) lead to uncertainties in the required number and types of analyses. For example, experimental estimates of soluble contaminant concentrations may depend on the filtration or other separations procedure; however, not performing a separation may lead to inclusion of non-representative solids in the analytical result. Questions concerning the nature of the soluble phase-limiting process also arise. For example, if a precipitation mechanism is assumed, a knowledge of only the aqueous phase composition would be required. (Unless, of course, experimental confirmation of the solubility limiting precipitate is desired.) A presumed adsorptive mechanism *a priori* requires individual phase surface characterizations that are difficult to reconcile in even laboratory pure phase studies.[32] (For example, the presumed specific surface area for amorphous iron oxide used in some models is presently estimated to be $600\,m^2/g$;[7,8] this value was not determined experimentally.)

Rapid progress can be expected in the technology for collecting sub-surface groundwater and aquifer material samples. Numerous commercial in-line monitoring systems should become available in the not too distant future. The recognition that well construction and development procedures may depend on the types of analyses desired will aid in this progress. Aquifer solids samples collected in split spoon sampler liner tubes have been used in the past for sub-surface bacterial population characterization and are also particularly well suited for inorganic analyses. Means of obtaining groundwater samples uncontaminated with oxygen is currently under investigation, as are improved procedures for measuring Eh.

The logistics of a project of this nature is such that a fast, multi-element analytical capability is nearly mandatory. Our experiences suggest that inductively coupled plasma spectrometry for multi-element analysis and ion chromatography for separation and detection of inorganic species provide complementary resources in this area. Limitations associated with the inability to detect background contaminent concentrations in groundwater are the subject of on-going research at ERL-Athens.

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