

JUN - 8 1987

SUMMARY REPORT

TRANSPORT OF CONTAMINANTS IN THE SUBSURFACE:
THE ROLE OF ORGANIC AND INORGANIC COLLOIDAL PARTICLES

Manteo, North Carolina

October 6-9, 1986

Organized and Hosted by

John F. McCarthy
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6036

In Cooperation With

Frank J. Wobber
Ecological Research Division
Office of Health and Environmental Research
Office of Energy Research
U.S. Department of Energy, Washington, D.C.

ACKNOWLEDGMENTS

The active participation of the speakers and all the attendees is gratefully acknowledged. Appreciation is expressed to those who helped organize the agenda, including P. Gschwend, J. Hunt, W. Penrose, A. Stone, J. C. Westall, and R. Schwardenbach. Several participants provided informal summaries of the material presented during platform presentations, posters, or discussions. These contributors included M. A. Anderson, B. Brownawell, R. W. Buddemeier, F. T. Ewart, P. M. Gschwend, R. W. Harvey, J. Hunt, J. Leenheer, P. F. Low, J. C. Means, W. Penrose, E. M. Perdue, T. F. Rees, P. H. Santschi, J. C. Westall, and J. M. Zachara. Their summaries provided the basis for much of the text of this report, and their contribution is acknowledged and greatly appreciated.

Special thanks are due to Laurence E. Roberson for arranging all of the technical details needed for a successful seminar and to Vicki Davidson for help in organizing the meeting and providing secretarial support. Thanks also to Mr. Rhett White and the staff of the North Carolina Aquarium in Manteo, North Carolina, for providing the space for the meeting and assisting in the details of the meeting.

Research sponsored by the Ecological Research Division of the Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Publication No. 2931, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

SEMINAR SERIES

U.S. DEPARTMENT OF ENERGY SUBSURFACE TRANSPORT PROGRAM

The International Series of Interactive Seminars (ISIS) has been organized to focus attention on scientific questions of importance of DOE's Subsurface Transport Program. The objectives of the seminars and the number of participants vary, but each seminar has common features that facilitate information exchange and a sharper definition of research questions.

Core participants are drawn from the academic, government, national laboratory, and international research communities. Each is a senior specialist in a specific field. Approximately 80% of core participants are from scientific disciplines that are relevant to the seminar; others are selected consciously from outside these core disciplines in such fields as mathematics, numerical modeling, and other scientific areas. This format encourages challenges to accepted scientific wisdom on a given problem.

Advanced notices about the seminars are distributed to scientists who have requested to be kept informed about DOE research activities in subsurface systems.

ISIS programs are organized using a detailed agenda that focuses on key subtopical areas of importance to the program. The agenda ensures that nearly equal time is given to formal presentations and to discussion. Visitors can participate substantively during discussion periods by informal presentations or questions. Brief reports on the technical results of each seminar are prepared by the organizers. These working papers are available through DOE's Technical Information Center or the National Technical Information Service, Springfield, Virginia.

Up to three seminars are organized annually. Initiative from outside DOE will be incorporated into the seminar series if accompanied by a willingness to host the seminar.

Meeting and travel costs are borne by the host and participants. Further information may be obtained from Frank J. Wobber, Office of Energy Research (301-353-5549).

LIST OF SPEAKERS AND DISCUSSION LEADERS

Dr. Marc A. Anderson
Water Chemistry Program
660 N. Park Street
Madison, WI 53706
608/262-2470

Dr. Bruce Brownawell
Department of Chemistry
Oregon State University
Corvallis, OR 97331
503/754-2591

Dr. Cary T. Chiou
U.S. Geological Survey
Water Resources Division
Box 25046, Denver Federal Center
Denver, CO 80225
303/236-3608

Dr. James Davis
Water Resources Division
U.S. Geological Survey, MS-65
Menlo Park, CA 94025
415/323-8111 Ext. 2145

Dr. Philip M. Gschwend
Assistant Professor
Dept. of Civil Engr., 48-154
Massachusetts Inst. of Tech.
Cambridge, MA 02139
617/253-1638

Dr. James Hunt
Dept. of Civil Engineering
University of California
Berkeley, CA 94704
415/642-0948

Dr. Jerry Leenheer
U.S. Geological Survey
Water Resources Division
Box 25046, Denver Federal Center
Denver, CO 80225
302/236-1925

Dr. Philip F. Low
Department of Agronomy
Purdue University
Lafayette, IN 47907
317/494-8047

Dr. John F. McCarthy
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831-6036
615/576-6606

Dr. Jay C. Means
Chesapeake Biology Laboratory
P.O. Box 38
Solomons, MD 20688
301/326-4281

Dr. William Penrose
Argonne National Laboratory
ER-203
Argonne, IL 60439
312/972-4262

Dr. E. Michael Perdue
Georgia Institute of Technology
School of Geophysical Sciences
Atlanta, GA 30332
404/894-2857

Dr. Terry F. Rees
U.S. Geological Survey
Box 25046, MS 424
Denver Federal Center
Denver, CO 80225
303/236-4053
FTS 776-4053

Dr. Peter H. Santschi
EAWAG, Swiss Fed. Inst. of Water Res.
CH-8600 Dübendorf, Switzerland
8235111

Dr. Frank J. Wobber
Ecological Research Division, ER-75
Office of Health and Environmental Re
Office of Energy Research
U.S. Department of Energy
Washington, DC 20545
301/353-5549

Dr. John M. Zachara
Earth Sciences Department
Battelle Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99320
509/375-2993

CONTENTS

Acknowledgments.....	iii
Seminar Series.....	v
List of Speakers.....	vii
Abstract of Meeting.....	xi
Background on the Role of Colloidal Particles on Subsurface Transport.....	1
References.....	13
Report of Seminar.....	16
Organization of Seminar.....	16
Fundamental Theory	18
Filtration Theory.....	18
Solution Theory for Nonpolar Organic Compounds.....	20
Electrostatic Interactions.....	23
Organic Colloidal Particles.....	26
Interaction with Metals.....	26
Interaction with Radionuclides.....	32
Interaction with Organic Contaminants.....	36
Mobility of Bacteria.....	41
Inorganic Colloidal Particles.....	43
Interaction with Metals and Radionuclides.....	43
Interaction with Organic Compounds.....	52
Discussion Topics.....	56
1. The Influence of Sorbent Concentration on Apparent Partition Constants.....	56
2. Sampling Problems in Colloid Research.....	58
3. Environmental Significance of Colloidal Transport.....	62
Research Needs in Colloidal Transport	66
Appendix	
I. Seminar Agenda.....	73
II. List of Participants.....	77

ABSTRACT OF MEETING

A meeting on "Transport of Contaminants in the Subsurface: Role of Organic and Inorganic Colloidal Materials" was held on October 5-9, 1986, in Manteo, North Carolina. The meeting was part of the series of International Seminars on the Subsurface held by the Subsurface Transport Program of the Office of Health and Environmental Research of the U.S. Department of Energy. The meeting was organized by Frank Wobber (OHER/DOE) and John McCarthy (Oak Ridge National Laboratory).

The purpose of the meeting was to review current knowledge about the role played by colloids on the mobility of contaminants in the subsurface environment, and to identify important long-term research needs in this area. Participants included senior researchers in this field from national laboratories, government agencies, universities, and research institutes in four countries. Recent findings on the occurrence and nature of colloidal material in the subsurface as well as on the association of colloids with organic, metal, and radionuclide contaminants were presented and discussed. Field studies have demonstrated that colloidal particles do move through aquifers and that radionuclides have been transported much further than predicted due to their association with mobile colloids in the groundwater. The consensus of the meeting was that colloids do occur in the subsurface environment, are capable of binding organic and inorganic contaminants, and do alter the mobility of contaminants. A major difficulty in understanding and predicting the role of colloids is their heterogenous nature that hampers precise chemical characterization. Clay and metal oxide colloids can be formed or dissolved due to changes in solution chemistry in the aquifer. Organic colloids have variable and diverse functional groups, making it difficult to predict their association with metal and radionuclide contaminants. Some important advances were reported toward understanding the assembly of organic colloids and the nature of their interactions with organic contaminants. Major research needs identified by the participants included studies in real systems on the occurrence of colloids in subsurface environments, and more rigorous characterization of the physical and chemical properties of the colloidal material. Methods for sampling colloids need to be improved to avoid production of artifacts during collection. In summary, the meeting concluded that colloidal material is important in contaminant transport and that further research in this area will significantly improve our capacity to predict the movement of energy-related contaminants in subsurface environments.

TRANSPORT OF CONTAMINANTS IN THE SUBSURFACE:
THE ROLE OF ORGANIC AND INORGANIC COLLOIDAL PARTICLES

BACKGROUND REVIEW OF THE PROBLEM

The movement of contaminants in the subsurface is controlled by interactions between the contaminants, the pore water, and the soil or aquifer material. Many chemicals have a high affinity for association with the solid phase rather than the aqueous phase. There is, however, an increasing body of literature suggesting that contaminants may associate with organic and inorganic colloidal particles and that such associations will alter the expected mobility of contaminants in subsurface systems. The objective of this meeting is to review our current understanding of the role of colloids on the subsurface mobility of contaminants. The scope will include consideration of both organic colloidal material as well as inorganic colloids. The interactions of the colloids with organic and inorganic contaminants will be addressed as will the interactions of the colloid-contaminant complex with the aquifer matrix.

The importance of basic research in the role of organic and inorganic colloidal particles was identified in 1983 by the Department of Energy's Subsurface Transport Program as a potentially important program element. Although the opportunities for scientific advances in this area appear to be significant, there is a need to review the existing information and establish research needs.

Given the very broad scope of the problem addressed during the course of this seminar, it was impossible to synthesize the large amount of published literature that relates to the potential role of organic and inorganic colloidal particles on the subsurface mobility of contaminants. Key investigators in various research areas were invited to present important aspects of the overall problem. To provide the interested reader an introduction to this research area, the following summary of some of the relevant literature is provided.

Colloidal Particles in the Mobile Phase
of Subsurface Systems

The transport of contaminants through aquifers is usually conceptualized as a chromatographic process involving the partitioning of a pollutant between an immobile adsorbed phase and a mobile aqueous phase (Freeze and Cherry 1979; Gilham and Cherry 1982). Many contaminants are generally considered to be virtually immobile in groundwater, and thus may not present a serious danger to groundwater supplies. Many radionuclides, such as cesium, bind strongly to mineral particles. Likewise, hydrophobic organic contaminants, such as DDT, polychlorinated biphenyls (PCBs) and dioxin, are strongly bound to organic matter on soil particles. Models of the sorption processes, which range from simple linear partitioning (K_d) to more complicated mechanistic descriptions of reactions at the solid solute interface are combined with convection-based flow codes to yield estimates of solute transport. These typically treat groundwater as a two-phase system, with contaminant partitioning occurring between immobile solid constituents and the mobile aqueous phase. In the absence of complicating phenomena, solutes that are more strongly sorbed move more slowly through porous media.

However, there is a general assumption that water and completely solvated solutes are the only constituents of subsurface systems that are mobile. In fact, components of the solid phase in the colloidal size range (nanometers to a few micrometers) may also be mobile in subsurface environments. The composition of colloidal particles is chemically similar to the clay and metal oxide surfaces or the organic coating of immobile aquifer material. These colloidal particles can also sorb organic and inorganic contaminants and stabilize them in the mobile phase. Association of contaminants with mobile colloidal particles may enhance the

transport of highly adsorbed pollutants, or deposition of colloidal particles in porous media may decrease permeability and reduce contaminant transport.

There is ample evidence that colloidal-size particles can move in aquifers. Reviews of pathogen transport report bacterial migration to 830 m and virus migration up to 400 m from their source (Gerba et al. 1975; Keswick and Gerba 1980; Gerba and Goyal 1985). Asbestos fibers were detected in an aquifer recharged from a reservoir containing high levels of fibers (Hayward 1984). Colloidal clay particles mobilized from surface soils were responsible for turbidity observed in wells several hundred meters distant from the recharge site (Nightingale and Bianchi 1977).

Organic Colloidal Particles

Organic macromolecules similar to the humic and fulvic acids that can be extracted from soils, sediments, or aquifer material are present in groundwater. Total levels of dissolved organic carbon (DOC) range from 0.5 to 0.7 mg/L in igneous, sand, or gravel aquifers, to 3 to 10 mg/L in oil shales and humic-colored groundwaters (Thurman 1985); the median DOC in groundwater is approximately 1.0 mg/L (Leenheer et al. 1974). Of the total DOC in groundwater, approximately 20 to 58% are humic or fulvic substances (Thurman 1985; Collins et al. 1986; Aho 1986), which refractory organic macromolecules formed by the decay and polymerization of biological material (Schnitzer and Kahn 1978). Humic substances from groundwater have less oxygen and more carbon and hydrogen than humics from surface water, suggesting a more aliphatic structure. The organic matter may have arisen from leaching of soil organic matter, or from kerogen deposited with sediments during formation of some aquifers (Thurman 1985).

Organic macromolecules with structures similar to natural humic substances have been reported to migrate with little retardation in some aquifers. Tannin and lignin from a waste pulp liquor traveled through a sand aquifer as fast and as far as the plume of sodium ions. The mobile organic material was colloidal in size (>2000 daltons) and its infrared spectra were very similar to that of soil fulvic acid (Robertson et al. 1984). Anionic detergents released from a sewage treatment facility traveled 3.5 km through a sand aquifer in Cape Cod, Massachusetts, at the same rate as specific conductance and boron, which are both assumed to be conservative tracers of the plume from the disposal beds. Chemical similarities between natural surfactants (humic substances) and the detergents suggest the potential for transport of humics in some aquifers (Thurman et al. 1986).

Humic substances from surface water or extracted from soil bind hydrophobic organic contaminants (Carter and Suffet 1982; Landrum et al. 1984; McCarthy and Jimenez 1985), enhance the pollutant's apparent solubility in water (Chiou et al. 1983, 1986), and reduce the chemical's apparent affinity for binding to sediment particles (Hassett and Anderson 1982; Gschwend and Wu 1985; McCarthy and Black 1987). Contaminant interactions with humic material from groundwater near peat deposits are similar to those observed in surface waters (McCarthy and Roberson, ORNL, unpublished). Association with mobile humic macromolecules could enhance the transport of hydrophobic pollutants and may explain why hydrophobic pesticides such as DDT have been reported to move much further under field conditions than predicted by computer models (e.g., Enfield et al. 1982). Although we are not aware of any direct field evidence for the cotransport of organic contaminants with organic colloids, laboratory studies have demonstrated that humic substances inhibit the binding of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polychlorinated dioxins to the immobile phase of

reverse-phase chromatographic columns (Landrum et al. 1984; Muir et al. 1986), and enhance the migration of dioxin from laboratory soil columns (J. C. Means, University of Maryland, personal communication).

The polyelectrolyte character of humic and fulvic acids enables them to associate with metal ions. Both laboratory and field studies have demonstrated the significance of humic substances in surface waters on the aqueous chemistry of metals (Alberts and Geisy 1983), although the multiligand nature of the humic macromolecules makes it difficult to develop general complexation models (Perdue and Lytle 1983). Colloidal organic material also alters the distribution of radionuclide contaminants in surface and groundwaters. The distribution of Pu(III,IV), Am(III), and Th(IV) in several North American lakes was highly correlated with only one limnological parameter, the concentration of DOC (Wahlgren and Orlandini 1982; Nelson et al. 1985; Nelson and Orlandini 1986). Colloidal organic matter (>1000 daltons, based on ultrafiltration) from lakes inhibited the adsorption of Pu(III,IV) and Am(III) to sediments (Nelson et al. 1985; Nelson and Orlandini 1986). Humic and fulvic acid extracted from soil and sediment strongly bound Th(IV), U(IV,VI), Eu(III), and Am(III), with binding constants appearing to be directly related to the ionization of the humic substances (Bertha and Choppin 1978; Nash and Choppin 1980; Li et al. 1980).

Field studies demonstrated that radionuclides in plumes from the Chalk River Nuclear Laboratories migrated more rapidly than predicted from laboratory-derived K_d measurements. Champ et al. (1984) attribute the increased mobility to complexation of the nuclides with organic ligands, although the complexes were not characterized. Gel filtration chromatography of groundwater near an intermediate-level radioactive disposal trench demonstrated that 5 to 10% of the

^{60}Co and 30% of the uranium was associated with high molecular weight organic material (Means et al. 1978).

Inorganic Colloidal Particles

Sheppard et al. (1980) demonstrated that radionuclides (^{85}Sr , ^{137}Cs , ^{233}U , ^{237}Np , and ^{241}Am) equilibrated with several soils were associated with three broad size classes of particles: (1) ionic particles (<1 nm); (2) complexes with material between 2 and 3 nm (8000-50,000 daltons), assumed to be humic colloids; and (3) larger soil particles (10-60 nm). The 2 to 3-nm size class dominated the distribution ratio, but there was no evidence that the colloid was organic. Inorganic colloidal particles exist in the subsurface environment and can mobilize chemical contaminants. Actinides formed complexes with organic and inorganic colloids in groundwater samples (Kim et al. 1984), and associated with iron oxide colloids in test solutions (Nakayama et al. 1986). Actinides in borosilicate glass leached with organic-free water eluted as colloidal particles that were retained by soil columns (Avogadro et al. 1982). While colloids may be filtered and retained by porous media, changes in aqueous chemistry of the groundwater can mobilize the colloids and enhance transport through the subsurface environment. Changes in pH, ionic strength, and storage time significantly changed the formation, net surface charge, and mobility of americium colloids in aluminum oxide columns (Olofsson et al. 1982). The pesticide, paraquat, bound to Li-montmorillonite particles was retained in the upper portion of a soil column rinsed with 1 M calcium, but was mobilized by distilled water, which dispersed the clay and its associated pesticide (Vinten et al. 1983). Pulses of low-conductivity recharge water dispersed submicron, poorly crystallized, clay colloids from surface soil and resulted in high turbidity in wells several hundred meters distant;

treatment of the recharge area with gypsum relieved the turbidity by destabilizing the colloids (Nightingale and Bianchi 1977).

Treatment facilities or disposal sites may provide conditions that alter groundwater chemistry. The presence of colloidal particles of ferric phosphate was attributed to a plume of sewage-derived phosphates in an iron-rich sand aquifer which caused the solubility product for the complex to be exceeded (Gschwend and Reynolds 1987). A phosphate detergent solution dispersed ^{46}Sc -labeled kaolin and enhanced the mobility of the colloid in a laboratory sand column (Champlin and Eichholz 1976). Laboratory simulation of anaerobic, reducing conditions below a nuclear disposal vault demonstrated that soluble U(VI) could form negatively charged submicron spherical colloids composed of mixtures of U(IV) and U(VI) oxides (Ho et al. 1986).

Association with clay colloids appears to have enhanced the transport of radionuclides from a nuclear detonation cavity at the Nevada Test Site. Essentially all the transition elements and the lanthanide nuclides were associated with colloidal (3-50 nm, by ultrafiltration) mineral particles. The presence of these colloiddally-associated nuclides outside of the detonation cavity suggests that they are moving by particle transport (Buddemeier 1986; Buddemeier and Isherwood 1985; R. W. Buddemeier, Lawrence Livermore National Laboratory, personal communication).

Implication of Colloidal Particles to Contaminant Transport

The preceding discussion supports the following statements concerning organic and inorganic colloidal particles: (1) they exist in at least some subsurface environments; (2) they are capable of associating with types of groundwater contaminants generally considered to be highly retarded due to strong interactions with immobile aquifer particles; and (3) they can, under certain conditions, move

through aquifers and thereby alter the mobility of associated contaminants. Can descriptive relationships be formulated to account for the role of colloidal particles in transport calculations? A complete treatment of this subject is beyond the scope of this section; however, some general approaches and their limitations can be addressed.

Colloidal material can be treated as another component of the unretarded mobile phase. While aqueous complexation of metallic ions by humic and fuvic acids has long been considered in calculations of free metal activity (Jenne 1979; Morel 1983 and references therein; Dzombak et al. 1986; Fish et al. 1986), the significance of interactions of inorganic ions with inorganic colloids or organic solutes with organic colloids has only recently been recognized. Mass action equations can be written between solutes and colloids akin to aqueous complexation if relevant concentration variables and equilibrium constants can be defined (Fig. 1A). Empirically, or for the sake of transport calculations, the colloid interaction can be factored into a distribution coefficient (K_d) if the solute conforms to a constant partition model (e.g., hydrophobic organic compounds) (Fig. 1B). The denominator of the distribution coefficient (K_d) used to calculate transport or retardation factors (Fig. 1) would then include the amount of contaminant in both the aqueous and colloidal phase.

An example of the results of this approach is illustrated in Fig. 1 for a hydrophobic organic contaminant and a mobile humic colloid. The presence of the colloid decreases the apparent K_d between the mobile and immobile phase (Fig. 1C), and thus decreases the retardation factor and enhances the transport of the pollutant (Fig. 1D). The magnitude of this effect is directly related to the hydrophobicity of the contaminant, the concentration of the organic colloid, and the relative magnitude of the distribution coefficients between the aqueous phase

FIGURES 1 A-D. The effect of colloidal particles is illustrated.

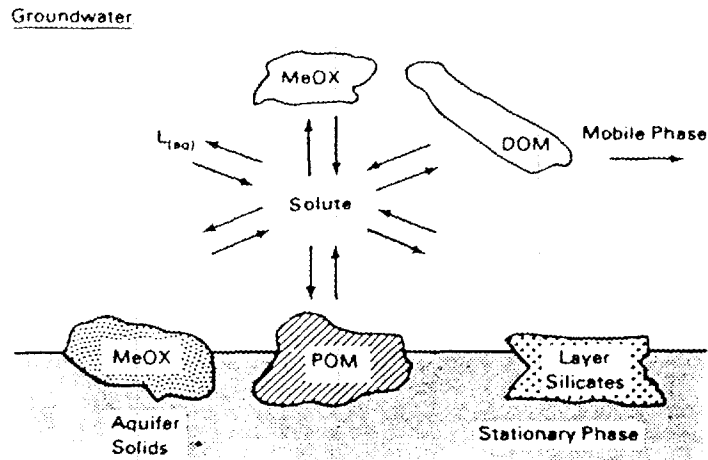


FIGURE 1A. Solutes react via site binding with multiple ligands (aqueous, solid, colloid) in an aquifer. Solute partition most strongly to ligands in high concentration and those with large equilibrium constants. The overall distribution coefficient reflects contributions from these reactions.

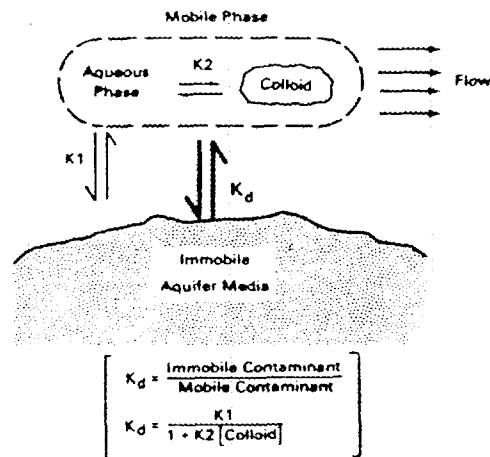


FIGURE 1B. Because of many uncertainties in the site binding approach (A), inapplicability to certain organic compounds, and difficulty in linkage with transport models, a K_d is often used. K_1 and K_2 are distribution coefficients between the aqueous phase and the colloidal and immobile phases, respectively. The K_d between the immobile and mobile phases is dependent on the relative magnitude of K_1 and K_2 , and the concentration of reactive colloid (68, 70, 98).

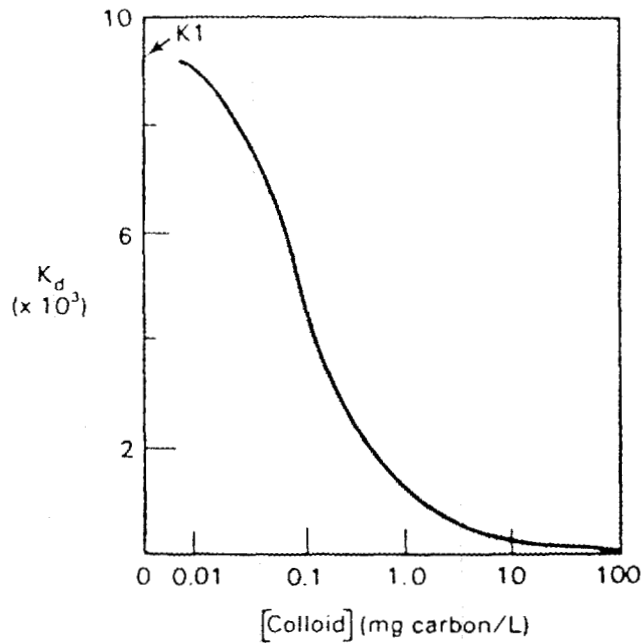


FIGURE 1C. As an example, consider the effect of organic colloids on the transport of a highly retarded HOC ($K_{ov} = 10^7$). Assume (i) organic content of the aquifer media = 0.1%, (ii) colloidal and particulate organic matter binding HOC equally, (iii) all phases are in equilibrium, (iv) distribution is defined by a constant partition model (after 103). Increasing colloid concentration reduces the K_d , thus lowering the retardation factor and increasing mobility of the HOC (D, below).

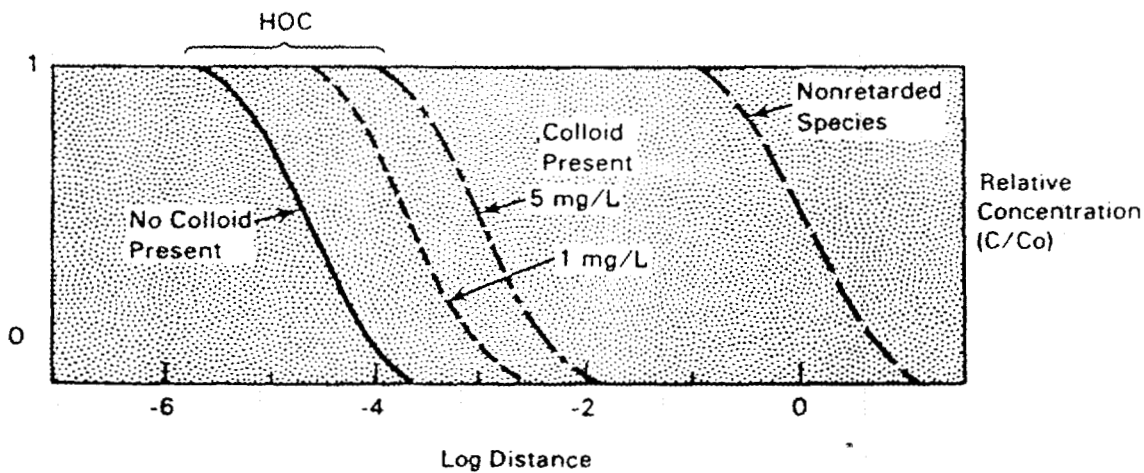


FIGURE 1D. Mobility increases by 10-50 fold in presence of 1 or 5 mg/L of organic colloid, respectively.

and the immobile and colloidal phases (K1 and K2, respectively). Enfield and Bengtsson (1987) developed an advection-dispersion model that incorporates a mobile organic macromolecule.

There are two limitations to this approach. First, it assumes that there are no spatial or temporal limitations preventing equilibration of all phases in the subsurface system. Rapid flow of water through soil macropores, especially during storm events, may quickly transport large quantities of mobile colloid-bound contaminants through the vadose zone to the saturated environment. Transport through fractures or solution channels in aquifers could also greatly enhance contaminant migration. Colloidal particles may be transported preferentially through larger channels within porous media; the macromolecule, blue dextran, eluted from a soil column before tritiated water, presumably by being forced to move through larger pores and being excluded from smaller pores (Enfield and Bengtsson 1987).

A second limitation to the constant partition approach is the assumption that colloidal particles are essentially unretained by the aquifer. The water treatment literature developed a considerable body of theory on the physical and chemical processes involved in filtration and coagulation of small particles (Yao et al. 1971; Stumm 1977; O'Melia 1980; McDowell-Boyer et al. 1987). Colloidal particles and immobile materials in aquifers possess surface charges controlled by surface groups and aqueous chemistry. Electrostatic and van der Waals forces determine if particle-media or particle-particle associations are favorable. Changes in aqueous chemistry may destabilize particles so that they flocculate with themselves and attach to media as aggregates via van der Waals attractive forces. Destabilization can occur by compression of the double layer of charge surrounding particles by high concentrations of inert electrolytes; by pH adjustment to neutralize the

particle surface charge; or by the presence of counter ions that preferentially adsorb onto particles and decrease the net surface charge so that attractive forces dominate.

While filtration theory attempts to address these processes, existing filtration data are not directly applicable to groundwater flow conditions. Groundwater flows are much slower than flows through porous media filters, and the direction of flow is typically horizontal rather than vertical. Filtration experience has involved uniformly sized media, compared to the heterogeneous reality of subsurface environments.

Predictions of the transport of contaminants in groundwater should consider the potential role of colloids, particularly if the following conditions pertain: (1) contaminants are known to associate strongly with organic or inorganic ligands (e.g., many metals, radionuclides, and hydrophobic organic contaminants); (2) groundwater contains relatively high levels of DOC; (3) aquifers are relatively porous or fractured and flow rates are relatively high; or (4) aqueous chemistry undergoes natural or contaminant-associated alterations that could mobilize colloidal particles.

References

- Aho, J. Arch. Hydrobiol. 1986, 107, 301-314.
- Alberts, J. J.; and Geisy, J. P. In "Aquatic and Terrestrial Humic Materials"; Christman, R. R.; Gjessing, E. T, Eds.; Ann Arbor Science: Ann Arbor, Michigan, 1983: pp. 333-348.
- Avogadro, A.; Murray, C. N.; Deplano, A.; Bidoglio, G. In Env. Migration of Long-Lived Radionuclides; International Atomic Energy Agency: Vienna, 1982, pp. 527-540.
- Bertha, E. L.; Choppin, G. R. J. Inorg. Nucl. Chem. 1978, 40, 655-658.
- Buddemeier, R. W. Eos 1986, 67, 955.
- Buddemeier, R. W.; Isherwood, D. In "Radionuclide Migration Project 1984 Progress Report", UCRL-53628; Lawrence Livermore National Laboratory, Livermore, CA, 1985: pp. 1-71.
- Carter, C. W.; Suffet, I. H. Environ. Sci. Technol. 1982, 16, 735-740.
- Champ, D. R.; Young, J. L.; Robertson, D. E.; Abel, K. H. Water Pollut. Res. J. Can. 1984, 19, 35-54.
- Champlin, J. B. F.; Eichholtz, G. C. Health Phys. 1976, 30, 215-219.
- Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E. Environ. Sci. Technol. 1986, 20, 502-508.
- Chiou, C. T.; Porter, P. E.; Schmedding, D. W. Environ. Sci. Technol. 1983, 17, 227-.
- Collins, M. R.; Amy, G. L.; Steelink, C. Environ. Sci. Technol. 1986, 20, 1028-1032.
- Dzombak, D. A.; Fish, W.; Morel, F. M. M. Environ. Sci. Technol. 1986, 20, 669-675.
- Enfield, C. G.; Carsel, R. F.; Cohen, S. Z.; Phan, T.; Walters, D. M. Groundwater. 1982, 20, 711-722.
- Enfield, C. G.; Bengtsson, G. Groundwater. 1987: in press.
- Fish, W.; Dzombak, D. A.; Morel, F. M. M. Environ. Sci. Technol. 1986, 20, 676-684.

- Freeze, R. A.; Cherry, J. A. "Groundwater"; Prentice-Hall: Englewood Cliffs, NJ, 1979.
- Gerba, C. P.; Goyal, S. M. In "Artificial Recharge of Groundwater"; Asano, T., Ed.; Butterworth: Boston, 1985: pp. 283-317.
- Gerba, C. P.; Wallis, C.; Melnick, J. L. Am. Soc. Civil Eng., J. Irrigation Drainage Div. 1975, 101(IR3), 157-174.
- Gillham, R. W.; Cherry, J. A. Geol. Soc. Am. Spec. Pap. 189 1982, pp. 31-62.
- Gschwend, P. M.; Wu, S.-C. Environ. Sci. Technol. 1985, 19, 90.
- Gschwend, P. M.; Reynolds, M. D. "Monodisperse Ferrous Phosphate Colloids in an Anoxic Groundwater Plume." Contaminant Hydrology, 1987, in press.
- Hassett, J. P.; Anderson, M. A. Water Res. 1982, 16, 681-686.
- Hayward, S. B. J. Am. Water Works Assoc. 1984, 76, 66-73.
- Ho, C. H.; Miller, N. H. J. Colloid Interface Sci. 1986, 113, 222-240.
- Jenne, E. A.; "Chemical Modeling in Aqueous Systems: Speciation, Sorption, Solubility, and Kinetics." ACS Symposium Series 93; American Chemical Society: Washington, D.C., 1979.
- Keswick, B. H.; Gerba, C. P. Environ. Sci. Technol. 1980, 14, 1290-1297.
- Kim, J. I.; Buckau, G.; Baumgartner, F.; Moon, H. C.; Lux D. Scientific Basis for Nuc. Waste Management, Vol. 7; Elsevier, New York, 1984, pp. 31-40.
- Landrum, P. F.; Nihart, S. R.; Eadie, B. J.; Garner, W. S. Environ. Sci. Technol. 1984, 18, 187-192.
- Leenheer, J. A.; Malcolm, R. L.; McKinley, P. W.; Eccles, L. A. U.S. Geol. Surv. J. Res. 1974, 2, 361-369.
- Li, W. C.; Victor, D. M.; Chakarbarti, C. L. Anal. Chem. 1980, 52, 520-523.
- McCarthy, J. F.; Black, M. C. In "Tenth Symposium on Aquatic Toxicology and Hazard Assessment"; American Society for Testing and Materials: Philadelphia, PA, 1987: in press.
- McCarthy, J. F.; Jimenez, B. D. Environ. Sci. Technol. 1985, 19, 1072-1076.
- McDowell-Boyer, L. M.; Hunt, J. R.; Sitar, N. Water Resour. Res. 1987, 22, 1901-1921.

- Means, J. L.; Crerar, D. A.; Duguid, J. O. Science 1978, 200, 1477-1481.
- Morel, F. M. M. "Principles of Aquatic Chemistry"; John Wiley and Sons: New York, 1983.
- Muir, D. C. G.; Yarechewski, A.; Knoll, A.; and Webster, G. R. B. Environ. Toxicol. Chem. 1986, 5, 261-272.
- Nash K. L.; Choppin, G. R. J. Inorg. Nucl. Chem. 1980, 42, 1045, 1050.
- Nakayama, S.; Moriyama, H.; Arimoto, H.; Higashi, K. J. Nuc. Sci. Technol. 1986, 23, 731-739.
- Nelson, D. M.; Orlandini, K. A. In "Speciation of Fission and Activation Products in the Environment"; Bulman, R.A.; Cooper, J.R., Eds.; Elsevier Applied Science: London, 1986: pp. 262-268.
- Nelson, D. M.; Penrose, W. R.; Kaltunen, J. O.; Mehlhaf, P. Environ. Sci. Technol. 1985, 19, 127-131.
- Nightingale, H. I.; Bianchi, W. C. Groundwater 1977, 15, 146-152.
- Olofsson, U.; Allard, B.; Andersson, K.; Torstenfelt, B. Scientific Basis for Nuc. Waste Mangement, Vol. 4; Elsevier, New York, 1982, pp. 191-198.
- O'Melia, C. R. Environ. Sci. Technol. 1980, 14, 1052-1060.
- Perdue, E. M.; Lytle, C. R. In "Aquatic and Terrestrial Humic Materials"; Christman, R. R.; Gjessing, E. T, Eds.; Ann Arbor Science: Ann Arbor, MI, 1983: pp. 295-313.
- Robertson, W. D.; Barker, J. F.; LeBeau, Y; Marcoux, S. Groundwater 1984, 22, pp. 191-197.
- Sheppard, J. C.; Campbell, M. J.; Cheng, T.; Kittrick, J. A. Environ. Sci. Technol. 1980, 14, 1349-1353.
- Schnitzer, M.; Kahn, S. U. Soil Organic Matter; Elsevier: New York, 1978.
- Stumm, W. Environ. Sci. Technol. 1977, 11, 1066-1070.
- Thurman, E. M. In "Humic Substances in Soil, Sediment, and Water"; Aiken, G. R.; McKnight, D. M.; Wershaw, R. L., Eds.; Wiley-Interscience: New York, 1985: pp. 87-104.
- Thurman, E. M.; Barber, L. B.; LeBlanc, D. J. J. Contam. Hydrol. 1986, 1, 143-161.
- Vinten, A. J. A; Yaron, B.; Nye, P. H. J. Agric. Food Chem. 1983, 31, 664-665.
- Wahlgren, M. A.; Orlandini, K. A. In "Environmental Migration of Long-Lived Radionuclides"; International Atomic Energy Agency: Vienna, 1982: pp. 757-774.
- Yao, K.-M.; Habibian, M. T.; O'Melia, C. R. Environ. Sci. Technol. 1971, 5, 1105-1112.

SUMMARY OF THE MEETINGORGANIZATION OF THE MEETING

The agenda was arranged so that the meeting addressed the interactions of contaminants with colloidal particles and the colloidal particles with the aquifer media:

CONTAMINANT	COLLOID	AQUIFER
- organics	- organic	- filtration
- metals	- clays	- chemical
- radionuclides	- metal oxides	interaction (sorption or repulsion)

The sessions were organized into four main parts:

PART I established the fundamental theoretical framework for the interactions between contaminants, the colloidal particles, and the aquifer.

PART II focused on organic colloidal particles and their interaction with organic and inorganic contaminants, as well as the fundamental forces that result in the aggregation of the organic macromolecules in the environment.

PART III focused on inorganic colloidal particles, their interaction with contaminants and their interfacial chemistry.

PART IV addressed several discussion topics that are critical for understanding the role of colloidal particles in the subsurface environment. Each topic was introduced by a discussion leader who then moderated an interaction among all the participants.

Several participants at the meeting presented posters communicating their research results. At the end of the seminar, participants divided into speciality groups to identify specific research needs critical to understanding the role of colloidal particles in the transport of contaminants in the subsurface environment.

This summary of the meeting will present the information from both the oral and poster presentations in a narrative form that follows the agenda outline. It was the concensus of the participants and speakers that this format was preferred for this summary report rather than a series of contributed abstracts.

Information on organic colloidal material will be presented first, along with summaries of the fundamental theory sections on filtration and solution theory. Information on inorganic colloidal particles will then be discussed. A summary of the discussion topics will be followed by the groups, recommendations for research needs.

FUNDAMENTAL THEORYFiltration Theory*

Transport of suspended particulate matter is widely recognized to occur in subsurface environments. Field data indicate that viruses, bacteria, and clay minerals can migrate considerable distances and that small particles and macromolecules are implicated in the transport of organic contaminants and radionuclides. Furthermore, media permeability can be significantly altered by changes in aqueous chemistry through particle release and capture. Quantitative models for predicting particle transport are available within the water filtration literature that account for the mechanism of particle-media collisions and the conditions for attachment. Predictions from the filtration transport models are in agreement with experimental data when electrostatic repulsive forces between particles are masked. As particles accumulate within media pores, available models become less predictive because of the coupling between retention and permeability reduction.

The fact that contaminants adsorbed to particles are mobile has important implications in understanding and predicting contaminant transport. The design of laboratory experiments and the collection of field samples often neglect contaminants transported by suspended colloids and particles.

Water filtration theory has been developing over the last few decades such that considerable predictive capability is available. Size-based filtration mechanisms include surface or cake filtration and straining filtration. For

*This summary was contributed by J. R. Hunt.

particles much smaller than the pore size of the media, particle retention is only successful if particles are transported to the media surface and if the particles stick when they collide. Particle transport processes are well defined in deep-bed filtration and include Brownian diffusion, interception of particles moving with the fluid flow path, and settling of particles onto media surfaces. An analysis of these collision mechanism reveals a strong dependence on particle size. For submicrometer-sized particles where Brownian motion dominates collisions, transport rate, and thus potential removal efficiency, increases as the particle size decreases. For micrometer and larger-sized particles, both interception and settling transport rates to media surfaces increase with increasing particle size. Thus, greatest mobility is expected for micrometer-sized particles where transport to media surfaces is least efficient. For conditions where attachment of particles following collision is favorable, particles are expected to be removed from flowing groundwater in less than a meter. Experimental data have confirmed these transport theories, but at high flow rates typical of deep-bed filters, 100-1000 m/d.

The condition for particle attachment following collision with a fixed surface is controlled by physical, chemical, and hydrodynamic forces. The dominant force hindering attachment is the electrostatic repulsion between the particle and the media because both are usually negatively charged. The London-van der Waals interaction provides an attractive force that operates over very short distances (a few nanometers). Hydrodynamic forces hinder particle attachment, and steric forces associated with polymeric material at particle surfaces can help or hinder attachment. The predictions are extremely sensitive to assumed surface potentials that control electrostatic forces. Small increases in surface potentials or decreases in ionic strength effectively stop particle attachment according to these predictions. Experimental data reveal that attachment efficiency is far less sensitive than theory would predict, indicating particle mobility through a clean

porous media is again fairly limited, on the order of tens of meters, although very limited data exist at typical groundwater flow velocities of less than 1 m/d.

The consequence of particle attachment to media surfaces is that media permeability and subsequent particle attachment are altered by the development of a deposit. Particle-media and particle-particle attachment results in the formation of a very porous aggregate that can partially clog media pores. There have been reports of extensive model development in the water filtration literature for particle accumulation and permeability reduction. These models can be fitted to experimental data but are not predictive under new situations. An examination of filtration data during clogging reveals that less than 1% solid matter in media pores can lower the media permeability to less than 1% of the clean bed value. This dramatic reduction is due to the very porous aggregates formed within the media pores. While filtration models frequently assume that attachment is reversible with a "desorption" reaction, there are no experimental data showing that particle release occurs if fluid flow rate and solution composition remain constant. Erosion of deposited material is possible if the fluid velocity is increased or if the solution chemistry is altered to disperse or restabilize the attached deposit.

Solution Theory for Nonpolar Organic Compounds*

Following the approach of Yalkowsky et al. (J. Pharm. Sci., 1975, 64, 48), one can quantify the tendency of nonpolar chemicals to dissolve in water by considering the "energetic costs" of forming a high-energy interfacial region between the solute molecule and the surrounding solvent molecules. Interestingly, this

*This summary was contributed by P. M. Gschwend.

microscopic interfacial surface tension appears to be directly proportioned to its macroscopic counterpart, that is the interfacial tension observed at the contact of hydrocarbon liquids and water (γ_{h-w}). Thus, the solubility of nonpolar organic compounds in water is given by

$$\ln x_{\text{water}} = \ln x_{\text{ideal}} - \frac{(N) (C) (\gamma_{h-w}) (HSA)}{RT},$$

where: $\ln x_{\text{water}}$ is the natural log of the mole fraction aqueous solubility,
 $\ln x_{\text{ideal}}$ is the ideal mole fraction solubility for gases or solids arising from the "energetic costs" of the condensing or melting of these materials as part of the dissolution process,
 N is Avogadro's number (individuals/mol),
 C is a correction factor accounting for the curvature of the microscopic solute-water interfacial region (≈ 0.55),
 γ_{h-w} is the macroscopic interfacial surface tension between a hydrocarbon liquid and water ($\text{kJ}/\text{\AA}^2$),
 HSA is the hydrophobic surface area of the molecule which is in contact with the water ($\text{\AA}^2/\text{individual}$),
 R is the gas constant ($\text{kJ}/\text{mol deg}$), and
 T is the absolute temperature (deg).

In light of this formulation, one predicts and observes a regular decrease in aqueous solubility as a function of increasing size of the congeners of nonpolar compound classes such as PAHs, chlorinated benzenes, or aliphatic alcohols. Further, if one changes solution composition (e.g., by adding salts or cosolvents), we can imagine that the solute:water interfacial costs can be divided into parts

proportional to the fraction of the cavity contact area which is no longer water:organic in nature but cosolvent or hydrated ion:organic contact. If this fraction corresponds directly to the mole fraction abundance of these constituents in the bulk water, Yalkowsky et al. (1976) derive:

$$\ln x_{\text{mix}} = \ln x_{\text{water}} + \frac{NC (Y_{\text{h-w}} - Y_{\text{h-cosolvent or satd salt water}}) (HSA) f}{RT}$$

where: $Y_{\text{h-cosolvent or satd salt water}}$ now reflects the macroscopic surface tension between a hydrocarbon liquid and the, pure solvent or saturated salt solution of interest, and
 f measures the fractional approach of the mixed bulk solution from pure water to pure solvent or saturated salt solution.

Such a formulation appears to successfully allow us to use available surface tension data to estimate a priori salting constants and cosolvent effects.

Finally, because colloid-nonpolar organic contaminant associations are expected to be inversely related to the chemical's solubility in the aqueous phase, this quantitative assessment of compound-to-compound or solution-to-solution differences in aqueous solubility allows us to immediately predict the differential tendency of such organic chemicals to sorb to colloidal or soil solids. Rao et al. (J. Environ. Qual., 1987 in press) have shown these predictions to fit the available data.

Fundamental Theory of Electrostatic Interactions*

Electrostatic interactions influence three processes that affect the transport of contaminants by colloids in the subsurface environment: (i) the adsorption of

*This summary was contributed by J. C. Westall.

the contaminant by the colloid or the aquifer matrix; (ii) the aggregation of the colloidal particles; (iii) the retention of the colloidal particles by the aquifer matrix. The magnitude of the electrostatic interactions depend on the nature of the contaminants and the colloids and solution variables such as pH and major ion composition. This discussion of fundamental theory examines the extent to which these interactions can be understood in terms of simple physical-chemical models.

The "dilute solution" approximations are used initially to define the problem: (i) solutions are aqueous with no cosolvent effects (ii) the composition of the colloidal particles resemble that of the aquifer matrix (iii) the contaminants do not affect the bulk properties of the solution, the colloids, or the matrix. Deviations from these assumptions are treated as special cases. Reference is made to both inorganic and organic surfaces and contaminants.

The framework for consideration of electrostatic effects is the classic Gouy-Chapman-Stern-Grahame theory for the structure of the interface, adapted for natural sorbents. The surface chemistry is represented in terms of a constant chemical affinity surface.

There are three phenomena through which information on electrochemical energies at the surface are obtained: (i) adsorption reactions, (ii) electrokinetic phenomena (e.g., colloid stability, electrophoretic mobility), and (iii) chemical reactions at surfaces (precipitation, dissolution, heterogeneous catalysis). Our understanding of these phenomena in terms of the models is examined.

Adsorption Reactions: The adsorption reactions considered in geochemical studies include surface hydrolysis, adsorption of metal ions by surface complexation, adsorption of anions by ligand exchange, and ion association. The chemical energy

of such a reaction is often expressed as the equilibrium constant for the reaction of a species in solution with hydroxyl groups on the uncharged surface. The electrostatic interactions associated with adsorption broaden the energy of the adsorption reaction from a single discrete value to a distribution of values; however, it is difficult to know how much of the broadening is attributable to the variation in electrostatic energy associated with variation in surface charge, and how much to the chemical heterogeneity of the oxide surface. In principle, the study of adsorption in electrolytes of different ionic strengths should allow the electrostatic and chemical components of adsorption energy to be distinguished. However, in practice, it is difficult to reach an indisputable conclusion from these experiments, for reasons to be discussed.

Electrokinetics: Surface equilibrium models are also applied in the study of electrokinetic phenomena, including (i) colloid stability, which is of great practical importance in geochemistry, and (ii) electrophoretic mobility, which is convenient for experimentation. The electrophoretic mobility of a particle is related to the electrostatic potential at a mean "slipping plane." Where this plane is located within the structural model of the interface is not clear, although there has been a great deal of thought on the subject.

The stability of colloids can be understood qualitatively in terms of electrochemical energies, but the quantitative understanding is not satisfactory. In well-controlled experiments involving the forces between two charged plates, the DLVO theory is quite satisfactory in explaining the observations. However, the same theory is not so satisfactory in explaining the stability of colloids with variable charged surfaces; the transition from stability to instability is more gradual than that predicted from the simple electrochemical equilibrium model.

Further work is needed to couple our understanding of electrophoretic mobility, colloid stability, surface charge, and interfacial potential difference.

Reactivity: A third phenomenon, the kinetics of surface reactions such as dissolution, precipitation, and surface-catalyzed reactions, could be among the most sensitive indicators of chemical and electrostatic energies at the surface. Chemical energies are specific (i.e., short-range and highly dependent on molecular structure), while electrostatic energies are not. However, up to the present, there have been only a very few of the studies on these sorts of reactions at oxide surfaces which have been cast explicitly in terms of electrochemical energies at the interface. As a better understanding of electrochemical potentials at the interface evolves, both electrical and chemical energies can be considered in studies of reaction kinetics at oxide surfaces. At some point in the future, it might even be possible to use data on the kinetics of these reactions to aid in separating interfacial energies into electrical and chemical components.

Summary: To return to the problem of interpreting interfacial phenomena in terms of chemical and electrostatic energies, we reach the following conclusion: many phenomena, if considered separately, can be interpreted reasonably well without a clear separation of electrostatic and chemical energies. Part of the reason for our moderate satisfaction with this less-than-perfect result is that natural surfaces and interfaces are so heterogeneous that an explicit mathematical description of them is impossible. However, if different phenomena are considered simultaneously, particularly for well-characterized interfaces, it should become possible to distinguish between electrostatic and chemical energies. The insight gained from study of these well-characterized interfaces can then be used to understand observations in poorly characterized natural systems.

ORGANIC COLLOIDAL PARTICLESInteractions of Metals with Organic Colloids*

Humic substances are described in the literature as polymers, heteropolycondensates, and complex mixtures. Their average molecular weights are reported to range from a few hundred to several hundred thousand grams per mole. Compositionally, they reportedly contain anywhere from virtually no aromatic carbon to virtually all aromatic carbon, depending on the sample and the method of characterization. Their complexation capacities for metal ions reportedly vary with the nature of the metal ion, pH, and ionic strength, and with the concentration of humic substance used in complexation capacity determinations. Literature "stability constants" for metal complexation vary considerably from one study to another. It is from such a background that we must try to separate facts from fiction and recognize those measurable properties that are unique to humic substances and not expected for ordinary polymers and/or mixtures.

Whenever any physical or chemical property of a humic substance is measured, it is critically important to realize that the measured property is that of a mixture and is not necessarily characteristic of any single component of the mixture. It is usually fairly simple to mathematically express the measured "average" property in terms of the corresponding properties of the individual components of the mixture, even though those components and their individual properties are not actually known. This procedure is a major tool for determining the conditions, if any, under which an average property can be represented by a

*This summary was contributed by J. R. Hunt.

single constant and for determining what type of weighting of the properties of the individual components of a mixture is embodied in the average property. Without such an analysis, it is almost inevitable that unwarranted and potentially misleading conclusions about the properties of humic substances will be reached.

Consider a complex mixture such as a humic substance that contains W grams and N moles of organic acids (N can be determined by colligative measurements). There exist w_i grams and n_i moles of the i^{th} individual component of the mixture, even though neither w_i nor n_i is known or determinable. An average property (P) of the mixture is some type of weighted average of the properties (P_i) of the individual components of the mixture. The general relationship between P and the individual P_i values is:

$$P = \frac{\sum P_i(\text{weight})_i}{\sum (\text{weight})_i} \quad , \quad (1)$$

where $(\text{weight})_i$ is some kind of weighting factor (mass, moles, mass fraction, mole fraction, etc.). If all $(\text{weight})_i$ are constant during experimental manipulations of the mixture, then P will be an average constant. Otherwise, P will be some type of continuously changing function. Some examples illustrate both types of average properties.

Example 1. Average Weight Percent Carbon

$$\% C = \frac{\text{Total C}}{\text{Total mass}} = \frac{\sum (\% C)_i w_i}{\sum w_i} \quad , \quad (2)$$

where $(\% C)_i$ is the percent carbon in the i^{th} component of the mixture. Unless the masses (or mass fractions) of the individual components of the mixture are somehow altered by experimental manipulations (e.g., by

unintentional fractionation of the sample through incomplete dissolution or partial adsorption/ precipitation), % C is expected to remain constant. It is clearly a meaningful average constant.

Example 2. Average Density

$$d = \frac{\text{Total mass}}{\text{Total volume}} = \frac{\sum d_i v_i}{\sum v_i} , \quad (3)$$

where v_i is the volume of the i^{th} component of the mixture. Volumes are not strictly additive, so, if a wide range of humic substance concentrations is used in a study, the density of the humic substances themselves will probably undergo some change. Density is thus almost, but not quite, an average constant.

Example 3. Number-Average Molecular Weight

$$M_n = \frac{\text{Total grams}}{\text{Total moles}} = \frac{\sum M_i n_i}{\sum n_i} = \frac{W}{N} , \quad (4)$$

where M_i is the molecular weight of the i^{th} component of the mixture.

Unless the sample is fractionated, M_n is expected to be an average constant.

Example 4. Average Rate Constant

The rate of the metal complexation reaction $M + L_i \longrightarrow ML_i$ is given by

$$(\text{Rate})_i = k_i [M][L_i] , \quad (5)$$

where k_i is the second-order rate constant for reaction of metal (M) with the i^{th} ligand (L_i) in a mixture of ligands. The overall rate of metal complexation by the mixture is simply

$$\text{Rate} = \sum (\text{Rate})_i = \sum k_i [M][L_i] . \quad (6)$$

Unfortunately, kinetic data are more often interpreted from the following kind of "overall" equation:

$$\text{Rate} = \bar{k}[M] \sum [L_i] \quad , \quad (7)$$

where \bar{k} is purportedly an "average rate constant" for metal complexation by the mixture of ligands. By equating Eqs. 6 and 7, it is readily shown that

$$\bar{k} = \frac{\sum k_i [L_i]}{\sum [L_i]} \quad . \quad (8)$$

Thus, \bar{k} is some kind of weighted average. As reaction with M preferentially decreases the concentrations of rapidly reacting ligands (those with larger k_i values), their weighting factors $[L_i]$ will decrease more rapidly than those of less reactive ligands. The inevitable result is that \bar{k} will be greatest at the beginning of a reaction and will steadily decrease as the reaction progresses. Accordingly, "average rate constants" are actually average rate functions. Tabulation of average rate constants from kinetic studies of humic substances is clearly misleading. It is also misleading to resolve the problem by hypothesizing the existence of two ligands, one that reacts more rapidly than the other.

Example 5. Average Equilibrium Constants

The equilibrium constant for the reaction $M + L_i \rightleftharpoons ML_i$ is

$$K_i = [ML_i]/[M][L_i] \quad , \quad (9)$$

where $[L_i]$ is the i^{th} ligand in a complex mixture of ligands. The overall extent of metal complexation by the mixture as a whole is often described in terms of an average equilibrium constant, which is given by:

$$\bar{K} = \frac{\sum [ML_i]}{[M] \sum [L_i]} \quad (10)$$

By substituting from Eq. 9 for $[ML_i]$ in Eq. 10, it is readily shown that

$$\bar{K} = \frac{\sum K_i [L_i]}{\sum [L_i]} \quad (11)$$

At extremely low metal:ligand ratios, all $[L_i]$ values are at their maximum values. As the relative amount of metal is increased, the strongly binding ligands (those with larger K_i values) react preferentially, thus reducing their weighting factors $[L_i]$ in Eq. 11 more rapidly than the weaker ligands. The inevitable consequence is that \bar{K} will be greatest at very low metal:ligand ratios and will steadily decrease as the metal:ligand ratio increases. This result has often erroneously been cited as evidence for the existence of two binding sites, one reacting more favorably than the other with the metal ion. Average \bar{K} values are actually not constant at all, despite their ubiquitous presence in the literature.

To characterize metal-humic interactions in surface waters or in the subsurface environment, whether from a kinetic or thermodynamic perspective, it is essential to recognize the functional nature of average rate "constants" and average equilibrium "constants" for metal-humic complexation reactions. Another characteristic property of a humic substance that must be determined before any

thermodynamic analysis can be made is the complexation capacity of the humic substance.

For a pure compound, even though complexes of higher stoichiometry (1:2, 1:3, etc.) may form at low levels of bound metal, 1:1 complexes predominate at higher levels of added metal. Thus, the complexation capacity is usually one mole of metal per mole of ligand. The important point is that complexation capacity is a compositional, rather than thermodynamic, parameter. The complexation capacity of citrate ion (L^{3-}), for example, is one mole of metal per mole of citrate, regardless of pH, ionic strength, nature of the metal, or the concentration of citrate ion used in the measurements.

The complexation capacity (CC) of humic substance or other complex mixture is, to a good approximation, a weighted average of the complexation capacities of the individual ligands in the mixture:

$$CC = \frac{\sum(CC)_i n_i}{\sum n_i} \quad (12)$$

If the mixture is not fractionated, CC is expected to be an average constant. Its value must be known to compute equilibrium parameters for metal complexation by the mixture. The metal-humic literature suggests that the complexation capacity of a humic substance varies considerably with almost every conceivable experimental variable: increasing at higher pH, decreasing at higher ionic strength, increasing at higher humic substance concentrations, and generally varying with the nature of the added metal ion. The differences between these reported results and theoretical expectations must be resolved.

At the heart of the problem are two fundamental misconceptions that have led to much confusion in the literature. First, the effects of experimental conditions on conditional equilibrium constants are erroneously interpreted as modifications of the complexation capacity of the humic substance; second, the effect of simple dilution on the position of the equilibrium in Eq. 11 is erroneously interpreted as a variation of complexation capacity with humic substance concentration.

Virtually all metal-humic complexation studies measure concentrations rather than activities of metal and ligand. Complexation capacity data are usually interpreted with no regard for the fact that conditional concentration-based equilibrium constants are effected by pH, ionic strength, and the nature of the reacting metal. It is simply easier to saturate ligands with metal at near-neutral pH and low ionic strength and with a strongly binding metal such as Cu^{2+} . This greater ease of formation of metal-humic complexes leads directly to apparently higher complexation capacities under these optimum conditions. Because metal complexation equilibria shift toward free metal and ligand with dilution, it is more difficult to saturate a dilute ligand mixture than a concentrated ligand mixture, which gives rise to the illusion that the complexation capacity of a humic substance varies with dilution.

Interaction of Radionuclides with Organic Colloids

One important area of concern in which the interactions of organic colloids with inorganic contaminants is especially important is understanding the potential role of these organic macromolecules in the transport and environmental distribution of radionuclides. Nuclear weapons testing in the 1950s and 1960s and the widespread use of nuclear reactors for power generation have created a

widespread distribution of radionuclides in the environment. In most water bodies, two processes are important in removing radionuclides: washout into the sea and sedimentation. For example, in Lake Michigan water outflow is very slow (about 1%/year), but time-series measurements have indicated a half-time of removal for plutonium of about ten years. This is due to annual sedimentation and resuspension of most of the plutonium inventory of the lake, with about 10% being irreversibly lost each year.

It is commonly thought that energy-related actinides (plutonium, americium, curium, thorium, and uranium) will inevitably be retarded by, and bound to, particulate phases, rocks, and soil of all kinds. It is now known that many water chemistry factors can interfere with this binding. At the Los Alamos National Laboratory, traces of Pu and Am travel distances of several kilometers in groundwater. This seems to be due to "source effects," or the nature of the discharged form of the elements; the Am does not exchange freely with added Am, for example, indicating that the ambient Am is present as a tightly bound form.

An important water chemistry factor controlling actinide mobility is "dissolved" (colloidal) organic carbon. By separating the >1000 MW material from water by ultrafiltration and then recombining the concentrate and ultrafiltrate, the concentration of colloidal organic carbon (COC) can be varied while retaining nearly constant composition of the ionic background. In this way, it could be shown that COC concentrations of 1 to 10 mg/L (in the normal range) could dramatically inhibit the binding of actinides to sediments. The resulting competition curves could be fit to a simple three-term equation that assumes the formation of both 1:1 and 1:2 actinide:COC complexes. The binding constants derived from this fit indicate that "old" organic carbon, such as that from the sea and from Lake Michigan, is the least effective at binding. Low pH, such as that

found in some bog waters, favors the formation of the 1:1 complex, whereas neutral and alkaline pH favors the 1:2 complex.

There are two competing views of the nature of metal binding to particulate material. One is the inorganic model, where binding occurs to the inorganic matrix of the particulate material, which may be clay, iron oxides, carbonates, etc. The other is that inorganic particles in nature are invariably coated with organic matter. This has been demonstrated in the past by electrophoretic and binding studies. Iodine-labeled humic acids will bind to most inorganic matrices. Furthermore, coating goethite, an iron hydroxide, with humic acids causes the pH behavior of lanthanide binding to adjust to more closely resemble that of natural particulates.

Lanthanide elements can be used to occupy the actinide-binding sites on natural particles. As the lanthanide concentration is increased, the inhibition of Am binding progresses from 0 to 100% over a very short range. This behavior fits the model of single type of binding site. The occurrence of the single type of binding site on a random polymer is very unusual. The behavior of tetravalent actinides is much more typical: inhibition of binding progresses much more slowly and is incomplete even over four orders of magnitude of lanthanide concentration. This fits the much more reasonable model of a variety of binding sites commonly observed with transition elements; the strongest sites fill first, while the weakest do not begin to be occupied until the lanthanum concentration is considerably higher.

The lanthanide-inhibition approach has demonstrated that the binding of actinides to humic acids and natural particles is similar to, and distinct from, binding to the inorganic matrix goethite.

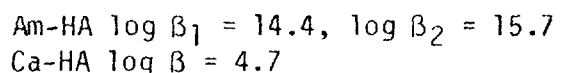
Hollow-fiber filtration has been found to be useful in the field for measuring the size-speciation of actinides. In a study of an artificial reactor-cooling lake

in Wales, United Kingdom (UK), about 85% of the actinides were found in the molecular size fraction >100K in surface waters, and in the 30 to 100K range in anoxic bottom waters. The remaining 15% are found in the lowest (<3K) size fraction. The <3K and >100K fractions contain only a small proportion of the organic carbon present in the lake; most is found in the 3K to 100K range where small amounts of the actinides are found. It is possible that, in this lake, the actinides are present in some form other than bound to humic substances.

One of the potential routes for the disposal of low-level wastes in the UK is in concrete vaults in a clay formation. Some of the UK clay formations contain significant quantities of organic material which could give rise to groundwaters containing 1 to 10 mg/L of dissolved organic carbon (DOC). These organics are high molecular weight acids, some of which could be regarded as colloids. Because of the acidic functional groups, these molecules may have the capacity to form complexes with some radionuclides which could enhance their solubility or reduce the sorption on components of the near field. Equally, because these complexes will be physically large, the result of the complex formation may be a net reduction in radionuclide transport because of filtration and entrapment in the pore structure of the concrete or the host clay.

Recent studies at the Harwell Laboratory in the UK have concentrated on the experimental determination of the effect of humic acid (HA) on the solubility and sorption of Am in cement systems.

The calculation of the effect of a small concentration of HA on the solubility of Am has been made using a geochemical speciation and mass transfer code (PHREEQE, Parkhurst et al, 1982, WRI 80-96, U.S. Geol. Survey). The formation constants for the calcium and the Am complexes were given the following values:



The simulation was achieved using a hypothetical solid phase so that the water composition corresponded to the prediction of aged cement water and contained 4×10^{-6} M HA sites. On the basis of a molecular weight of 10,000, a carbon content of 50%, and a complexation capacity of 4 meq/g, this gives a DOC content of 0.5 mg/L.

The solubility studies have used HA extracted from a sample of Oxford clay along with equivalent experiments, in the absence of HA. The HA has little effect at high pH which was attributed, on the basis of the modelling studies, to competitive formation of hydroxides and the calcium-humic complex. However, because the solid and liquid phase separation in these experiments was by a 25,000-dalton cut-off filter, it is possible that some of the Am-HA complexes were rejected to the solid phase on the basis of their size.

A different set of experiments using a commercial HA and a slag cement equilibrated water showed a thirtyfold increase in Am solubility with 5 mg/L of HA. Higher concentrations of HA could not be achieved in this water because the colloids coagulated, which was attributed to the increased ionic strength of this water.

Sorption experiments conducted on a PFA/OPC concrete show a tenfold or greater reduction in sorption coefficient at HA concentrations over 10 mg/L. The solid-liquid phase separation in these experiments was accomplished by centrifuging at 25 g for a few minutes. The reduction in sorption is possibly due to the formation of complexes between Am and HA which inhibit sorption but were not found in the solubility experiments because of the restrictive filtration used.

Interactions of Organic Contaminants with Organic Colloids

Organic colloidal material such as humic substances also have a high affinity for association with hydrophobic organic contaminants (HOC) such as polycyclic

aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and chlorinated benzenes and alkanes. The affinity of the association is inversely related to the solubility of the HOC. The highly structured molecular properties of water limits the aqueous solubilities of HOC, which is dependent on the molecular surface area of the HOC. The association of HOC with organic colloids has been measured by several methods, including equilibrium dialysis, vapor phase analysis, and solubility enhancement; although the techniques vary, they measure the same interaction. Solubility enhancements of relatively insoluble HOC may be described in terms of a partition-like interaction of the solutes with the microscopic organic environment of the high molecular weight organic colloid. The apparent solubilities increase linearly with colloid concentration and show no competitive effect between solutes. With a given organic colloid sample, the solute partition coefficient (K_c) increases with a decrease of solute solubility or with an increase of the solutes octanol-water partition coefficient. The K_c values of solutes with soil-derived HA are approximately four times greater than those with soil fulvic acid (FA) and 5-7 times greater than those with aquatic HA and FA. The effectiveness of organic colloids in enhancing solubility appears to be related largely to the molecular size and polarity of the macromolecules.

There is continuing discussion, however, about how the molecular size and polarity are related mechanistically to the affinity of the colloidal material for binding HOC. The concept of HOC partitioning into organic material in proportion to their hydrophobicity suggests that natural organic coatings and colloids exist as liquid-like phases that act to extract nonpolar contaminants from water. Contaminant transport models that portray natural organic colloids as detergents with amphiphilic properties have been questioned because colloid concentration

levels in groundwater are much too low to form detergent-type micelles involving nonpolar mechanisms, and the nature of natural organic colloids is much too hydrophilic to form detergent-type micelles.

Studies comparing organic colloids from several aquatic and groundwater environments suggest that the hydrophobic nature of the colloid itself is not a sufficient condition for binding of HOC (binding affinity was measured by equilibrium dialysis). The affinity for binding hydrophobic PAH was negatively correlated with the fractional contribution of a hydrophobic neutral component of the total "dissolved" organic carbon (DOC) content of the water (the hydrophobic neutral fraction was defined as that component of the total DOC which binds to XAD-8 macroporous resin and is not eluted with either acid or base). There was, however, a strong positive correlation with the hydrophobic acid content of the DOC and binding affinity. The hydrophobic acid component is the fraction of the DOC which binds to the hydrophobic XAD-8 resin under acid conditions, but is eluted with base, suggesting the presence of ionizable acidic groups, such as carboxyl or phenol moieties, in a large organic macromolecule. These ionizable groups would interact with the resin when the acidic groups were protonated at low pH.

Binding affinity was also highly correlated with the molar volume of the organic colloid, as measured by fluorescent polarization techniques. The best predictor of the affinity of the different water samples for binding HOC was the extinction coefficient for absorbance at 260 nm. This portion of the spectrum reflects absorption by pi-pi orbitals of aromatic structures, and should be a measure of the aromatic content of the organic colloid. These observations are consistent with a hypothesis that colloidal matter which has a high affinity for binding HOC can be described as a large, open macromolecule, predominantly aromatic

in character, with an abundance of acidic functional groups. Charge repulsions between the acidic groups maintain the open structure at neutral pH, and the aromatic structure of the molecule provides the basis for intermolecular associations with the HOC. Water sources that contain organic colloids that were predominantly aliphatic in composition (i.e., characterized by low absorbance at 260 nm and few ionizable acidic functional groups) had a lower affinity for binding HOC.

Chemical studies on the primary aggregation phenomena of organic substances in groundwater appear to be consistent with these observations. Evidence was presented that polar interactions, based on hydrogen-bonding and pi-electron bonding mechanisms, are largely responsible for intra- and intermolecular interactions that create lower-polarity domains in natural organic colloids and surface coatings. The evidence was based on deviations of experimentally measured densities of organic colloids in water from calculated densities.

Densities of organic colloids were calculated by application of Traubes rule which states that partial atomic volumes are additive, and experimentally measured carbon, hydrogen, and oxygen distribution data were used to calculate densities of organic colloids. The density-concentration dependence suggested that intermolecular association phenomena predominate when organic colloids are in the free-acid form, but intramolecular association phenomena predominate when the organic colloids exist in salt forms.

Comparison of C-13 NMR data of organic colloids in the solid-state, liquid state dissolved in water, and liquid-state dissolved in dimethylsulfoxide suggest that the carboxyl groups, ketone groups, phenol groups, and pi-electrons of the aromatic rings are involved in the polar interactions that cause inter- and intramolecular interactions.

Conceptual models were presented that illustrate polar interactions for organic coatings on a particle surface. These polar interactions can lower the polarity of organic aggregates and give liquid-like properties that explain contaminant partitioning behavior.

Regardless of the precise mechanisms that underlie the aggregation of natural organic colloids, there is evidence that the organic colloids can alter the migration of hydrophobic organic contaminants (HOC, such as PCBs and dioxin) through porous media. Colloids have been recognized as modifiers of the solubility of organic contaminants in natural waters. This observation has led to intensive research because the solubility of compounds seemed to dominate their fate, transport, and bioavailability in aquatic systems. Early studies of the sorption of HOCs on colloids indicated that sorption appeared to be a simple partitioning process occurring between water and an organic-rich phase, in this case colloidal organic matter rather than a soil/sediment particle. The sorption of HOCs on colloids was found to be predictable within reasonable precision using regression equations developed for the sorption of HOCs on soil/sediments. However, sorption of HOCs on colloids was found to be more dependent on bulk solution properties than sorption on soil/sediments. Factors such as pH and ionic strength appeared to not only influence the solution properties of the HOCs but also the "solution" properties of the colloids, resulting in dramatic changes in sorption behavior.

The presence of cosolvents such as short-chain alcohols and aldehydes significantly affects the sorption and transport properties of HOCs such as dioxins and PCBs in soils and aquifer materials. These cosolvents can profoundly but predictably alter the sorption equilibrium of dioxins and PCBs in soils, making them much more mobile in model soil columns. The influence of organic colloids on the enhanced transport of dioxins and PCBs has also been examined in the presence

of cosolvents. Preliminary studies on the effect of colloids on the solubility of tetrachlorodibenzo-p-dioxin (TCDD) in selected cosolvent mixtures compared to the controls (solubility in the cosolvent mixtures only) have demonstrated that colloids do significantly enhance the solubility of TCDD in cosolvent systems. The effect becomes greater as the percentage of water in the mixture is increased. While more detailed studies are needed, at colloid concentrations in the range of 20 mg/L, no flocculation of the added colloids was observed at high percentages of co-solvent (e.g., 50-100% methanol).

In studies of the transport of dioxins in soil columns, the presence of cosolvents profoundly influences the mobility of TCDD. For example, while TCDD is essentially immobile in pure water systems, it will begin to elute from the same column in approximately five bed volumes of 50:50 methanol:water. In preliminary studies of the interactions of colloids and cosolvents as they relate to transport in soil columns, the transport of TCDD is enhanced in the presence of approximately 20 mg/L of colloid in soil columns eluted with cosolvent mixtures in the range of 50 to 100% methanol in water. The magnitude of the effect is poorly defined at this time; however, the general trend observed seems to parallel the effect on solubility, as would be anticipated. Much more information needs to be gathered in this research area before a true enhancement can be confirmed. Also, the potential influence of the cosolvent on the soils themselves needs to be investigated before any enhanced transport observed can be attributed to "added" colloids alone.

Transport of Bacteria through Porous Media

The basic chemical and structural features of the natural organic colloidal material affect the mobility of the colloid in porous media. There has been little direct and quantified evidence that colloidal-sized particles can be transported

through aquifers and at what rates. The transport of bacteria has been recently studied in this respect. Bacteria can serve not only as surrogates for nonliving organic colloidal particles, but their transport also has implications for microbial mineralization of chemical contaminants. Biodegradation of organic compounds that are mobile and persistent in moving groundwater may depend, in part, on the relative mobility of acclimating aquifer bacteria. The movement of indigenous bacteria and bacteria-sized fluorescent microspheres under a variety of hydrologic conditions is currently being investigated in a series of forced-gradient groundwater-injection experiments in Cape Cod, Mass. Methodology has been developed to collect, concentrate, and label morphologically diverse populations of indigenous aquifer bacteria with deoxyribonucleic acid (DNA) specific fluorochromes and to study their transport through aquifer sediments. In a recent divergent tracer experiment, downgradient breakthrough curves of aquifer bacteria stained with 4',6-diamidino-2-phenylindole (DAPI) were similar to those of a conservative tracer (bromide). Fractional breakthrough (C/C_0) of carboxylated microspheres at peak abundance at 1.5 m from point of injection was highest for the 1.2- μm diam size class, followed by 0.7 and 0.2 μm microspheres, respectively. This suggests a differential filtration effect that is inversely related to particle size for the size range tested. However, fractional breakthrough of DAPI-stained bacteria (0.2-1.6 μm long) was 100, 149, and 288-fold higher than that for the 1.2, 0.7, and 0.2 μm carboxylated microspheres, respectively. Breakthrough of uncharged microspheres was not detected. These results demonstrate that under certain conditions the mobility of some bacteria may approach that of a conservative tracer and that bacterial transport through aquifer sediments may depend on cell size, aquifer properties, and the nature of the bacterial surface.

INORGANIC COLLOIDAL PARTICLES

Inorganic colloidal particles include clays, metal oxides, and inorganic precipitates in the submicrometer size range. The meeting addressed aspects of interactions of both metals and organic chemical binding to the colloids, as well as the effect of organic solvents on the flocculation and stabilization of clays.

Interaction of Radionuclides and Metals with Inorganic Colloids

A first step in gaining a better understanding of colloidal transport of pollutants is to identify and characterize systems in which inorganic colloids are present. The Sheeler Seeps on Whitewood Creek, South Dakota, is one such system being examined by the U.S. Geological Survey.

The Sheeler Seeps are located on Whitewood Creek approximately 1 km from its confluence with the Belle Fourche River near Newell, South Dakota. The seeps are a result of downcutting through a historic meander of Whitewood Creek that was filled with tailings washed down from the Homestake Mine near Lead, South Dakota. After the meander filled, Whitewood Creek changed course, eroded through the meander sediments, and into the underlying shale bedrock. Groundwater percolates through the tailings until it encounters the relatively impermeable bedrock. Further flow is then directed laterally across the surface of the shale, until the water discharges at the land surface near the creek. Emergent groundwater then flows over the shale into small, quiescent pools before mixing with the stream water.

Samples for this study were collected from Whitewood Creek immediately upstream and downstream from the seeps, from a quiescent pool, from water flowing over the face of the outcrop, and from several inches into the outcrop. Analyses were performed for various chemical components on filtered (400-, 100-, and 50-nm

Nucleopore filters) and unfiltered fractions. The presence of suspended colloids was determined using photon correlation spectrometry (PCS). Samples for PCS analysis were collected and sealed in ampules under N_2 atmosphere to minimize oxidation. Finally, the materials retained on the filters were examined using SEM/X-ray analysis.

Iron and manganese concentrations are approximately 10 times greater in the seep than the stream. Concentrations of several other species -- As, Ca, Ni, Si, Sr, and SO_4 -- were two to three times greater in the seeps than in the stream. Filtration resulted in decreases in Fe and As concentrations, suggesting these elements may be associated with particulate or colloidal materials.

To ascertain the presence of colloids, samples were analyzed 2 to 4 h after collection using PCS. This technique provides information about particle-size distributions and particle concentrations. In all samples, the scattering intensity decreased with decreasing pore size of the filter. This is strong evidence for removal of colloids by filtration. The translational diffusion coefficient (D_t) which is inversely related to particle size also shows the expected trend, i.e., D_t increases as the pore size decreases. These data indicate median particle diameters in the filtrates that are too large to have passed through the filters used. If the assumption of particle sphericity is reasonable, then the data are consistent with two alternative explanations. First, that small particles that passed through the filters aggregated before PCS analysis; or second, that despite the precautions taken, some iron oxidation and precipitation of $Fe(OH)_3$ occurred between the time samples were collected and PCS analysis. The presence of the larger particles indicate the importance of measuring colloids quickly after collection to preclude temporal changes in size and surface distributions.

The most interesting results were from the SEM/X-ray analyses. Samples collected taken from the creek contained mostly clay with little iron. After filtration through 400-nm filters, virtually no particles were retained on the 100-nm filter and those that were present were calcite and some amorphous iron oxides.

Particles with a dimension larger than 400 nm collected from the quiescent pool included several noncrystalline calcium-potassium aluminosilicates with Si:Al ratios of approximately 5:1. Large particles (1 x 4 μm) of well-crystalized gypsum also were present. Polyframboidal iron pyrite approximately 5 μm in diameter and large (5 x 7 μm) magnesium-calcite crystals were identified, as well as a particle high in titanium with associated calcium and phosphorous. This latter particle may be rutile, brooksite, or anatase. Amorphous-iron masses were observed with either adsorbed calcium or perhaps calcite nuclei. Potassium silicates were observed that had no iron coatings.

The 100 nm filter used for the pool sample retained individual pyrite framboids that had diameters of 400 to 500 nm. Trace quantities of arsenic were associated with these framboids. Iron sulfide also was present as an amorphous phase. The diameters of individual particles of this amorphous phase were less than 100 nm. Numerous calcite and silica particles were retained.

Frequently the calcite had sulfur associated with it, suggesting formation of surface coatings of gypsum. Many small particles that should have passed through the 100-nm filter were retained, and at least one particle impacted the filter and was pushed toward a pore, as indicated by a scratch on the filter. These observations indicate that the filtration process might promote coagulation of small particles into larger aggregates that would then be retained by the filter.

Particles collected from the seep consisted of spheroids of amorphous iron oxides and hydroxides, crystalline silica with no iron coatings, and platy calcium silicates with iron coatings. Individual particle dimensions ranged from 200 to about 1000 nm. A large gypsum crystal with a maximum dimension of about 700 nm was also identified. In general, particles with dimensions ranging from 100 to 400 nm are much more abundant in seeps and pools than in the creek, a trend that is also indicated in the chemical data.

This preliminary study determined that particles of colloidal dimension are present in water from the Sheeler Seeps. An association of arsenic with iron-sulfide phases also was determined. Future work at the site will attempt real-time analyses of particle size, shape, and surface charge using in-situ PCS analysis, and will include a systematic approach to establish if arsenic at the site is moving in association with colloidal particles.

The significance of colloidal association on the geochemistry and distribution of inorganic contaminants is illustrated by studies on the scavenging of thorium isotopes in natural waters. Thorium isotopes occur in nature either as the mother nuclide of a decay series (^{232}Th) or as being produced by longer-lived and more soluble radioisotopes of uranium or radium. The latter isotopes (e.g., ^{234}Th , ^{228}Th , ^{230}Th) are ideally suited to be used for residence time calculations in closed systems under steady state or nonsteady state conditions. Thorium isotopes occur in natural waters as $\text{Th}(\text{OH})_4$ or polyhydroxy species or possibly adsorbed to preexisting organic or inorganic colloids. The solubility of ThO_2 is low, but all Th isotopes occur in natural waters at or below saturation concentrations (10^{-15} to 10^{-20} M). This is likely to form "adsorption-colloids" (i.e., Th attached to organic or inorganic colloidal matter or DOC). The analysis of Th isotopes in natural waters often requires large volume samples (e.g., 10-1000 L),

chemical separation steps in the laboratory, and alpha- (^{232}Th , ^{230}Th , ^{228}Th), beta- or gamma- (^{234}Th) counting of the purified samples.

There are a respectable number of results available from the Pacific and Atlantic oceans, very few from lakes, and a few from pore waters of marine surface sediments and from groundwater systems. The residence times from the time of production to its disappearance from the closed system can be calculated from the disequilibrium of particle-reactive Th-isotopes with their soluble mother nuclide (U or Ra isotopes) in unfiltered or filtered samples. Results obtained by different investigators over the past one to two decades indicate that oceanic residence time of thorium (T_T), ranging from decades in the open ocean to days in coastal or lake waters, is related to the particle flux through the system.

While long-lived ^{230}Th appears to be in adsorption-desorption equilibrium, with both time constants of the order of 1 year^{-1} , short-lived ^{234}Th is not fully equilibrated with available surfaces. The residence time needed for a Th(IV) ion to be attached to a particle of filterable or sinkable size is much slower than would be expected if it were simply a surface adsorption process onto larger particles. These residence times are on the order of days to weeks in coastal waters and lakes and up to months or years in the open ocean. They appear to be predictable from the uptake kinetics of Th isotopes by natural sediments in laboratory batch experiments, when corrected for different particle concentrations.

If we assume that Th uptake by particles from Narragansett Bay, Rhode Island, (mainly composed of resuspended sediments) is representative of uptake by particles from other coastal areas, and that Th uptake by particles from the North Atlantic caught in sediment traps (mostly planktonic remains) is representative of uptake by particles in other areas of the open ocean, the observed scavenging kinetics of the short-lived ^{234}Th for vastly different oceanic environments can be predicted.

It can be shown that the observed scavenging kinetics of Th isotopes in the ocean is consistent with a simple, reversible uptake model in which the radionuclide, attached to colloidal sized particles, is "scavenged" by larger filterable particles ("Brownian Pumping" with differential settling). These colloidal-sized particles carrying the radioactive tracer have been identified by ultrafiltration or resin-type separations under near-natural conditions in model ecosystem experiments and in laboratory batch experiments. These nuclide-carrying colloids are responsible for the slower than expected removal of radionuclides from coastal marine ecosystems.

The distribution coefficient K_d (= activity on particles/activity in filtered waters) of ^{234}Th in open ocean waters and sediment pore waters is proportional to $C_p^{-0.5}$ (C_p = particulate matter concentration). This is not inconsistent with the original kinetic data calculated from ^{230}Th and ^{234}Th distributions in the open ocean. The observation that K_d is a function of time and $1/C_p^{0.5}$ has been frequently reported from laboratory sorption experiments with natural particles for the radionuclides of hydrolyzable ions, phosphates, selected trace metals, and hydrophobic organics. Models to explain these phenomena in the laboratory invoke diffusion-controlled reactions through surface films, coagulation, or incomplete separation of natural colloidal matter (e.g., hydrous oxyhydroxides of Mn and Fe, humic acids, clay minerals) during batch uptake experiments.

Because this particle concentration effect appears to promote a higher than expected apparent solubility of ^{234}Th in marine sediments and groundwater aquifers, colloids carrying hydrolyzable ions such as Th isotopes could also be important in groundwaters. Not much work has been done in this area: U-Th series

nuclides in groundwaters could also provide kinetic information needed to better understand colloid transport in groundwaters.

The kinetics of coagulation and peptization of natural colloidal-sized particles is difficult to observe directly in natural waters by spectroscopic methods. However, it appears that this process is traced by Th isotopes, which might therefore also be used as natural colloid tracers and "coagulometers" in subsurface waters.

The significance of radionuclide association with inorganic colloids is also apparent in the subsurface environment around nuclear weapons facilities. Water samples were collected and analyzed from inside and outside an underground nuclear detonation cavity at the Nevada Test Site. The mobile species (^3H , ^{99}Tc , and ^{125}Sb) exhibited conservative behavior and were found at similar concentrations inside and outside the cavity. Lanthanide and transition element isotopes were observed outside the cavity but at much lower concentrations than inside. In both locations these nuclides were not found in ultrafiltrates, but were completely associated with particles >0.6 nm. Their presence at the external sampling site indicates transport in particulate, probably colloidal, form. Although ^{137}Cs is traditionally treated as relatively immobile, a substantial fraction of the total ^{137}Cs activity at both sampling locations passed through the 0.6-nm ultrafilter. This suggests that the field applicability of laboratory data on Cs sorption and retardation requires careful review. The chemical characteristics of the colloids involved are under investigation; preliminary results show that the colloidal fraction (<50 nm, >0.6 nm) contains natural clay minerals, and that at ambient pH values the groundwater may be supersaturated with respect to $\text{Fe}(\text{OH})_3$.

Information derived from the use of tracers of colloidal particles can be used to develop and validate models to predict the transport of chemical species. A vital problem that constrains the use of solute transport models is a lack of knowledge about the mechanisms and rates of reactions that govern partitioning of chemical species between aqueous and solid phases (including colloidal particles). Trace metal concentrations in natural aqueous systems are usually less than the solubilities of pure solid phases that contain the metal ion, and adsorption and ion exchange processes are frequently invoked as an explanation for this phenomenon. Research on this topic has emphasized the role of adsorption by hydrous oxides and clays, since these phases are presumed to be the predominant sorbents in natural waters. An abundance of literature is now available on adsorption of metal ions by hydrous oxides, and numerous theoretical models have been presented that describe the physical and chemical characteristics of the oxide/water interface. However, carbonates are a major component of sediments in subsurface systems as well as in freshwater and marine environments, and few studies of the sorptive behavior of carbonate surfaces have been undertaken. Recent observations indicated that Cd(II) sorption by an aquifer sand was dominated by reactions with carbonate minerals rather than by the more abundant hydrous oxides.

The rates of metal ion sorption by calcite are usually characterized by fast and slow processes, with half-times of reaction on the order of minutes (fast) and hours to days (slow). Authors generally have concluded that the fast process is due to adsorption of metal ions on the surface, and the slower process is due to nucleation and growth of a surface precipitate [e.g., MnCO_3 , CdCO_3 , or $\text{Cu}_2(\text{OH})_2\text{CO}_3$]. Little evidence to support these conclusions has been available, although electron spin resonance spectra demonstrated that MnCO_3 had

formed on the calcite surface in systems that were supersaturated with respect to MnCO_3 .

The mechanism of these processes has been examined in further detail. The rate of Cd^{2+} sorption by calcite was determined as a function of pH and Mg^{2+} concentration in aqueous solutions saturated with respect to calcite but undersaturated with respect to CdCO_3 . The rate of Cd^{2+} sorption was characterized by two reactions steps, with the first step reaching completion within 24 h. The second step proceeded at a slow and nearly constant rate for at least seven days. The rate of calcite recrystallization was also studied as a function of pH and Mg^{2+} concentration, using a Ca^{2+} isotopic exchange technique. Both the recrystallization rate of calcite and the rate of slow Cd^{2+} sorption decreased with increasing concentration of pH or with increasing Mg^{2+} . The recrystallization rate could be predicted from the number of moles of calcium present in the hydrated surface layer. A model is presented that is consistent with the rates of Cd^{2+} sorption and Ca^{2+} isotopic exchange. In the model, the first step in Cd^{2+} sorption involves a fast adsorption reaction that is followed by diffusion of Cd^{2+} into a surface layer of hydrated calcium carbonate that overlies crystalline calcite. Desorption of Cd^{2+} from the hydrated layer was slow. The second step is caused by solid solution formation in new crystalline material that grows from the disordered mixture of cadmium and calcium carbonate in the hydrated surface layer. Calculated distribution coefficients for solid solutions formed at the surface were slightly greater than the ratio of equilibrium constants for dissolution of calcite and cadmium carbonate, which is the value that would be expected for an ideal solid solution in equilibrium with the aqueous solution.

The importance of carbonates as sorbents for trace elements in natural systems and the reversibility of sorption reactions in general appears to deserve more attention. While it is widely assumed that sorption of trace elements in natural systems is reversible, this conclusion has rarely been confirmed by experimental

observations. Understanding the time scales of desorption reactions is important in the formulation of transport models, because these rates will generally determine whether the coupling of chemical and hydrologic models should be based on a kinetic model or an assumption of local equilibrium. Recent results described here suggest that a kinetic approach would be most appropriate for models of the transport of Cd(II) through calcareous soils and aquifers.

Interaction of Organic Solutes with Inorganic Colloids

The same basic knowledge about the mechanisms and chemical reactions is required to understand the interactions of organic contaminants with inorganic colloids. The chemical mechanisms involved in the association of model organic chemicals to a colloidal iron oxide were discussed. Bonding mechanisms of benzoic and phenolic compounds at the goethite (α -FeOOH)/water interface were studied in situ using cylindrical internal reflection (CIR)/Fourier transform infrared (FTIR) spectroscopy. Comparisons between CIR/FTIR spectra of salicylate, phthalate, 2,4-dihydroxybenzoate, benzoate, o-nitrophenol, phenol, and other related compounds in solution and spectra of these organics added to goethite suspensions showed whether adsorption at the interface occurred and in what manner. The primary probe organic was salicylate (2-hydroxybenzoate) and it bonded to surface iron via a chelation structure involving one carboxylic oxygen and the phenolic oxygen. Phthalate bonded to goethite probably in a binuclear fashion (involving only one of the two carboxylate groups), and 2,4-dihydroxybenzoate resembled salicylate in its bonding. Benzoate weakly adsorbed as evidenced by the observation that adsorption occurred only at high solid concentrations. Phenol and o-nitrophenol did not adsorb at all. Adsorption isotherm experiments employing (^{14}C) organic tracer and/or ultraviolet techniques qualitatively verified the CIR/FTIR findings.

Results demonstrated the importance of salicylate-, phthalate-, benzoate- or phenolic-type groups in adsorption on this soil metal oxide.

The interaction of organic compounds with inorganic colloids has two types of implications: the association can alter the transport and fate of the contaminant, and the presence of organics can alter the state of aggregation of the colloid, and thus its interaction with the aquifer matrix. The permeability of a soil or aquifer governs the convective flow of water through it and, thereby, the transport of dissolved organic molecules. The permeability, in turn, is strongly influenced by the state of aggregation of the clay particles within the soil or aquifer. As the clay deflocculates or swells, the permeability decreases, and as the clay flocculates or shrinks, the permeability increases. It is important, therefore, to understand the interactions between organic molecules and clay particles and how these interactions affect the flocculation and swelling of clays.

The effect of several organic molecules on the flocculation and swelling of Na-saturated Upton montmorillonite, a well-known clay, was reported. The organic molecules were selected as being representative of different classes of organic molecules having characteristic structures and functional groups. To determine the effects of these molecules on flocculation, solutions containing them were mixed with the clay to form dilute suspensions. The absorbance, A , of each suspension was then measured by means of an infrared spectrometer at a frequency where the radiation was scattered but not absorbed. According to the theory of light scattering, A is proportional to the square of the floc volume and, hence, is a measure of the degree of flocculation. Similar suspensions were also used to determine the value of m_w/m_c , the mass ratio of water to clay, that existed in each suspension after excess solution was expressed from it under an applied

pressure of 3 atm (3.04×10^5 Pa). The value of m_w/m_c can be regarded as a criterion of the degree of swelling of the clay.

The results lead to the conclusions that (1) organic molecules affect the flocculation and swelling of clays, (2) any given organic molecule may affect flocculation and swelling differently, (3) one factor affecting both flocculation and swelling is the degree of ionization of the organic molecule, and (4) the organic molecule can affect flocculation and swelling without being adsorbed.

The alteration in permeability due to flocculation or swelling will reduce the transport of organic contaminants associated with the mobile phase of groundwater systems. However, many organic contaminants, particularly ionogenic solutes, bind to inorganic colloids. If the colloids are mobilized and advectively transported, the migration of the contaminant will be enhanced. Mobile inorganic colloids may exist in groundwater as a result of dispersion of clay-sized materials or polymerization/nucleation of inorganic solids in the aqueous phase. These stable colloids can enhance the migration of contaminants that bind strongly to their surfaces. Sorption experiments of quinoline ($pK_a = 4.93$), aminonaphthalene ($pK_a = 3.95$), and carbazole on amorphous silica, montmorillonite, and a natural clay demonstrate how ionogenic and hydrophobic compounds sorb to typical subsurface mineral surfaces. Contaminant binding was investigated in various electrolyte and cosolvent mixtures to affirm the sorption mechanisms and generalize about the possibility of colloid-assisted transport.

The ionogenic compounds (quinoline and aminonaphthalene) were sorbed significantly by all sorbents through electrostatic interaction while carbazole was weakly bound. Charge location was significant because quinoline was more strongly sorbed over aminonaphthylene at comparable ionization fractions. The effect of ionic strength, electrolyte, and cosolvent on sorption was consistent with

DISCUSSION TOPICSThe Influence of Sorbent Concentration on Apparent Partition Constants*

The transport and biogeochemical cycling of hydrophobic organic compounds (HOCs) in aquatic environments are strongly influenced by their distribution between aqueous and nonaqueous phases. The extent and rates of these sorption reactions are controlled by solute, sorbent, and environmental properties. In the case of relatively nonpolar HOC, a large number of experimental observations have led to an organic phase partitioning model to describe aqueous sorption. Sorption isotherms can be generally described by linear partition coefficients, K_p (L/kg), and are not influenced by sorbate competition. K_p can be well predicted by the solute's aqueous phase activity coefficient and the organic matter fraction of the sorbent. Sorption is seen to be analogous to a partitioning process where HOCs dissolve into the organic matter coating of a heterogeneous sediment or soil matrix (i.e., sorption is volume- or mass-dependent and not surface-area- or specific-site-dependent).

This mechanistic view of sorption (as well as our ability to predict K_p in a range of environmental situations) is severely challenged by a number of investigations which report that the experimentally determined concentration distribution ratio, D_c , decreases with the concentration of suspended solids (P) used in batch sorption experiments. D_c does not necessarily represent the ratio of thermodynamic aqueous and nonaqueous phases. There are several possible explanations for these observations:

*This summary was contributed by J. C. Westall and B. Brownawell.

electrostatic and solvation considerations, with cosolvent inducing a dramatic reduction in sorption. The results imply that transport of ionizable N-heterocyclic compounds on mobile mineral constituents will be significant only at low pH or where large colloid loads exist. Colloid-assisted transport of hydrophobic compounds on mineral surfaces is not expected unless organic coatings are present.

Research needed to improve predictions of organic contaminant-clay interactions and to assess the importance of colloid-assisted transport was identified. Research areas include (1) nature, concentration, and surface properties of inorganic colloids; (2) molecular aspects of surface reactions of ionogenic and hydrophobic organic compounds on mineral surfaces; (3) the role of adsorbed DOM on surface reactivity, and (4) lability and reversibility of organic contaminant/inorganic colloid complexes and their susceptibility to microbiological alteration.

(1) Incomplete separation of sorbed and dissolved phases in typical batch sorption experiments can lead to erroneous estimates of actual sorbed and dissolved concentrations when crossover phases are not accounted for. For highly sorbed HOC, colloid-sorbed compounds in the analytically determined aqueous phase will contribute to that measurement. Because the concentration of colloids is known to increase with P , D_c will decrease with P as the colloid-sorbed phase becomes more important. On the other hand, when $K_p \times P$ becomes small (i.e., in experiments where the fraction sorbed is quite low), analytical separation and measurement of the sorbed phase is difficult, and contamination of water (and associated dissolved solutes) in the solid phase measurement can be very important. In this case, D_c increases with decreasing P , as residual water becomes more important.

(2) An increase in suspended solids concentrations may result in an increase in aggregation and aggregate size of soil or sediment. An increased state of aggregation may block sorption sites or volumes. It has also been suggested that increased particles may compete for sorption sites by an unknown mechanism. These possible effects are at odds with the organic phase partitioning model which assumes that sorption is a volume-dependent process where all organic matter is accessible to sorption. Alternatively, increased aggregate size is expected to impede sorption kinetics through an intraparticle diffusion mechanism. Thus, solids concentration may have an effect on nonequilibrium measurements of D_c .

(3) When radiolabeled HOCs are used in batch sorption experiments, small quantities of soluble, radiolabeled contaminants may contribute to low measured D_c , and would result in a decreasing D_c as P increases.

(4) Increasing the solids concentration may affect the structure of solvency of water in the bulk solution and affect aqueous phase activity coefficient negatively. However, available data suggest that this possibility can be safely ignored.

Several studies have shown a constant D_c when crossover phases were minimized or accounted for, or when the dissolved phase activity was directly measured without using artifact-prone phase separations. It is likely that many instances of observed sorbent concentration effects on D_c are due to problems associated with incomplete phase separations, and also to possible nonequilibrium effects [explanation (2)]. Sorption experiments need to be "fine-tuned" to minimize the potential artifacts noted above. Future studies of sorbent concentration effects should carefully determine the amount and properties of crossover phases, or use nonseparation methods to determine D_c .

Sampling the Subsurface Environment for Colloidal Materials:
Issues, Problems, and Techniques*

Our understanding of the subsurface environment is necessarily conditioned and limited by the techniques we use to characterize it. The discussion addressed several of the aspects of well (or other sampling point) installation and sampling which may affect studies of groundwater colloids. Because the intention was to develop a reasonably complete list of potential issues, no individual study or locale will be affected by all of the points raised; however, the underlying issues require consideration in the design and interpretation of colloid studies.

Drilling Techniques: Drilling operations, by their nature, disrupt the subsurface environment. The drilling redistributes materials and creates fine particles as a result of the occurring and abrasion. In addition, many drilling techniques involve the injection of foreign materials into the borehole -- drilling muds,

*This summary was contributed by R. W. Buddemeier.

water, compressed air, etc. In general, boreholes designed for colloidal transport investigations should be installed by the least disruptive technique available; for shallow holes in unconsolidated material, auguring is probably the method of choice. In deeper holes or harder materials, casing drive techniques may be useful. However, there will be occasions when the more traditional drilling methods are necessary, or where one wishes to sample a well installed for some other purpose. In these situations, careful evaluation of the probable impacts of the drilling techniques and materials on the samples is essential.

Well Construction: Typical materials that go into the construction of test or monitoring wells include either plastic or metal casing; cement, sand, or gravel as a pack around the well screen; often bentonite or some similar material for a seal; and some type of well screen (frequently metal). All of these materials may have an impact on the subsurface chemical environment, and will come in contact with at least some of the water that may be drawn into the well and sampled. In particular, the sand pack may be a source of fine particles itself, or it may function as a filter medium with different characteristics from that of the aquifer with respect to well water particulate material being drawn through it.

Aquifer Characterization: To assess groundwater transport phenomena, it is essential to understand the physical and chemical characteristics of the groundwater and the aquifer that carries it. One approach to this is by use of cores obtained during the drilling process. This normally requires no disruptive impacts above and beyond what would normally occur during drilling. A second means of obtaining information about the geological system is by borehole logging techniques. These are generally benign, although some of them require additions of water. A somewhat more disruptive approach to obtaining information about the

hydrologic system involves testing of aquifer, traditionally by some sort of pump or test; however, slug tests are sometimes used in place of this approach. As a precursor to such testing, well development is performed. Although surge techniques are sometimes used to develop wells, the traditional method is prolonged and rapid pumping. The purpose of this is to remove drilling muds, and fine particles created during the course of drilling, or added with the sand pack, and generally to open up or develop the permeability of the well and surrounding aquifer. This obviously involves the dislocation and transport of particles within the system. Although the target is the artificial particles, there is no question but that this will influence naturally existing particulate material as well. Well development and pump testing thus involve serious trade-offs. They are informative and, to some extent, necessary in order to provide reasonable samples. On the other hand, they are potentially disruptive to the natural system.

Sampling: The well itself is a conduit for the surface atmosphere to contact the groundwater in an artificial fashion. In addition, waters in the zone of installation of the well are in contact not only with the atmosphere, but with the materials of construction of the well -- none of which are in any way comparable to the natural environment. For this reason, it is standard practice in groundwater monitoring to withdraw some predetermined volume of water before taking the sample, for the purpose of drawing in fresh and presumably representative formation water. Excessively rapid pumping, however, may change the natural groundwater gradient and flow patterns and may affect the distribution of suspended particles in the sampled water if the flow field is dramatically different from the natural groundwater velocities. Here again, trade-offs must be considered.

Natural Variability: Frequently, one of the problems in relating groundwater data to the geologic system is a lack of detailed knowledge about the stratigraphy and

the relative water-bearing importance of different zones within the aquifer. In an inhomogeneous aquifer, only coring and packer tests can tell you what the distribution of water-bearing zones actually is. Another factor to consider is variability over time in relation to the sampling program. Surface aquifers are seldom absolutely constant as to their chemistry, water level, or gradients, and will almost certainly exhibit seasonal changes. In some case these changes may be reflected well below the actual water table surface. In designing a sampling program, it is important to obtain enough information to distinguish between sampling uncertainty and the actual "noise" imposed on the system by natural variations. Finally, there is the issue of the zone of water table fluctuations and the capillary fringe. This is an area of interest that is normally monitored in contaminant studies because most contaminants reach the groundwater by going across the zone into the water table surface. However, from the standpoint of sampling or monitoring for particulate materials in groundwater transport, this raises a number of questions because the wetting/drying cycle near the water surface may very well result in some form of weathering, which will influence the production and the aggregation of particles. Also, there may well be as yet undetermined effects which make the water table -- the actual water surface -- a region of either enhanced transport or retardation of specific materials.

Unsaturated Zone: Finally, it is worth noting that most contaminants travel to the water table through the unsaturated zone, whether in gas, liquid, or particulate form. Transport of fluids in the unsaturated zone is still poorly understood; transport of particles has hardly been investigated. The most common method of sampling soil moisture in the unsaturated zone is by use of the suction lysimeter. This device has pores on the order a few microns diameter, and there has been no characterization of its behavior with respect to colloidal particles. At first

guess, one would assume that it would do a reasonably good job of excluding them from the water samples collected.

In applying these various considerations to any planned study or the results of an existing study, the question of scale is important. If monitoring wells are in close proximity to each other, or to a source of contamination, then the problems associated with the withdrawal of large volumes of water, or with rapid pumping, are much greater. In a setting where the installations are in close quarters, withdrawal of a significant amount of water may induce the flow that one is attempting to study in its natural state, may alter the flow patterns, or may disrupt a large enough zone of the aquifer so that the experiment observes no natural conditions at all. When larger distances are involved, the disruptions of flow or aquifer alteration immediately around the well installation becomes somewhat less important, if the system is allowed to stabilize after installation. In this case, the assumption would be that there is enough undisturbed aquifer so that the flow system in general is representative of the natural state.

Environmental Significance of Colloidal Transport

The purpose of this portion of the meeting was to delimit the types of contaminants and types of subsurface environments for which colloidal transport might be particularly important. Several specific questions were presented and the discussion of those topics is described.

1. What Colloids are Important?

In general, it was felt that much more is known about organic colloids than about inorganic colloids. Three categories on organic colloidal material were

discussed: (a) "biocolloids", such as bacteria, spores, or viruses, or fragments resulting from lysis of these organisms; (b) humic substances, high molecular weight polymers or aggregates resulting either from leaching of organic matter from the surface, from decomposition and polymerization of subsurface microbiota, or from kerogen deposited during formation of sedimentary aquifers; and (c) nonaqueous-phase liquids, including colloidal-sized oil droplets or detergent micelles which may be associated with waste disposal activities. Very little is known about the concentrations or properties of these colloids. In the saturated zone, the total concentration of dissolved organic carbon ranges from 0 to approximately 20 mg carbon/L, of which about 50% is high molecular weight (>1000-dalton) macromolecules.

Very little is known about the quantities or character of inorganic colloids in the subsurface. The nature of inorganic colloids is likely to be a function of the lithology and chemistry of the system, and may vary considerably with changes in aqueous chemistry of the groundwater.

2. Where are Colloids Important to Transport?

Organic colloids may be of particular importance to contaminant transport in sites which codispose highly organic leachates, particularly if the leachate is basic, which will favor mobilization of the organic matter. Changes in groundwater chemistry due to codisposal of either acidic or basic wastes can result in formation of inorganic colloids. From a hydrogeological perspective, aquifers that might permit rapid flow through larger pores or channels would be of concern. Karst aquifers, very porous aquifers composed of large and heterogeneous material, or fractured terrain could permit rapid migration of colloidal particles and associated contaminants. The velocity of flow, per se, may be of limited influence

to the deposition of colloidal particles, but may promote detachment of particles which have been deposited. Very little is known about the relationship between flow velocity and its implications to particle detachment.

3. For What Contaminants Will Colloid Interactions Be Significant?

For organic contaminants, the potential for association with organic colloids increases with the hydrophobicity of the contaminant. Compounds with an octanol-water partition coefficient $>10^5$ can exhibit a significant enhancement in mobility due to association with mobile colloids. Ionogenic organic contaminants may associate strongly with inorganic colloids with $K_{Na} >1000$, if the pH of the groundwater promotes ionization of the compound. The significance of adsorption of inorganic contaminants to colloids will be related to the charge-to-radius ratio of the contaminant. Precipitation of inorganic solutes will be dominated by heterogeneous nucleation.

4. What Hydrodynamic Properties Promote Colloid Transport?

Fractured, highly porous, or karst aquifers will promote colloid transport. The presence of surfactants, perhaps due to codisposal of wastes, will also enhance the potential for colloid-assisted transport.

5. What are the Greatest Concerns for Environmental Health or Bioavailability?

Four areas of concern were discussed that raised significant health and environmental concerns:

(a) Association of contaminants with colloids could increase the movement or dissemination of hazardous wastes through the environment. Because design

criteria for disposal of hazardous wastes do not account for the potential role of colloids in contaminant transport, risks to health or the environment may be more significant than currently calculated.

(b) The potential for microbial degradation of contaminants may be affected by the presence of mobile colloids in the subsurface environment. Compounds bound to colloidal particles may not be available for uptake and metabolism by microbiota. Conversely, organic colloidal material may serve as a substrate for bacteria and enhance growth and promote degradation of contaminants. There does not seem to be sufficient information available at this time to evaluate the significance of these interactions.

(c) The discussion of colloid transport highlighted the potential significance of pathogen transport through aquifers. The same interactions of physical, chemical, and hydrodynamic factors which would govern the transport of colloidal particles would pertain to the movement of viruses and bacteria. Advances in understanding of colloid transport will provide insights on the mobility of pathogens through the subsurface.

(d) Association of contaminants with colloids raised concerns about the possibility for enhanced biological exposure to contaminants. Compounds generally considered to be highly retained by aquifers could be transported to wells or to surface waters, leading to ingestion by humans or by feral organisms. The potential increase in risk of human exposure to toxic contaminants highlights the need for research to improve capabilities to accurately predict the transport of contaminants through the subsurface environment.

IDENTIFICATION OF RESEARCH NEEDS

The participants decided to divide into three groups to identify research needs in specific areas: (a) the importance of organic colloids to contaminant transport; (b) the importance of inorganic colloids to contaminant transport; and (c) hydrodynamic and hydrogeochemical aspects in colloid transport. However, before breaking into individual groups, the participants met together to discuss a research need that transcended any individual speciality.

1. Occurrence, Characterization, and Sampling of Subsurface Colloids

There was unanimous agreement that much more needs to be learned about where and at what concentration colloids exist in subsurface systems. Basic characterization of the chemical and structural properties of the colloidal particles is essential. However, great care needs to be exercised so that sampling procedures do not introduce artifacts into the analyses. In recognition of the problems addressed in the discussion of sampling problems, an effort to investigate colloids truly suspended in situ will require several precautions during groundwater sampling:

- (1) To minimize the inclusion of immobile soil solids in the water sample, pumping should be performed at very low volumetric flow rates (e.g., 100 mL/min).
- (2) Under such a slow pumping regime, it is critical to minimize the standing well water to be flushed by using packers, and parameters such as temperature, conductivity, dissolved oxygen, and pH must be monitored to ascertain when sufficient flushing is complete.
- (3) Once the water arrives at the ground surface, it must not be filtered because many studies have demonstrated the ability of filters to collect submicron particles.

(4) If precautions are not taken to exclude all contact with air, the introduction of oxygen can lead to colloid production (esp. Fe(III) oxides).

(5) Finally, water samples should be stored in the dark and at temperatures comparable to those in situ to minimize colloid ripening, aggregation, or other transformations.

There was a suggestion that a practical guidebook is needed on the problems of sampling colloidal material to provide researchers with a consistent set of procedures. Only by standardizing sampling methods and sample handling will a consistent and comparable data base be assembled on colloidal particles in groundwater systems.

The development of new approaches to sampling colloids was encouraged. Suggestions included in situ observation using fiber optic devices for light scattering and spectrophotometric or fluorescence analyses. "Miniature" wells, perhaps drilled with lasers, might permit sampling or direct observation with minimal disturbance of the aquifer.

2. Importance of Organic Colloids to Contaminant Transport

A subcommittee of the attendees of the workshop considering the priorities for research in the area of the role of organic colloids in subsurface transport of contaminants identified the following research needs:

1. A detailed intercomparison of methods for collection and concentration of organic colloids is needed. Filtration techniques versus adsorption techniques may influence the types of organic colloids collected from the subsurface (e.g., polar vs hydrophobic colloids, different molecular weight ranges, amounts of inorganic matter associated with the organics, and seasonal variations in colloids).

2. Rigorous chemical characterization of the forms of carbon present in the colloids (e.g., aliphatic vs aromatic, polar vs nonpolar functional groups, etc.) is required, followed by physical characterization of the colloids (e.g., molecular weight distribution, light scattering, x-ray diffraction, etc.).
3. The physicochemical properties of organic colloids must be studied as a function of bulk solution properties as pH, ionic strength, major element ions (i.e., Ca, Mg, Fe, Al).
4. The factors that may influence the mobilization/immobilization of organic colloids in the subsurface environment must be examined in relation to the properties of the subsurface media - binding, aggregation, disaggregation.
5. A set of experimental conditions should be identified such that sorption studies of colloids can be calibrated and intercompared.
6. A study is needed to define the influence of the use of ambient levels vs "elevated" levels of organic colloids in sorption studies.
7. The role of subsurface microbial populations as possible sources or sinks of organic colloids needs to be defined.
8. There is a critical need for research on the role of colloids in transport processes occurring in the unsaturated zone of the subsurface environment.
9. Detailed studies of the kinetics and reversibility of sorption processes occurring on organic colloids as well as equilibrium studies need to be performed.
10. The role of potential modifiers of the sorption processes need to be investigated, particularly in the near-field relative to sources of contaminants (i.e., hazardous waste disposal dumps). Potential modifiers to be investigated should include, at a minimum, cosolvents, immiscible phases, competing sorbants, detergents, or other surfactants.

3. The importance of Inorganic Colloids in Subsurface Transport

A major problem affecting the study of inorganic colloids is one of definition -- What constitutes a colloid? Several lines of research to address this issue were proposed:

1. Analytical definition of a colloid could be based on particle size as defined by laser light or neutron-scattering studies.
2. Chemical definition is more complex. Should the colloid be examined with and/or without coatings? Extraction of the coating in a nondestructive fashion will not be easy. The cleansed colloids should be structurally examined using techniques such as X-ray or electron diffraction, scanning electron microscopy and transmission electron microscopy, neutron activation, and wet chemical analysis.
3. Electrophoretic mobility studies and surface charge measurements of both cleaned and uncleaned colloids should also be performed. This would serve to characterize the charge properties of these systems.
4. Further characterization using both dry (ESCA, FTIR), and in situ surface techniques (RAMAN and CIT-FTIR) would be valuable.
5. Coatings should next be investigated concerning their physical and chemical characteristics to determine how these coatings affect the behavior of the primary particles.

Further studies are needed with both model colloids and natural colloids (with their surface coatings removed). Such studies include:

1. Basic laboratory studies involving the adsorption of both inorganic and organic species onto field-recovered and model colloids (e.g., polystyrene latex particles). These could be on both coated and noncoated colloids. Coatings could be made to duplicate those found in the field.

2. Model systems to test the particle-particle dynamics of both coated and uncoated particles. Laboratory column studies in which a model colloid coated with organics is introduced for purposes of studying its interaction with the soil bed.
3. Combined field and laboratory studies in which field studies are designed to optimize a certain variable and laboratory studies are designed to mimic the behavior of that variable under laboratory conditions.

Several general research needs on inorganic colloidal particles were also identified:

1. A study of the dynamics and thermodynamics of coatings.
2. Carefully designed sequential extractions of coatings.
3. Speciation of adsorbed species and coatings.
4. Studies related to the chemical reactivity of low crystalline materials.
5. Better field collection of colloidal materials including their recovery without change and their cleanup.
6. Studies related to particle movement dynamics under controlled laboratory studies.
7. Tracer experiments with radionuclides in the field with both adsorbents and adsorbates attached to well-characterized colloids.
8. Studies related to the fundamental thermodynamics of the formation of humic materials.
9. Redox experiments in both the field and laboratory.
10. Particle-particle bridging studies as related to the adsorption of solutes on those particles.

4. Hydrodynamic and Hydrogeochemical Considerations

Particle migration and adsorbed contaminant transport are possible in the subsurface environment. The transport processes are well defined, and considerable experimental data are available that verify theoretical predictions when electrostatic repulsion between particles and media is not significant. However, mechanistic models are not available for predicting contaminant and colloid transport under conditions typical of the subsurface environment.

Research needs are extensive because colloid and particle transport research has been empirical until recently and no theoretical foundation is available to unify the empiricism. The dominant controlling factor in all transport processes is colloid size, and for submicrometer sizes, colloid characterization techniques are limited. Of particular importance is the distribution of sizes, not the average size, since transport cannot be predicted from a mean size. There is some doubt as to the usefulness of colloidal tracers not representative of the actual physical system until mechanism controlling colloid collection are well defined. The issue of deposit formation and erosion is critical to assess contaminant migration and potential isolation but it cannot be predicted at this time.

Specific research needs identified by the group included:

1. Development of techniques to characterize colloids, especially in terms of properties affecting their transport, such as size and surface charge. The use of tracers was suggested.
2. Colloid formation needs to be elucidated and the role of processes such as precipitation needs to be clarified.

3. The deposition of colloids on aquifer solids needs to be examined in relation to the processes resulting in changes in permeability. The controls exerted by both advective water flow and by chemistry of the system need to be studied.
4. Transport must be studied in the laboratory under controlled conditions that mimic field conditions. Model systems should consider both porous and fractured aquifers and unsaturated as well as saturated environments.
5. Natural hydrogeochemical systems must be examined to provide field data that can be used as analogs for other field situations.

APPENDIX I

AGENDA OF THE MEETING

INTERACTIVE SEMINARS IN THE SUBSURFACETRANSPORT OF CONTAMINANTS IN THE SUBSURFACE:
THE ROLE OF ORGANIC AND INORGANIC COLLOIDAL PARTICLES

Organized by: Dr. John F. McCarthy
Environmental Sciences Division
Oak Ridge National Laboratory
(615) 576-6606

and: Dr. Frank J. Wobber
Subsurface Transport Program
U.S. Department of Energy/ Office of Energy Research
(301) 353-5549

OCTOBER 5 - 8, 1986
MARINE RESOURCES CENTER, MANTEO, NORTH CAROLINA

Objective of the Meeting: To review our current understanding of the potential significance of natural colloidal particles, including organic macromolecules and inorganic colloidal particles, in modifying the mobility of chemical substances in the subsurface environment, and to prioritize long-term fundamental research needs.

Sunday Evening, October 5
- Reception and mixer

Monday, October 6
8:00 - Purpose and Objective of Meeting
(J. McCarthy, ORNL)
8:30 - Scope of DOE Subsurface Transport Program
(F. Wobber, DOE)

I. REVIEW OF FUNDAMENTAL THEORY

Objective: The purpose of this session is to establish the theoretical framework for the interactions between contaminants (organics, metals, and radionuclides), the colloids, and the aquifer itself.

9:00 - Filtration Theory
(J. Hunt, U. Cal. Berkeley)
10:00 - Solution Theory
(P. Gschwend, MIT)
11:00 - Break

Monday, October 6

II. ORGANIC COLLOID PARTICLES (continued)

II.A. INTERACTIONS WITH INORGANIC CONTAMINANTS:

- 11:30 - Binding of Metals to Organic Colloids in Dilute Solutions
(E. M. Perdue, Georgia Tech)
- 12:00 - LUNCH
- 1:00 - Association of Radionuclides with Organic Colloids
(W. Penrose, ANL)

II.B. INTERACTIONS WITH ORGANIC CONTAMINANTS:

- 1:30 - Physical and Chemical Factors Influencing the Solubility Enhancement by Organic Material
(C. Chiou, USGS)
- 2:00 - Changes in Binding Affinity During Subsurface Migration
(J. McCarthy, ORNL)
- 2:30 - Break
- 3:00 - Effect of Partitioning to Colloids on the Migration of Dioxins and PCBs in Soil Columns
(J. Means, Univ. of Maryland)

II.C. INTERACTIONS IN THE SUBSURFACE ENVIRONMENT:

- 3:30 - Potential Effects of Primary Aggregation Phenomena on Partitioning of Contaminants into Organic Substances in Groundwater
(J. Leenheer, USGS)
- 4:00 - Movement of Colloids in Groundwater: Field Investigations
(T. Rees, USGS)

Tuesday, October 7, 1986

REVIEW OF FUNDAMENTAL THEORY, PART II

- 8:30 - Electrostatic Theory
(M. Anderson, Univ. Wisconsin; J. Davis, USGS; and P. Low, Purdue Univ.)

III. CLAY COLLOIDS

- 9:30 - Scavenging of Thorium Isotopes in Natural Waters
(P. Santschi, EAWAG)
- 10:00- Metal Sorption Processes on Mineral Surfaces
(J. Davis, USGS)
- 10:30- Break
- 10:45- Behavior of Some Benzoate Type Compounds at the Geothite/Aqueous Solution Interface
(M. Anderson, Univ. Wisconsin)
- 11:15- Interactions of Organic Contaminants with Clays
(J. Zarchara, PNL)
- 11:45- Clay-Water-Organic Interactions and the Effect on Flocculation and Deflocculation
(P. Low, Purdue Univ)
- 12:15-1:00 - Lunch

IV. DISCUSSION TOPICS

Objective: To focus the individual expertise of the participants on interdisciplinary topics that are critical for understanding the role of colloids in the subsurface environment.

IV.A. THE INFLUENCE OF SORBENT CONCENTRATION ON APPARENT PARTITION CONSTANTS:

- 1:00 - Review of the problem (B. Brownawell)
- 1:50 - Group discussion concerning the significance to subsurface transport

IV.B. TECHNICAL ASPECTS OF RESEARCH ON COLLOIDS IN THE SUBSURFACE:

- 2:15 - Sampling and storage of colloids (P. Gschwend)
- 2:35 - Group discussion of technical and analytical problems in colloid research in the lab and in the field
- 3:30 - Break

IV.C ENVIRONMENTAL SIGNIFICANCE OF COLLOIDS

- 3:45 - Group interaction to attempt to delimit and prioritize the types of contaminants and subsurface environments in which colloids may play a significant role in altering contaminant mobility (J. Zachara, discussion leader)

Wednesday, October 8, 1986

V. IDENTIFYING RESEARCH NEEDS

- 9:00 - Identification of three to four major research areas, based on preworkshop input and group discussions
- 9:30 - Participants separate into working groups to define specific research needs and establish research priorities
- 10:30- Reports assembled into a list of research needs
- 11:45- DOE research plans and proposal preparation
- 12:00- Adjournment

APPENDIX II

LIST OF MEETING PARTICIPANTS

Dr. Calvin C. Ainsworth
Battelle, Pacific NW Laboratory
P.O. Box 999
Richland, WA 99352
509/375-2670

Dr. Marc. A. Anderson
Water Chemistry Program
660 N. Park Street
Madison, WI 53706
608/262-2470

Dr. Michael A. Anderson
Savannah River Ecology Lab.
Drawer E
Aiken, SC 29801
803/725-2472

Dr. Joel E. Baker
Environ. Eng. Sciences
122 CivMinE Bldg.
University of Minnesota
Minneapolis, MN 55455
612/625-5522

Dr. Roger Bales
Dept. Hydrology & Water Resources
University of Arizona
Tucson, AZ 85721
602/621-7113

Dr. Bruce Brownawell
Department of Chemistry
Oregon State University
Corvallis, OR 97331
503/754-2591

Dr. Robert W. Buddemeier
Lawrence Livermore National Laboratory
University of California
P.O. Box 808
Livermore, CA 94550
415/422-1100

Dr. Michael M. Carrabba
EIC Laboratories, Inc.
111 Downey Street
Norwood, MA 02062
617/769-9450

Dr. Shizheng Chen
Agronomy Department
Purdue University
West Lafayette, IN 47906
317/494-8093

Dr. Cary T. Chiou
U.S. Geological Survey
Water Resources Division
Box 25046
Denver Federal Center
Denver, CO 80225
303/236-3608

Dr. James Davis
Water Resources Division
U.S. Geological Survey, MS-65
Menlo Park, CA 94025
415/323-8111 Ext. 2145

Dr. Brian A. Dempsey
212 Sackett Hall
Pennsylvania State University
Dept. of Civil Engrg.
University Park, PA 16802
814/865-1226

Dr. Steven J. Eisenreich
Env. Engineering Sciences
122 CivMinE Bldg.
University of Minnesota
Minneapolis, MN 55455
612/625-3082

Dr. Alan Elzerman
Environmental Systems Engineering
Clemson University
Clemson, SC 29634-0919
803/656-5568

Dr. F. T. Ewart
B10.30
Harwell Laboratory
Oxford, OX11 0RA UK
235/24141

Dr. Michael J. Graham
Battelle Pacific Northwest Labs.
P.O. Box 999/Sigma V Bldg.
Richland, WA 99352
509/376-8314

Dr. Philip M. Gschwend
Assistant Professor
Department of Civil Engineering
48-154
Massachusetts Institute of Technology
Cambridge, MA 02139
617/253-1638

Dr. Ronald W. Harvey
U.S. Geological Survey
345 Middlefield Rd., MS-465
Menlo Park, CA 94025
415/323-8111 Ext. 2834

Dr. James Hunt
Dept. Civil Engr.
University of California
Berkeley, CA 94704
415/642-0948

Dr. Cady Johnson
Miffin & Associates
2700 Sunset
Suite 13
Las Vegas, NV 89120
702/798-0402

Dr. Pierre LaFrance
INRS-EAU
Universite de Quebec
2700 Einstein, C.P. 7500
Ste-Foy, Quebec G1VC7, Canada
418/654-2543

Dr. Jerry Leenheer
U.S. Geological Survey
Water Resources Division
Box 25046
Denver Federal Center
Denver, CO 80225
302/236-1925

Dr. Philip F. Low
Department of Agronomy
Purdue University
Lafayette, IN 47907
317/494-8047

Dr. Donald L. Macalady
Professor of Chemistry & Geochemistry
Colorado School of Mines
Golden, CO 80401
303/273-3996

Dr. M. Machesky
Pennsylvania State University
Geosciences Dept., 208 Deike
University Park, PA 16802
814/863-0170

Dr. R. L. Malcolm
U.S. Geological Survey
Water Resources Division
Box 25046
Denver Federal Center
Denver, CO 80225

Dr. John F. McCarthy
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831-6036
615/576-6606

Dr. Jay C. Means
Chesapeake Biology Laboratory
P.O. Box 38
Solomons, MD 20688
301/326-4281

Dr. Cass T. Miller
The University of North Carolina
Dept. of Env. Sciences & Eng.
School of Public Health 201H
Chapel Hill, NC 27514
919/966-2643

Dr. Laila A. Moustafa
104 Westbury Ct.
Chapel Hill, NC 27514
919/942-0430

Dr. William Penrose
Argonne National Laboratory
ER-203
Argonne, IL 60439
312/972-4262

Dr. E. Michael Perdue
Georgia Institute of Technology
School of Geophysical Sciences
Atlanta, GA 30332
404/894-2857

Dr. Wilfred L. Polzer
Environmental Science, HSE-12
Los Alamos National Laboratory
Los Alamos, NM 87545
505/667-3073

Dr. Terry F. Rees
U.S. Geological Survey
Box 25046, MS 424
Denver Federal Center
Denver, CO 80225
303/236-4053
FTS 776-4053

Dr. Lawrence E. Roberson
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831-6036
615/576-6606

Dr. Peter H. Santschi
EAWAG, Swiss Federal Institute of Water Research
CH-8600 Dübendorf, Switzerland
8235111

Dr. Alan T. Stone
405 Ames Hall
Johns Hopkins University
Baltimore, MD 21218
301/338-8476

Dr. Cynthia L. Stubbs
Savannah River Ecology Lab.
Drawer E
Aiken, SC 29801
803/725-2472

Dr. I. Suffet
Env. Studies Institute
Drexel University
Philadelphia, PA 19104
215/895-2270

Dr. John E. Tobiason
Dept. of Geol. and Env. Eng.
Johns Hopkins University
Baltimore, MD 21218
301/338-7092

Dr. Vijay S. Tripathy
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831-6036
615/574-7824

Dr. Richard F. Unz
116 Sackett Bldg.
Pennsylvania State Univ.
University Park, PA 16802
814/863-2940

Dr. John C. Westall
Chemistry Dept.
Oregon State University
Corvallis, OR 97330
503/754-2591

Dr. Rudolph C. White
American Petroleum Institute
1220 L Street, Northwest
Washington, DC 20005
202/682-8225

Dr. Frank J. Wobber
Ecological Research Division, ER-75
Office of Health and Environmental Research
Office of Energy Research
U.S. Department of Energy
Washington, DC 20545
301/353-5549

Dr. John M. Zachara
Earth Sciences Department
Battelle Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99320
509/375-2993