CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: Soil Science Society of America Annual Meeting

DATE/PLACE OF TRIP: October 21-26, 1990, San Antonio, TX

AUTHOR: D. Turner

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AUTHOR: D. Turner

PERSON PRESENT: CNWRA
David Turner

BACKGROUND:

This meeting is a joint annual meeting of the Soil Science Society of America, the Crop Science Society of America, and the Agronomy Society of America. Talks presented in the Soil Physics and Soil Chemistry Divisions of the SSSA included research that is applicable to sorption modeling in variably saturated media.

CONFERENCE TOPICS:

Topics of interest at the meeting included: colloidal transport of actinides, sorption and geochemical equilibria modeling, subsurface solute transport, and the results of field and laboratory experiments. Abstracts presented at the meeting were published in a single volume entitled "1990 Agronomy Abstracts", available in the CNWRA library.

SCIENTIFIC ACTIVITIES:

I attended sessions sponsored by the Soil Physics and Soil Chemistry to follow current research in coupled hydrogeochemical transport. I have contacted principal investigators and requested reprints and copies of articles on research relevant to the sorption modeling project of the CNWRA.

PROBLEMS ENCOUNTERED:

None

PENDING ACTIONS:

None

RECOMMENDATIONS:

Much of the research presented at the meeting was not, at first glance, directly applicable to radionuclide migration and retardation. However, a number of the studies dealt with processes and utilized computer codes that are relevant to the objectives of the sorption modeling project of the CNWRA. It is recommended that several of the computer codes (e.g., LEACHM, MINTEQA2/VADOFT) presented be evaluated for application to sorption modelng, and the results and methodology of several studies of solute transport be examined more in depth.

SIGNATURE:

David R Turner

David Turner

11/12/90

Date

CONCURRENCE SIGNATURES:

John L Russell

John L. Russell

11/12/90

Date

Allen R. Whiting

Allen R. Whiting

11/12/90

Date

SOIL SCIENCE SOCIETY OF AMERICA

54th Annual Meeting

SOIL SCIENCE DIVISIONS

President: W. R. Gardner, University of California, Berkeley, CA

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Chair: G. C. Topp, Central Experimental Farm, Land Resource Research Institute, Ottawa, Ontario, Canada
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Chair: D. C. Adriano, Savannah River Ecol. Lab., Aiken, SC
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S-3 — Soil Microbiology and Biochemistry
Chair: J. M. Duxbury, Cornell University, Ithaca, NY
Chair-Elect: J. W. Doran, USDA-ARS, Lincoln, NE

S-4 — Soil Fertility and Plant Nutrition
Chair: N. W. Christensen, Oregon State University, Corvallis, OR
Chair-Elect: G. W. Hergert, University of Nebraska, Lincoln

S-5 — Soil Genesis, Morphology, and Classification
Chair: N. E. Smeck, Ohio State University, Columbus, OH
Chair-Elect: M. J. Singer, University of California, Davis

S-6 — Soil and Water Management and Conservation
Chair: J. W. Bauder, Montana State University, Bozeman, MT
Chair-Elect: Birl Lowery, University of Wisconsin, Madison, WI

S-7 — Forest and Range Soils
Chair: J. R. Boyle, Oregon State University, Corvallis, OR
Chair-Elect: J. A. Burger, Virginia Polytech Institute, Blacksburg, VA

S-8 — Fertilizer Management and Technology
Chair: Jim Thorup, Chevron Chemical Co.-Fertilizer, San Ramon, CA
Chair-Elect: B.R. Bock, TVA-NFDC, Muscle Shoals, AL

S-9 — Soil Mineralogy
Chair: J. W. Stucki, University of Illinois, Urbana, IL
Chair-Elect: Hideomi Kodama, Agriculture Canada, Ottawa, ON

SOIL SCIENCE SOCIETY OF AMERICA
ANNUAL MEETING, SAN ANTONIO, TEXAS
OCTOBER 21-26, 1990

The following is a brief summary of abstracts and poster sessions presented from October 21-26, 1990 at the 82nd Annual Meeting of the Soil Science Society of America, the American Society of Agronomy, and the Crop Science Society of America in San Antonio, TX. Presentations summarized are primarily related to geochemisty, fluid flow, and adsorption in the unsaturated zone, and represent the results of a combination of field, laboratory, and computer modeling studies. In general, those studies considered relevant to characterization of the Yucca Mountain Site are summarized. Copies of the meeting program and abstracts are available in the CNWRA Library.

Summary of Talks and Poster Sessions--Monday, October 22, 1990

Talk/Author: AFFINITY CONSTANTS AND BEHAVIOR OF Cd SORPTION IN SOME ACID SOILS: S. Kuo* and E.J. Kellum, Washington State Univ.

Summary Cd-sorption is pH dependent in a variety of soils. This dependence is modeled using one- and two- surface Langmuir models, which have generally been shown to be oversimplifications. This study proposed an alternative model: the simplified surface complexation model. Potentiometric titration was used on acid soils ranging in pH from 5 to 5.5, and determined protonation constants (two-site acidic constants pKa_1 and pKa_2) were used to estimate the number of exchange sites. Cd retention was observed to increase with pH. References cited include: Anderson and Christensen (1988); Turner and Steele(1988).

Talk/Author: EXPERIMENTAL OBSERVATIONS OF CADMIUM SORPTION TO NATURAL SORBENTS OF MIXED MINERALOGY: C.E. Cowan*, J.M. Zachara, S.C. Smith, and C.T. Resch, Batelle Pacific Northwest Laboratories, Richland, WA.

Summary Cd-sorption was measured for kaolinite standards and natural kaolinite-bearing soils over a range in pH, ionic strength (I), and solute concentrations. For natural soils, one split containing Fe-oxides, and a second split with Fe-oxides removed by DCB treatment were studied. While Cd-sorption was found to increase abruptly for Fe-oxide soils at pH between 6 and 8, it was also found to be relatively insensitive to changes in I. Removal of Fe-Ox by DCB treatment was found to increase Cd-sorption, and sorption in the DCB-treated soils was found to increase with pH and decrease with increasing I. Fe-oxide was added back to these soils in two forms: amorphous FeOx and crystalline Al-goethite. The amorphous form was found to have little effect, while addition of Al-goethite resulted in sorption profiles close to those of the untreated soils. This effect was most pronounced at lower ionic strengths. In general, Layer-silicates are the dominant sorbant for pH and I conditions typical of soils (pH=4 to 5; $I < 0.01$ M).

Talk/Author: NUMERICAL SIMULATIONS OF UNSATURATED FLOW RELATED TO RADIOACTIVE WASTE DISPOSAL: B.R. Scanlon*, Bureau of Economic Geology, Univ. Texas-Austin, and P.J. Wierenga, Univ. of Arizona, Tucson, AZ.

Summary An arid system in the Chihuahua Desert of West Texas was monitored through a series of subsurface wells and tensiometers. The unsaturated zone is approximately 150m thick, essentially 10-15m of relatively coarse loam above 140m of less-permeable clay. Vertical fluid flow was numerically modelled as 1-D infiltration using the TRACRN implicit finite-difference code of Travis and Birdsell(1990), and calibrated from field observations using ^{36}C as a tracer. Sensitivity analysis were performed to evaluate the effects of mositure content, saturated hydraulic conductivity (K_s), initial water potential, and applied flux on wetting front penetration. The system was found to be most sensitive to variations in the applied flux, and wetting front penetration increases sharply as initial water potential increases by 60%. The system is relatively insensitive to K_s. 2-D models were used to investigate lateral heterogeneities. Lateral spread of perched water tables were controlled by anisotropy in the medium, and the extent depends on the magnitude of the applied flux relative to K_s.

Talk/Author: SIMULATION OF SOLUTE TRANSPORT IN VARIABLY SATURATED POROUS MEDIA BY THE MODIFIED METHOD OF CHARACTERISTICS: R.W. Healy*, U.S. Geol. Surv., Lakewood, CO.

Summary The purpose of the talk was to compare the Modified Method of Characteristics(MMOC) to Forward, Backward and Central Finite-Difference (FDM) computer techniques. The latter method is widely used, but problems of numerical dispersion and oscillation limit its application in systems with high Peclet(Pe) and Courant (Cr), which are, respectively, measures of the degree of domination of advective processes, and distance travelled during a given time step. Input includes degree of saturation(S) and head(h). The MMOC solves separately for advective and dispersive components of the advection-dispersion equation, and essentially tracks particle wandering. A FDM was derived using fine discretization and a small time step for 1-D infiltration of a solution in an unsaturated sand column. The results of MMOC and FDM are compared to this "true" solution. For Pe > 2, oscillation and dispersion effects become untractable for FDM, while MMOC remains relatively unaffected for higher Pe, and closely reproduces the observed solution.

Note: In the question period, it was noted that the MMOC does not explicitly conserve mass in the system.

Talk/Author: (Replacement for F.C. Ugolini)

Summary This talk is a survey of theory and application of clay colloid chemistry to both case studies and in a generalized sense. Microscopic evidence of colloid transport includes clays occurring as coatings along pores, and transport is restricted to pores. Fluctuations in saturation levels suggest changes in redox potential. Drainage of soils removes Fe

and Mn by organic acids, accompanied by a loss of cement. Low tension or positive pore-pressure encourages dispersion, and biological respiration keeps continuous channels open for colloid transport.

Talk/Author: SUBSURFACE TRANSPORT OF CONTAMINANTS: ROLE OF MOBILE COLLOIDAL PARTICLES: J.F. McCarthy*, Oak Ridge National Laboratory, Oak Ridge, TN.

Summary A survey of possible roles of colloids in transport of hazardous substances. The author notes that both organic and inorganic colloids are found in natural groundwaters. The lack of controlled lab-work has only recently been addressed, and several questions are being formulated, such as partitioning of a given contaminant between the solution and the colloids, where do the colloids come from, and how long do they remain in solution? The author identifies several processes that need to be evaluated: Genesis, mobilization, and suspension of colloids; Stabilization of colloids in solution, and; transport, aggregation, and filtration of colloids. He reports some of the results of a recent field study at Clemson Univ. that used ^{36}Cl to monitor the injection, velocity, and dispersion of a natural solution in the subsurface over a distance of 5m. The solution contained dissolved organic carbon (DOC), which has been proposed as a possible colloid. In general, breakthrough occurred rapidly, at about the same time for all three layers in the sampled system. Predicted breakthrough profiles agreed only poorly with observed profiles; both deeper and downstream breakthrough occurred much more rapidly than predicted. This suggests that transport somehow bypasses the porous media. Small particles are preferentially transported.

Talk/Author: PREDICTING COLLOID MOBILITY IN THE SUBSURFACE: J.R. Hunt*, Univ. of California-Berkeley.

Summary A survey of mechanisms controlling the transport and retardation of colloids in the subsurface. The theory of particle removal by surface (cake formation), straining, and physical-chemical processes is described. The ability of particles to penetrate a porous medium is dependent on particle size. For particle diameter(d_p) > 0.1*media pore size(d_m), particles will not readily enter the medium, and surface cake formation will be the dominant method of retardation. For $0.05d_m < d_p < 0.1d_m$, straining will result in a permeability reduction, and for $d_p < 0.05$, physical-chemical processes will dominate. Clean-Bed Kinetics introduces the concept of a filter coefficient(lambda), and a characteristic migration distance (1/lambda). Modeling colloid particles as spheres, there is a peak in the migration distance for a particle size $\sim 10^{-6}$ m. Double-layer electrostatic theory can also be used to describe colloid transport through capture efficiency. However, there is smearing of observed capture efficiency relative to the sharp front predicted. These discrepancies may be due to irregular particle surfaces, surface heterogeneity, or the fact that particle properties have distributions rather than point values. Finally, the talk described the theory of transport in a fractured porous media using parallel-plate geometries.

Talk/Author: DISPERSION PROCESSES IN SEMI-ARID REGION SOILS: I. Shainberg*, Inst. of Soils and Water, ARO, Israel.

Summary Stresses the importance of flocculation in controlling clay particle dispersion. The greater the tendency of a mineral to flocculate, the less dispersive and the less stable it will be as a colloid. As flocculation value (minimum electrolyte concentration needed for flocculation to occur) increases, dispersion of a given mineral will decrease. Experimental results suggest that illite has a lower flocculation value than smectite, and is therefore more dispersive.

Talk/Author: FORMATION AND TRANSPORT OF COLLOIDAL SUSPENSIONS TO SURFACE WATERS: W.P. Miller*, Univ. of Georgia-Athens, Athens, GA.

Summary Colloids are formed in surface waters primarily by two methods: Disaggregation and dispersion. Dispersion is especially critical for primary clay particles $< 2 \times 10^{-6}$ m. Colloid production is affected by soil composition. Na results in more dispersive clays, and more colloids, while Ca dampens colloid production due to flocculation. Factors leading to particle destabilization include: (1) Charge neutralization via adsorption; (2) Adsorption of bridging compounds; (3) Salt addition resulting in double-layer compression.

Summary of Talks and Poster Sessions--Tuesday, October 23, 1990

Talk/Author: ION ACTIVITIES OF CU^{2+} AND PB^{2+} IN SOILS USING COMPETITIVE CHELATION AND COMPUTER SPECIATION: T.A. Tawfic*, and W.L. Lindsay, Colorado State Univ., Ft. Collins, CO.

Summary This study used a variety of techniques to directly measure pH and activities in alkaline soils using competitive chelation with Ca as the competitive ion. This method uses metal-DTPA shake solutions with the soils of interest, and determines the unique composition where Cu and Pb are neither gained nor lost by the soil. Equilibrium speciation was also modeled using the MINTEQA2 computer code. It was determined that modeled and observed pH-activity relationships agree fairly well, and that some of the discrepancy is due to the uncertain effects of organic metal complexing.

Talk/Author: ZN^{2+} AND FE^{3+} ACTIVITY MEASUREMENTS IN CONTAMINATED SOILS: Q. Ma*, and W.L. Lindsay, Colorado State Univ., Ft. Collins, CO.

Summary Competitive chelation as described in the above abstract of Tawfic and Lindsay(1990) was used to determine Zn^{2+} and Fe^{3+} activities in three soils from Colorado. Competitive chelation increases the detection limits of these two metals, and avoids problems resulting from inorganic and organic complexes of the metal. Activities of both Zn^{2+} and Fe^{3+} are inversely related to pH, and are higher in the contaminated soils than in

uncontaminated soils. Lab results also indicate that Zn and Fe solubility in the contaminated soils is controlled by different mineral phases than in uncontaminated soils. For example, Zn solubility is controlled by $ZnSiO_4$ and Zn_2O_4 as opposed to "soil" Zn.

Talk/Author: MEASUREMENTS AND CHARACTERIZATION OF COLLOIDS IN GROUNDWATER: P.M. Gschwend*,

Summary A survey of practical considerations required prior to measurement of colloids in groundwaters. Of particular importance is the contamination of the sample resulting from the sampling techniques themselves. These include shearing of soils in the sides of the well, resuspension of solids at the bottom of the wells, and contamination by exposure to the atmosphere. An additional requirement for the adequate characterization of groundwaters is good background well control. Contamination can be minimized using careful and consistent techniques. Shearing forces can be minimized by using slow pumping rates (1 L/min) until equilibrium colloid concentration is obtained. Using packers above and below the sampling tool can isolate the sampling area from contaminants. Open-air storage of the samples should be minimized to preserve the oxidation state and P_{CO2}. All characteristics (Eh, pH, DO, etc.) will level out with slow pumping, but at times different from leveling of groundwater turbidity. The limitations on various analytical techniques is also discussed. 1mg/L is defined as the useful detection limits for most techniques. Laser light scattering is not good for a heterogeneous fluid, SEM and EDX-ray are limited by the degree of resolution (1 cubic micron), and are not suited to a heterogenous medium. Finally, the author suggests TiCeB as a better reductant than DCB. There is less dissolution of aluminum, and TiCeB can be applied at lower temperatures (25° vs. 80° C). References cited include: Gschwend and Reynolds(1988); Gschwend et al(1990)--Jour. Contam. Hydrol.

Note: The author also quoted unnamed studies that determined that artesian wells near Yucca Mountain contained no measurable colloids.

Talk/Author: ACTINIDE MIGRATION VIA FACILITATED TRANSPORT WITH COLLOIDS: A REVIEW: J.S. Gaffney*, N.A. Marley, and K.A. Orlandini, Environ. Res. Div., Argonne National Laboratory, Argonne, IL.

Summary A survey of literature relating actinide transport and colloid concentration. Particular emphasis was placed on the correlation between particle size and Pu,Am concentration. Pu and Am have high affinity for particles in the 25 to 450 nm size range, while only U is tied up in the larger fraction (450-1000 nm). The smaller fraction is also very active in tightly binding ^{228}Th, which shows up out of equilibrium with the fluids by a factor of 34. Chemistry is important, and the large fraction becomes more important in an anoxic environment. Studies in tuff in Mortandad Canyon, New Mexico and lake waters in Wales reveals that Pu activity is correlated with DOC, and K_D changes with distance migrated. For field studies, hollow fiber ultrafiltration techniques can process more water with less clogging, and is the preferred technique. DOC needs

to be characterized more carefully, and ^{13}C NMR, Laser Raman Spectroscopy, Pyrolysis Gas Chromatography, and especially Fourier Transform IR Spectroscopy (FTIR) are potential analytical methods.

Talk/Author: STUDIES OF SAMPLING AND CHARACTERIZATION OF GROUNDWATER COLLOIDS: C. Degueldre*, PSI, Villigen, Switzerland.

Summary Presents the results of three sampling studies at Grimsel, Switzerland, Pocos de Caldas, Brazil and Menzenschwand, Germany. Several groups set up colloid sampling in the Grimsel Site, and the samples were analyzed for a variety of elements by 12 different labs. Significant differences were encountered. Colloid concentration was found to be dependent on particle size, and pH changed from ~9.5 to 8 in a sample left open to air for a matter of hours. In Brazil, colloid sorption was found to decrease with the valency of the element of interest.

Talk/Author: DEVELOPMENT AND APPLICATION OF AQUEOUS GEOCHEMICAL MODELS: D.K. Nordstrom*, U.S. Geol. Survey, Menlo Park, CA.

Summary A survey of the history and development of numerical codes designed to solve geochemical problems. A few of the more prominent include: EQ3/EQ6, MINTEQA2, GEOCHEM-PC, SOLMNEQ.88, PHREEQE, WATEQ4F, PHRQPITZ, BALANCE, and HYDRAQL. These models use a variety of techniques to address the problems of modeling geochemical systems. Still needed are: sensitivity analysis of the various models; manageable kinetics, especially redox kinetics; better field data; cricial evaluation of the available thermodynamic data; and improved education in the geological and physical sciences.

Talk/Author: SELECTION OF CRITICAL STABILITY CONSTANTS: R.M. Smith and A.E. Martell*, Texas A&M University, College Station, TX.

Summary A survey of the validity and value of published stability constants. This study is the result of a systematic analysis of the available data and the conditions under which the experiments were performed. If experimental conditions or the purity of the materials used were not sufficiently documented, or T and I were not controlled, the data was discarded. Data was not necessarily discarded in cases where the calibration of the instruments was not explicitly given, but more credence was given to data were documentation was more complete. Under these guidelines, a large amount of the published data can be considered of little or no use.

Talk/Author: DEVELOPMENT AND APPLICATION OF AQUEOUS THERMODYNAMIC MODELS: THE SPECIFIC ION-INTERACTION APPROACH: A.A. Felmy* and J.H. Weare, Batelle PNL, Richland, WA and Univ. of California-San Diego, San Diego, CA.

Summary Gives the results of a new predictive model that incorporates the semi-empirical relations of Pitzer and others. Previous activity

coefficient models were relatively good for dilute solutions and for some 1:1 compounds. However, these models are less successful in predicting higher-order systems (2:2, 3:2, and 4:2) where strong ion interaction becomes less important at higher ionic strengths. Traditional ion association models attempt to add ion pairs. In contrast, the Specific Ion-Interaction approach uses virial expansion of excess Gibbs energy, and incorporates the semi-empirical Pitzer equations. This method is a reanalysis of Debye-Huckel theory and focuses on hard-core interactions. The model as presented uses all available data, and adequately models a variety of systems from zero to high concentrations. The model has been applied successfully to brines in Searles Lake, CA.

Talk/Author: ENVIRONMENTAL APPLICATIONS OF THE GEOCHEMICAL SPECIATION MODEL MINTEQA2/PRODEFA2: D.S. Brown*, USEPA, J.D. Alison, Comp. Sci. Corp., N.T. Loux, USEPA and T.L. Allison, Comp Sci. Corp.

Summary A review of the capabilities and options of the numerical codes MINTEQA2/PRODEFA2. A flow chart of the logic structure and expressions solved by the systems is given. MINTEQA2 is an equilibrium model using a Newton-Raphson iteration technique. Seven different sorption models are available, and up to 40 components and 500 species can be considered. Other codes indirectly coupled to MINTEQA2/PRODEFA2 include VADOFT for 1-D transport in the unsaturated zone, EPAMCL(?) for 3-D steady flow in the saturated zone, and MULTIMED, an exposure assessment model incorporating air and groundwater travel times. The system is applied to evaluation of lead hazards, and is even used to model its biological uptake.

Summary of Talks and Poster Sessions--Wednesday, October 24, 1990

Talk/Author: ADSORPTION MODELS: J.C. Westall*, Oregon State Univ., Corvallis, OR.

Summary Addresses the incorporation of adsorption into geochemical models. Discusses two basic aspects, fundamental theory and applied studies of adsorption. Theory deals with clean systems such as oxide surfaces, while applied studies include semi-empirical field studies. Theory assumes water attaches to a dry surface, protons dissociate, resulting in a "coating" of hydroxyl anions at the surface. Mathematical formulation of the processes includes solving 5 equations (chemical reaction, mass action, mass balance, chemical and electrostatic equations for charge balance) with 5 unknowns. Different approaches include Triple-Layer, Stern, Diffuse-Layer, and Constant Capacitance models. In field systems, objectives of modeling are to take into account the effects of nonlinear sorption isotherms, variable saturation, competition for sites, pH and major ion compositions, and compatibility with some solution speciation model. Property distribution can be modeled either as discrete (using a code such as FITEQL) or continuous (Gaussian, etc.). Several examples dealing with the different distributions are presented for a Langmuir model, which the author presents as a better approach.

Talk/Author: APPLICATIONS OF CHEMICAL EQUILIBRIUM INVOLVING TRANSPORT PROCESSES: J.L. Hutson* and R.J. Wagenet, Cornell Univ., Ithaca, NY.

Summary LEACHM uses Richard's equations to solve for transient water and chemical transport. Sorption isotherms can be modeled as Linear, Freundlich, Langmuir, and multisite processes. In applications presented in this talk, models are constrained to processes in surface irrigation. To make these applications tractable for personal computer solution, the model is modified to couple the convection-dispersion equation with simple reversible linear sorption isotherms, assuming local equilibrium. For multiple species, there is decoupling of solute transport, chemical, and water flow and transport routines. Water transport can be calibrated assuming the ideal behavior of a non-interacting tracer which obeys the convection-dispersion equation. The author suggests that tritium is the only tracer that meets these requirements. Most behavior, however, is non-ideal, including: kinetics of sorption/desorption, diffusion-limited equilibration, water flux variability, spatial variability, and multi-site sorption. It is also difficult to tell whether the coupling of models duplicates effects observed in the system.

Talk/Author: APPLICATIONS OF A PITZER EQUATIONS-BASED MODEL TO HYPERSALINE SOLUTIONS: G.R. Smith*, K.K. Tanji, J.J. Jurinak, and R.G. Burns, Univ. California-Davis, and Utah State Univ.

Summary The talk presents the results of modeling observed dessication sequences using the chemical equilibrium model C SALT. C SALT can use either the Pitzer or Davies equations to calculate activity coefficients at high ionic strengths, similar to those encountered in natural brines. Input includes: T; P_{CO2}; pH; thermodynamic data; solution osmotic coefficient, and an evaporation concentration factor. C SALT successfully modeled dessication sequences observed for seawater, and three evaporation ponds in California. References cited include Smith et al(1990) and Harvie et al(1980).

Talk/Author: APPLICATIONS OF MINTEQ TO LEACHATES FROM COAL ASH: A.P. Schwab*, Kansas State Univ., Manhattan, KS.

Summary The chemical equilibrium model MINTEQ was used to predict speciation related to the leaching of coal ash by infiltrating rainwater. This is particularly challenging due to the extreme alkalinity of the ash (pH ~12). MINTEQ successfully modeled many element solubilities observed in the ash (Ca, Ba, SO_4^{2-}, Ni, Al, and CO_3^{2-}), but its predictions are poor for Pb and Zn. Some of the discrepancy is due to coprecipitation of $PbCO_3$ and $ZnCO_3$ with $CaCO_3$ that cannot be discriminated by the model. MINTEQ also adequately matches experimental IAP determinations, within 0.5 orders of magnitude. Observations of the authors include: The coprecipitation of phases must be considered in both solid solution and adsorption processes; the current MINTEQ data base lacks high pH species.

Talk/Author: VALIDATION OF CHEMICAL EQUILIBRIUM MODELS: S.V. Mattigod*,

Batelle Pacific Northwest Laboratories, Richland, WA.

Summary A review of the processes by which geochemical equilibrium models are validated. Chemical models must be validated by comparison of results with field and laboratory observations. Complete validation requires corroboration for categories of interaction such as the aqueous, solid, and gas phases. Parameters involved in validating aqueous phases include free ionic concentrations, concentration of complex species, pH and Eh. Additional parameters include the identity and selective dissolution of solid phases. Validation in the gas phase includes the correct prediction of partial gas pressures. Partial validation entails the corroboration of a limited number of components or parameters, or of only one or two categories. Conditional validation implies restriction of the parameters considered. Sources of error that lead to invalidation of geochemical models include: Filtration problems, complex speciation, free-ionic concentration interference, mixed potentials. Future work will require additional data on the interactions of metals and natural organics, solid solution effects, and adsorption onto mixed substrates.

Poster/Author: REDISTRIBUTION OF DEPLETED URANIUM(DU) IN SOILS AND WATER AT TWO U.S. ARMY PROVING GROUNDS: M.H. Ebinger, E.H. Essington, E.S. Gladney, B.D Newman, and C. Reynolds, Los Alamos National Laboratory, Los Alamos, NM.

Summary The study investigated depleted uranium (DU) with depth in soils at the Aberdeen(APG) and Yuma(YPG) Army Proving Grounds. At the more humid APG, the isotopic signature of DU was detected to depths of 30 cm, and solution transport was assumed to be the dominant mechanism. At the more arid YPG, DU penetrated only to depths on the order of 10 cm or less, and erosion of the site was assumed to have removed the DU before solution transport could become significant. EQ3/6 was used to model the dissolution of DU, and predicted that DU is unstable in the soils at both sites, and that DU concentrations are dependent on the redox conditions. A simple 1-D model was developed to investigate vertical solution transport of DU. For the conditions modeled (retardation(R) > 1), it was determined that DU transport was retarded relative to water velocity.

Poster/Author: UNCERTAINTY IN PREDICTED SOLUTE MOVEMENT DUE TO ESTIMATED SOIL-WATER CHARACTERISTICS: J.S. Chen, D.L. Nofziger, and S.D. Alspach, Oklahoma State Univ.

Summary This study evaluated the results of water characteristic curves calculated for four soils from Oklahoma using four different techniques. The four techniques used were: Campbell(1985)-Soil physics with BASIC; Gregson et al.(1987)-Jour. Soil Sci.; Saxton et al.(1986)-Soil Sci. Soc. Amer. Jour.; and the fractal model of Tyler and Wheatcraft(1989)-Soil Sci. Soc. Amer. Jour. Uncertainties in chemical movement calculated using the CMLS code of Nofziger and Hornsby(1986)-Applied Agric. Res. were evaluated using Monte Carlo techniques. The model of Gregson et al. was judged to be best at calculating field capacity and wilting point, necessary input for CMLS, followed closely by Campbell's model. The model of Saxton et al. tends to overestimate water content for water

tensions near saturation. The model of Tyler and Wheatcraft was judged unsatisfactory. The authors determined that for the satisfactory models, variation due to soil and water characteristics is much larger than that due to the differences in the methods used.

Poster/Author: CATION TRANSPORT DURING VARIABLE SOLUTION NORMALITY AND UNSTEADY, UNSATURATED LIQUID FLOW IN SOIL: R.S. Mansell, S.A. Bloom, Univ. of Florida, Gainesville, FL and W. Bond, CSIRO, Canberra, Australia

Summary The model of Mansell et al.(1988)-Soil Sci. Soc. Amer. Jour., a modified multi-species, convective-dispersive Valocchi et al.(1981) model, was further modified to include mobile/immobile flow zones in a two-region model approach. Exchange selectivity coefficients were allowed to vary locally in space and time with solution normality and compositional changes. The model was successful in predicting Na^{+} and Mg^{++} transport in laboratory experiments conducted on Brucedale soils.

Poster/Author: HEAVY METALS ADSORPTION BY SOILS: DEDUCTION OF REACTION MECHANISMS: N.T. Basta and M.A. Tabatabai, Iowa State Univ., Ames, IA

Summary Cd, Cu, Ni, Pb, and Zn sorption in soils was investigated by laboratory studies. A correlation was observed between heavy metal sorption and soil pH. The study determined that heavy metal transport in soils was controlled by adsorption mechanisms. Sorption was accomplished by soils through formation of hydrocomplexes such as $CuOH^{+}$ and $PbOH^{+}$ and through ion-exchange reactions.

Summary of Talks and Poster Sessions--Thursday, October 25, 1990

Talk/Author: ANALYSIS OF VARIABLES CONTROLLING FIELD-SCALE DISPERSION: J.S. Dyson*, W.A. Jury and R.E. White, Univ. of California-Riverside.

Summary An investigation of the extrapolation of small-scale measurements to field-problems using the Transfer Function Model (TFM). This model incorporates spatial variability in water flux, dispersivity equivalent, and solute transport volume. The goal of the model was to represnet data at a calibration depth in 18 soil columns, and find which aspects of dispersion best represent the results. Assumptions include a log-normal distribution of both critical column-scale variables and travel time. The model was calibrated agains Cl composition, and matched the observed distributions within 95% confidence limits.

Talk/Author: PREDICTING SOLUTE TRANSPORT IN THE VADOSE ZONE: R.C. Rice* and D.B. Jaynes, USDA-ARS, Phoenix, AZ.

Summary A field/computer study of the downward transport through the vadose zones of conservative tracers and pesticides following irrigation.

High water application rates were used to speed up studies. The water table in the system studied was at 47 feet. Volumetric water content was observed to increase gradually with depth from 0 to 0.05 at 11.5 m, and increased rapidly to the water table (~0.4 at 12m). KBr was used as a conservative tracer in the field studies, and was applied to the surface prior to irrigation. It took more than 100 days for the peak to reach monitor wells following application, a time which computer models using surface sample characteristics and the convection-dispersion equation underpredicted by approximately 75 days. An increase in the water table occurred after the peak in KBr, indicating that there were preferential flow zones available to KBr, due to immobile water.

Talk/Author: SOLUTE TRANSPORT THROUGH UNSATURATED SOIL: THE FIELD EVIDENCE: K. Roth*, W.A. Jury, Univ. of California-Riverside, and H. Fluhler, ETH Zurich.

Summary Field experiments were designed to investigate the effects of preferential flow and spatial variability for a variety of soil types. Examples include the increase in variance of Cl and Br breakthrough curves with depth. A convective-dispersion model may not be appropriate in this case since it assumes convective solute transport is much greater than dispersion, which may not be valid in areas where immobile water leads to preferential fluid flow. Such effects were observed to increase observed concentrations in Cl and Br by factors of 20 to 40 relative to predicted values. A Stochastic Convection Model is a better description of the observed breathrough curves. Assuming sorption processes, large retardation can model some, but not all, or the pesticide motion observed in preferential flow regions. It was noted in the field studies that the presence of a gravel layer broke up preferential flow regions. References cited include: Butters(1989) and Ghodrati(1989).

Talk/Author: SOLUTE TRANSPORT IN A LAYERED FIELD SOIL: C. Hamlen* and R.G. Kachanoski, University of Guelph, Ontario, Canada.

Summary The purpose of this study was to examine transport across the A/B horizon boundary and determine if transport in the layers of a two-layer system is correlated or uncorrelated. Consideration of relationships between variance and covariance of transport within and between two layers leads to simple expressions that can be used to determine the degree of correlation. This expression is $VAR(t_{A+B}) = VAR(t_A) + VAR(t_B)$, and the $COV(t_{A+B}) = 0$. Checking against field experiments indicates that, at least for the experiment considered, the laters are correlated, and the horizon boundaries do not represent discrete discontinuities.

Talk/Author: FIELD DETERMINATION OF SOLUTE TRANSPORT IN A HETEROGENEOUS VADOSE ZONE: R.S. Bowman*, D.P. Grabka and D.B. Stephens, New Mexico Tech, Socorro, NM.

Summary The purpose of this study is to evaluate the effects of field-

scale heterogeneities on subsurface transport. The field studies entailed dividing a heavily instrumented (tensiometers, etc.) surface plot in an arid-zone alluvial deposit into four sections. Trenching of areas near the plot indicated the heterogeneous nature of the subsurface, with lenses of clays, sands, and cobbles. Water was applied through a drip irrigation system for two months to establish steady-state flow in the unsaturated zone. Four different tracers were applied in each of the four subdivisions in order to evaluate lateral flow in the subsurface, and KBr was applied over the entire surface. Tracers migrated laterally as much as 75cm for each meter of vertical infiltration. A 1-D convection-dispersion model was shown to be inadequate. Observed vertical transport was generally less than that predicted, probably due to lateral transport. In a related experiment, a sorbent dye was used, which showed the existence of preferential flow paths.

Talk/Author: SPATIAL SCALE DEPENDENCE ON IN SITU SOLUTE TRANSPORT: I.J. van Wesenbeeck* and R.G. Kachanoski, Univ. of Guelph, Ontario, Canada.

Summary This study tries to establish the nature of the transition in solute travel-time between local and field-scale cases. In order to make this extrapolation, a horizontal scale-dependence of solute travel-time variance was determined for cultivated and forested soils. It was found that horizontal velocity is varied, and there are zones of preferential vertical fluid flow due to immobile water. For the two soils examined, minimum horizontal scales of 2.8 m(forested) and 3.8 m(cultivated) were needed to incorporate all major horizontal variations in the systems.

Talk/Author: VALIDITY OF THE CONVECTIVE-DISPERSIVE EQUATION FOR PREDICTING POLLUTANT TRANSPORT: S.A. Aburime*, Alabama A&M University and T.S. Steenhuis, Cornell University:

Summary The purpose of this study was to evaluate the applicability of the convective-dispersion equation for solute transport to field problems. Input parameters were determined by soil column experiments. Comparing predicted and observed $CaCl_2$ concentrations in field studies indicates that the equation may not be suitable in predicting first breakthrough of transported pollutes, and preferential fluid flow needs to be considered for accurate predictions.

Talk/Author: MODELING THE TRANSPORT OF DISSOLVED ORGANIC CARGON IN LABORATORY SOIL COLUMNS: P.M. Jardine*, F.M. Dunnivant, and J.F. McCarthy, Oak Ridge National Laboratory, Oak Ridge, TN.

Summary Dissolved organic carbon (DOC) is a possible agent of transport in the form of colloid particles. This study reports the results of laboratory batch studies, which were used to determine equilibrium and kinetics of DOC adsorption isotherms. Rapid breakthrough with Pe > 60 was observed. Three models were used to predict observed breakthrough: (1) CXTFIT-Parker and Van Genuchten(1984) assumes linear adsorption isotherms, and both local equilibrium and first-order reaction kinetics

on two sites; (2) DISPER-Fluhler and Jury(1983) assumes that both sites obey nonlinear Langmuir adsorption and first-order reaction kinetics; (3) SOTS-Selim and Amacher(1988) assumes second-order kinetics at both sites. Batch studies model tailing of concentration curves, but not the initial breakthrough. The transport models used model initial breakthrough, but are less accurate in predicting tailing. DOC transport is biphasal, is best fit by a two-site model assuming either first-order reaction kinetics and nonlinear adsorption with respect to solid DOC, or second-order kinetics with respect to both solid and solution phase DOC.

Talk/Author: FIELD STUDY OF BROMACIL TRANSPORT UNDER CONTINUOUS FLOOD IRRIGATION: D.B. Jaynes*, USDA-ARS, Ames, IA.

Summary This study compared movement of a reactive tracer (herbicide) to that of a conservative tracer as a means of evaluating the suitability of batch-derived retardation factors. Br was used as a conservative tracer, while bromacil was used as a reactive tracer. In general, batch-derived retardation factors are not suitable due to dhemical kinetic effects. While prediction was fairly close at the surface, the degree of agreement decreased with depth, and in some instances, predicted retardation was the reverse of that observed at depth.

Talk/Author: EVALUATION OF WICK LYSIMETERS FOR SOLUTE SAMPLING IN THE VADOSE ZONE: T.S. Steenhuis*, J. Boll, and S. Saul, Cornell Univ., Ithaca, NY.

Summary Braided fiberglass wick lysimeters are proposed as alternatives to pan and suction lysimeters for sampling waters from the vadose zone. Advantages include the fact that the lysimeters are non-mechanical, self-priming, and properties can be systematically varied with respect to the wick diameter. Dispersion matches fairly well, and suction is observed to decrease with increasing flow rate, and wick flux is correlated with wick diameter. There is a small hysteretic effect during the wetting of the wick. Travel-time through the wick is related to velocity such that V = (Wick Flux)/(0.38 + Wick Influx). One notable advantage of wick lysimeters is their limited effect on the sampled environment. Use of mechanical suction lysimiters frequently disturbs the environment itself.

Talk/Author: USE OF SURFACE COMPLEXATION MODELS TO EVALUATE ANION ADSORPTION MECHANISMS: S. Goldberg*, USDA-ARS, U.S. Salinity Lab, Riverside, CA.

Summary Surface complexation models require independent modeling of inner sphere and outer sphere adsorption. In this study, surface site density effects on anion sorption on goethite are examined. Constant capacitance and triple-layer surface complexation models both describe anion adsorption by goethite using either inner- or outer-sphere models. Inner-sphere models are found best for small site densities, while an outer-sphere model best fits large site densities. Different techniques, however, yield differences of up to an order of magnitude in measured site densities, indicating that independent experimental determinations are needed to find active sites for anion-complexation prediction.

Talk/Author: PROPERTIES OF SYNTHETIC GOETHITES AND THEIR EFFECT ON SULFATE ADSORPTION: M.A. Munoz*, J.M. Bigham, S.J. Traina and C.T. Johnston, Univ. of Puerto Rico and the Ohio State Univ.

Summary Goethite is a common anion sorbing mineral. Since aluminum substitution is up to 30 mol %, the goal of this study was to evaluate the effect of Al-substitution on sulfate adsorption. Microscopic examination of low-temperature synthetic goethites indicates that with increased Al-substitution, crystal morphologies become more anhedral. Additionally, calculated surface area decreases with increased aluminum, from $42m^2/g$ at 0% Al to 32 m^2/g at 9.3% Al. The study also synthesized Al-free goethite at higher temperatures. Surface areas and crystal morphologies were similar to those described for low-T Al-goethites. In the experiments, sulfate adsorption did not change for Al-free goethites with increasing temperature from 0-200° C. However, sorption was observed to increase with Al-substitution in the 0.5 to 1.5 micromoles/ml sulfate adsorption range. Part of this is probably due to the creation of a limited number of high affinity sites.

Talk/Author: COUPLED DIFFUSION OF EXCHANGEABLE CATIONS IN SOIL: R.D. Rhue*, Univ. of Florida, Gainesville, FL.

Summary Numerical models of cation flux in an isothermal, unsaturated system need to incorporate relatively constant water contents and bulk densities. The models also need to account for another cation diffusing against K^+, since experiments examining Ca^{++} and K^+ counter-diffusion end up with a surplus of metal cation charge for every run. Lab experiments examining the Na-Ca-K system, identify a transient Na^+ flux equal to approximately 20% of the K^+ flux and 100% of the Ca^{++} flux diffusing counter to K^+. Soil experiments also indicate that exchangeable Na and K are more mobile than Ca. Concentration distributions predicted by computer models incorporating coupled diffusion are in good agreement with measured concentrations of Ca-Na-K. A high degree of coupling is expected in systems with high concentration gradients, and/or counter diffusing ions exhibit large differences in ionic mobility.

Talk/Author: KINETICS OF CATION EXCHANGE ON CLAY MINERALS USING PRESSURE-JUMP RELAXATION: C. Aharoni, L. Tang*, and D.L. Sparks, Univ. of Delaware.

Summary This experiment was designed to examine the kinetics of cation exchange in montmorillonite. This exchange is generally very quick, on the order of milliseconds, and the rate-limiting step is duffusion/mass transport. Traditional methods are too slow to examine this exchange. Pressure-jump relaxation relies on an "instant" drop in pressure on a system at equilibrium. The experiment then monitors the rapid changes in the system as it seeks a new level of equilibrium. K_{eq} can be determined using static techniques, or for kinetic models such as the pressure-jump relaxation technique, $K_{eq} = k_+/k_-$. Comparison of results in K_{eq} determined for Ca and Mg exchange on Na- and K-montmorillonite by both static and

kinetic methods are in reasonably good agreement.