Journal of Contaminant Hydrology, 13 (1993) 249–259
Elsevier Science Publishers B.V., Amsterdam

Assessment of radionuclide retardation: uses and abuses of natural analogue studies

Ian G. McKinley[a] and W. Russell Alexander[b]

[a]*NAGRA, Hardstrasse 73, CH-5430 Wettingen, Switzerland*
[b]*RWIG, University of Berne, Balzerstrasse 1, CH-3012 Berne, Switzerland*

(Accepted for publication January 8, 1993)

ABSTRACT

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: uses and abuses of natural analogue studies. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 249–259.

Various techniques which have been reported for the in situ determination of radionuclide sorption or retardation as part of natural analogue studies have been critically assessed. In particular cases, the tacit assumptions used to derive retardation data from field observations can be shown to be questionable or, indeed, totally incorrect. Some problems identified are due to ambiguous or inconsistent use of terminology, but a fundamental error which commonly arises is the failure to distinguish between sorption and precipitation — processes which are treated quite differently in transport models. Natural analogue studies can be used to test radionuclide migration models and their associated databases, but considerable efforts are required to adequately characterise the geochemical process occurring. Without such extensive studies, the general applicability of data produced is limited and claims to derive parameters usable in repository performance assessment should be treated with considerable caution.

1. INTRODUCTION

In repository performance assessment, retardation of radionuclides in the geosphere is usually identified as one of the key parameters which determine predicted consequences (doses to the population). National waste management research programmes inevitably include laboratory sorption studies to provide data for nuclide transport models and may also include costly field migration experiments to test these models and their associated databases. "Natural analogue" studies of the migration of trace elements in relevant geological environments provide a complementary approach to model/database testing, which has the particular advantages of applying to an undisturbed system and allowing access to natural events and mechanisms occurring over long timescales. It has often been claimed that analogue studies

0169-7722/93/$06.00

can provide sorption/retardation data which is superior to that from laboratory/field experimental work. In most cases (if not all), such claims are unjustified.

This paper examines the various approaches which can be used to examine retardation in natural analogue studies, identifies pitfalls and proposes approaches which ensure that analyses are sufficiently well justified to be used in performance assessment.

2. SORPTION AND RETARDATION

The radionuclide sorption literature is, unfortunately, a morass of poorly defined concepts and inconsistent nomenclature. Sorption can be defined for static aqueous systems containing a solid phase as the partitioning of solute between solution and an adsorbed phase associated with the solid. Retardation is a measure of the retention of a solute relative to bulk solution in a dynamic system due to interaction with solid phases (e.g., by sorption). As discussed in detail elsewhere (e.g., Bear, 1979; Mangold and Tsang, 1991), many mathematical models exist which evaluate the extent of retardation due to sorption in a defined flow system. Such models generally incorporate some kind of sorption function which relates the concentration in the sorbed phase to that in the aqueous phase. Sorption must thus be very carefully distinguished from precipitation (in which the quantity of precipitated phase is unrelated to the solubility-limit concentration). It is also important to identify saturation of available sorption sites as, after such saturation has occurred, solution concentrations can increase "indefinitely" without affecting the concentration in the sorbed phase. For ease of modelling, it is often assumed that the sorbed concentration is linearly proportional to the concentration in solution. The gradient of this "linear sorption isotherm" is referred to as a partition or distribution coefficient — often represented as K_d. Fig. 1 illustrates the form of a general sorption isotherm of the type which may be measured in laboratory studies. In natural systems, the element or isotope studied may also be present in an inaccessible form (e.g., isolated from water, within mineral grains or impermeable parts of the rock) or as precipitates. The total concentration associated with the rock phase is thus the sum of the sorbed concentration plus a "matrix" concentration.

3. IN SITU K_d's

The limitations in the applicability of simple sorption concepts to geological systems are discussed in detail elsewhere (McKinley and Alexander, 1992). Nevertheless, even the simplest requirements for a meaningful sorption terminology have been misunderstood in many cases — particularly in the natural analogue field.

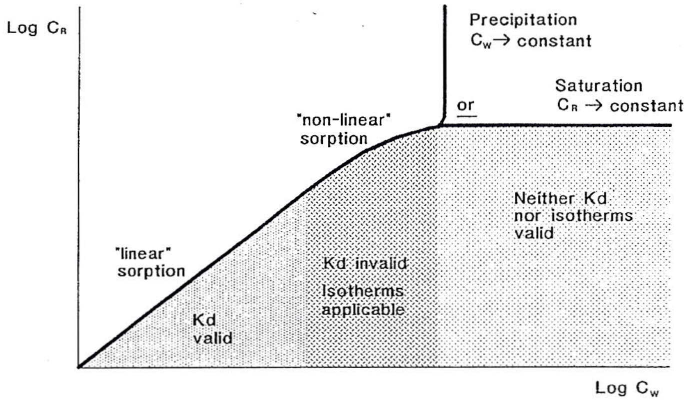

Fig. 1. Diagrammatic representation of a general sorption isotherm, where C_R is the nuclide concentration measured on the rock and C_W the concentration in the aqueous phase. At very low concentrations, the distribution of a radionuclide between rock and aqueous phases is usually linear (isotope exchange). At higher concentrations, either precipitation or saturation of the available sorption sites will occur.

To take one example, consider Table 1 presented in an invited review at the last Migration symposium (Ivanovich, 1991). The "secondary solid phases" are supposed to contain only sorbed nuclide and it is claimed that this approach

> "should give more realistic and site specific retardation information than laboratory derived K_d-values currently used in transport assessment modelling".

Table 2 presents the same basic data expressed as isotope ratios. It is very clear that, in most cases, the "sorbed" and "pore water" phases are not in isotopic equilibrium. Such massive differences in isotopic ratios cannot possibly be caused or maintained by any type of sorption process as defined above — they can only arise by the physico-chemical effects of radioactive decay (recoil) possibly coupled to aging in a closed system (if it were feasible, the nuclear industry would not need the exotic methods developed for isotope enrichment!). In fact, the data demonstrate that the interpretation is incorrect and the "sorbed" phase includes a matrix component (probably due to problems in the sequential extraction scheme — cf. references in McKinley and Alexander, 1992). Whatever such rock/water concentration ratios may signify, it has nothing to do with sorption. Such data are of no possible use in any type of transport modelling!

Unfortunately, even worse examples exist. In many cases, in situ K_d-values have been obtained by simply measuring the trace-element concentrations in both the rock and associated pore water (e.g., Jackson and Inch, 1989). This

TABLE 1

Derived effective distribution coefficients (R_d) for isotopes of uranium and thorium in cores from clay (Bradwell, Essex, U.K.) and limestone (Fulbeck, Lincolnshire, U.K.) formations (from Ivanovich, 1991)

Radionuclide	Pore water (10^{-3} dpm mL^{-1})	Solid secondary phases only (dpm g^{-1})	R_d (10^4 mL g^{-1})
Bradwell core (B/*101*/*22.78-23.0* M/C):			
^{238}U	1.3±0.1	18.4±0.5	1.4±0.1
^{234}U	2.2±0.1	29.1±0.3	0.6±0.1
^{230}Th	0.03±0.01	17.4±0.3	62±2
^{232}Th	0.012±0.007	20.8±0.5	173±101
^{228}Th	0.03±0.02	19.8±0.8	71±40
Fulbeck core (F/*31720.3-20.7*):			
^{238}U	0.7±0.1	16.0±0.2	2.3±0.2
^{234}U	6.2±0.3	12.1±0.3	0.20±0.01
^{230}Th	0.9±0.01	7.3±0.2	0.8±0.1
^{232}Th	0.04±0.03	11.0±0.2	28±20
^{228}Th	0.6±0.1	21.6±0.5	3.4±0.7

All quoted errors are 1σ uncertainties due to nuclear counting statistics only.

totally ignores the fact that such measurement cannot distinguish between sorption and precipitation and produce data of no relevance to radionuclide retardation (see the discussion in McKinley and Alexander, 1992). More importantly, so-produced K_d-values are generally non-conservative from a safety assessment viewpoint as they would lead to overprediction of contaminant retardation. This makes recent reports which support the use of such work, published by national and international radwaste organisations, particularly worrying.

TABLE 2

Isotope ratios derived from Table 1

Ratio	Pore water	"Secondary phases"
Bradwell core:		
^{234}U/^{238}U	1.7±0.2	1.6±0.05
^{230}Th/^{232}Th	2.5±1.7	0.8±0.02
^{228}Th/^{232}Th	2.5±2.2	1.0±0.04
Fulbeck core:		
^{234}U/^{238}U	8.9±1.3	0.8±0.02
^{230}Th/^{232}Th	23±17	0.7±0.02
^{228}Th/^{232}Th	15±12	2.0±0.06

For example, the Sediment Barrier Task Group (SBTG) of the Organization for Economic Cooperation and Development–Nuclear Energy Agency (OECD–NEA) study on deep-sea disposal of radwaste, concluded that deep-sea sediments would "provide a very effective barrier" radionuclide migration from a HLW (high-level radioactive waste) sub-seabed repository (Brush, 1991). Unfortunately, for four of the fifteen critical elements studied (U, Th, Ra and Zr), the conclusions were based on "in situ K_d-values" obtained by the bulk-rock analysis method and, as such, are worthless. In studies of fracture flow systems (Landström and Tullborg, 1990), even more pointless in situ K_d-values are reported by using analyses of groundwaters which, in several cases, were collected up to 34 m (vertically) away from the fracture material studied and, when no groundwater was available for two other fractures, the calculations were based on "average values for the three analysed groundwaters"!

4. CRITERIA FOR DERIVING RELEVANT SORPTION DATA FROM NATURAL SYSTEMS

In principle, the transport modeller requires a sorption isotherm (cf. Fig. 1) covering the range of concentration of interest. To derive such an isotherm from a natural system requires a series of measurements of equilibrium solute concentration in the sorbed and dissolved phase. It is important that the isotherm covers the concentration range of interest as, in general, these are fairly empirical and can only be used for interpolation.

This can be readily seen by the sorption data from two separate experimental runs on the same rock–water–nuclide system, illustrated in Fig. 2 (from McKinley and West, 1987). Although the datasets overlap rather well, the isotherms which would be derived from these individual datasets differ considerably, i.e.:

database *A*: $C_R = 1148 C_W^{1.08}$; $r = 0.99$

database *B*: $C_R = 0.74 C_W^{0.66}$; $r = 0.99$

where C_R is the sorbed concentration (kg kg^{-1}); C_W is the aqueous concentration (kg L^{-1}); and r is correlation coefficient for a linear fit to log-log transformed data.

As is evident from the figure, extrapolation of the isotherms could readily lead to incorrect estimates of sorption by several orders of magnitude. Obtaining the data required to derive an appropriate isotherm would only be

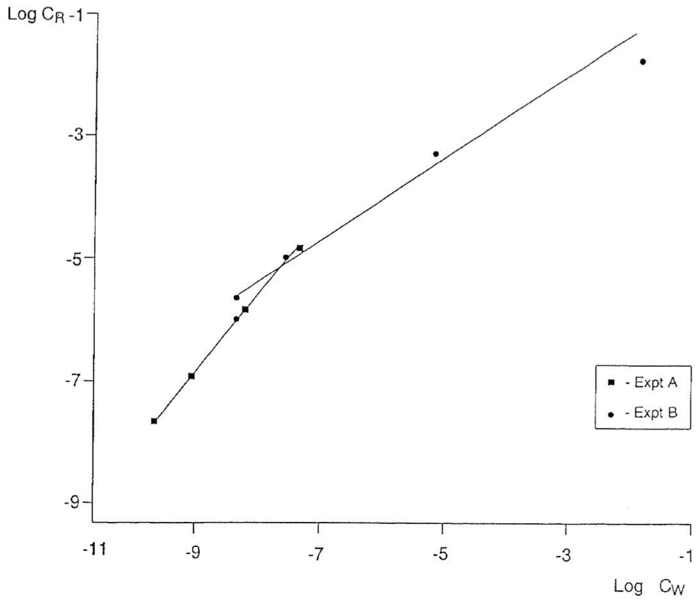

Fig. 2. Sorption isotherms for Sr on granite fracture infill measured in two separate experiments covering different concentration ranges (from McKinley and West, 1987). C_R = rock phase concentration (kg kg^{-1}); C_W = aqueous phase concentration (kg L^{-1}) .

possible in a very few natural systems (e.g., by sampling several points along a geochemical gradient or a contaminant plume). Nevertheless, even partial isotherms may clearly show up precipitation or sorption phase saturation (Fig. 1) which invalidate the sorption approach.

The wide range of concentrations examined in laboratory batch sorption studies necessitates the log-log plots illustrated in Figs. 1 and 2. When natural systems show only a narrower range of concentrations, a linear plot may be more relevant. Such a plot has the advantage of not only showing precipitation and exchange site saturation effects, but also indicating that the basic sorption approach is applicable at low concentrations when the extrapolated isotherm passes through the origin. Deviations from such ideal behaviour are diagnostic; if C_R tends to a positive value as $C_W \rightarrow 0$, this indicates that some of the solute is inaccessible within the rock matrix; tendency to a negative value (i.e. C_W is positive as $C_R \rightarrow 0$), indicates the presence of solute in a non-sorbing form — probably colloidal in most cases.

5. ASSESSING RETARDATION IN NATURAL SYSTEMS

As retardation is the characteristic of a dynamic system, it can be rigorously evaluated only by a series of measurements. Such series of measurements may provide a profile in either time or space, but a single measurement cannot be used to evaluate retardation without many speculative assumptions. Any references in the literature to retardation factors derived from measurements on a single rock/water sample must thus be regarded as extremely dubious, at best, and in most cases totally nonsensical.

Krishnaswami et al. (1982) developed an approach for determination of in situ retardation coefficients based on analysis of natural decay series radionuclide ratios in water. Although this approach has been uncritically adopted in several natural analogue studies (e.g., Laul et al., 1985), it is based on numerous unproven assumptions which are debateable for the gravel aquifer originally studied by Krishnaswani and certainly inappropriate in environments more relevant to nuclear waste disposal. The problems with this approach are discussed in more detail by McKinley and Alexander (1992).

Profiles resulting from bomb fallout and other releases of radioactive and stable pollutants have been studied for many years to determine the extent of sorption or retardation in natural systems. For most elements of interest, however, the extent of penetration is very limited and thus these studies are confined to the upper soil zone where interpretation is complicated by the effect of biological activity. Studies of deeper systems have included sources such as underground nuclear weapon tests and leachates from waste disposal trenches. As discussed by Chapman et al. (1984), the sources in these studies are rather ill defined and data produced tend to be more qualitative in nature.

The redistribution of other well-dated geochemical anomalies may be used in a similar manner. For example, the redistribution of various elements from a well-defined marine band within the lacustrine sediments in Loch Lomond, west Scotland, U.K., has been extensively studied and analysed to derive "best fit" retardation factors (Fig. 3) (MacKenzie et al., 1984, 1990; Hooker et al., 1985).

In these cases, when profiles are analysed, it is important to distinguish between interpretative models (or simulations) and predictive models. In the very simplest case of the fallout profiles, the ratio of peak transit times of a sorbing and "nonsorbing" tracer directly yield a retardation factor under the assumption of fast, concentration independent, reversible sorption (i.e. "K_d type"). If sorption is more complex, for example non-linear (concentration dependent), then the concept of a constant retardation factor is completely inappropriate and any value thus derived is meaningless (e.g., Smith, 1990).

More sophisticated models of solute transport can be derived to analyse the entire shape of the breakthrough curve in order to examine "tailing" which

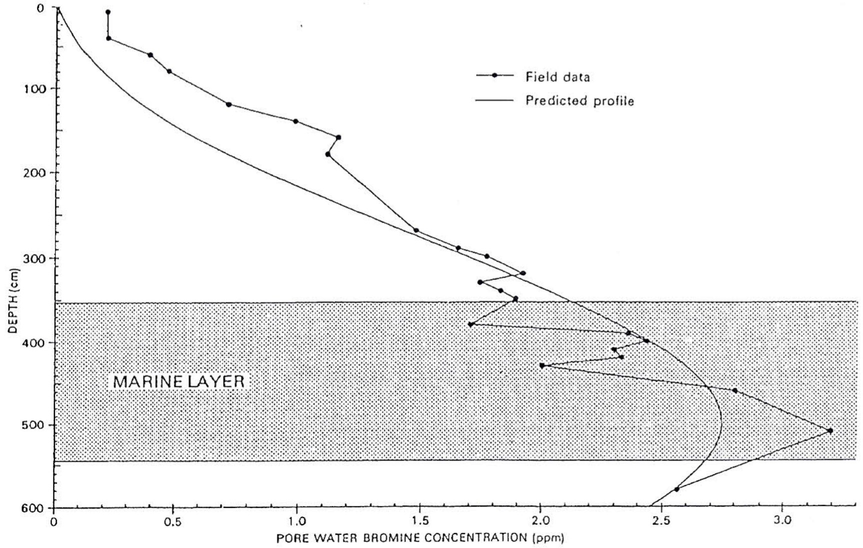

Fig. 3. Measured and predicted profiles of Br in Loch Lomond, west Scotland, U.K., sediments (from Hooker et al., 1985).

may be due to non-linearity, slow kinetics or partial irreversibility. If the mathematical model is mechanistically based and utilises only independent sources for input data, agreement of predicted profiles with those observed would greatly increase confidence in the modelling approach/database used (even if not validation, in the most rigorous sense). In most cases, however, a mechanistic model is used which contains several variables which are "fit" to simulate the observed profile. There is generally no indication that any such fit parameters have any physical meaning or that they can be extrapolated beyond the particular case examined. This is especially true if several parameters are fit — any model with three or more free parameters can be fit to almost any regular profile!

6. TESTING RADIONUCLIDE TRANSPORT MODELS USING NATURAL ANALOGUES

The discussion above indicates that it is extremely difficult, if not impossible, to derive meaningful sorption or retardation coefficients for relevant rock–water–radionuclide systems. This does not, however, imply that migration analogues are worthless. A key aspect of analogue studies is testing the applicability of the models and databases used for repository performance assessment (McKinley, 1990) and this is still possible.

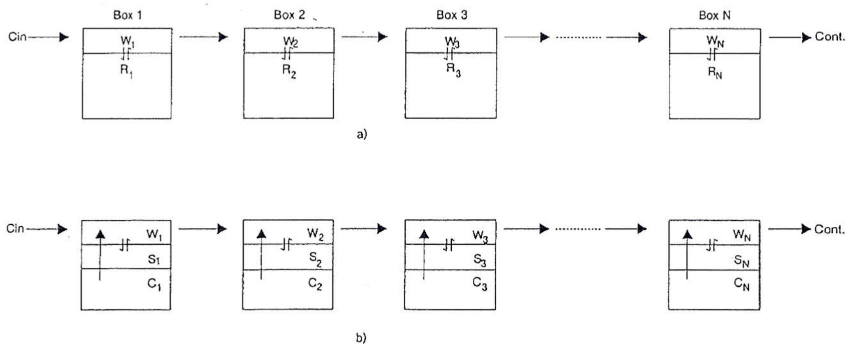

Fig. 4. Schematic outline of: (a) single rock phase box model; and (b) double rock phase model with sorbing and leaching phases. W_i represents the aqueous phase in box i, R_i the rock phase when only sorption occurs, S_i the sorbed phase when leaching may also occur from a separate mineral phase C_i.

The methodology involved in deriving laboratory sorption data and the relevance of such data to real systems can be tested by measuring such data on material from the analogue site studied and comparing the sorption (or retardation) predicted from the laboratory work with that actually observed. In dynamic systems, it may be advantageous to use an extremely simple transport model as, in general, more complex models have more free parameters and hence more flexibility to fit observations. In particular, a simple box model can be applied to most advective transport systems (cf. Fig. 4) and this can be readily analysed numerically for any particular empirical sorption relationship (non-linear isotherms, partial irreversibility, kinetics, etc.). A very simple example of this approach is given by McKinley (1982), and a much more complex example which considers natural decay series chains is described by Golian (1991). The latter, which explicitly includes inaccessible mineral phases and recoil processes (cf. Fig. 4b) could generate isotopic disequilibrium of the type evident in Table 2.

An appropriate application of the box model computer code to natural analogue data would be to examine whole-rock elemental profiles across a water-conducting fracture (e.g., Smellie et al., 1986). To date, such studies have (justifiably) been used only to assess the availability of the host rock matrix to retard contaminants migrating along fractures, away from a source such as a breached repository. Further information could be derived from these profiles by utilising the code in connection with appropriate laboratory data.

7. CONCLUSIONS

Natural analogue researchers (and others) persistently misuse sorption/retardation nomenclature and often report in situ parameters which are either poorly defined or simply incorrect. Much of this may be attributed to misunderstanding the mechanisms involved in sorption, but it may also be that the production of in situ K_d-values by selective chemical leaches or bulk-rock analyses are simply seen as a quick and easy alternative to laborious and expensive laboratory-based experimental programmes. This paper illustrates some of the more common errors in the definition of in situ K_d-values and formulates criteria which must be met in derivation of sensible sorption or retardation data.

Fundamental flaws in the present generation of in situ K_d or retardation factor determinations could have potentially serious consequences on the safety assessment of repository designs. It may be possible to derive in situ K_d-values which are robust, but only when great care is taken to fully characterise the rock–water system of interest. To date, this simply has not been the case, although it is encouraging to note that, in the Alligator Rivers natural analogue project, Northern Territories, Australia, a large amount of effort is currently being expended on the detailed study of selective leaching of the solid phase (e.g., Murakami et al., 1990; Yanase and Isobe, 1991). Until such procedures are established, the main application of sorption/retardation analogues is the testing of predictions made on the basis of laboratory sorption studies and transport modelling of the type illustrated.

REFERENCES

Bear, J., 1979. The Hydraulics of Groundwater. McGraw-Hill, New York, NY, 569 pp.

Brush, L.H., 1991. Summary of laboratory investigations of radionuclide migration through deep-sea sediments. Radiat. Waste Manage. Nucl. Fuel Cycle, 15: 133–143.

Chapman, N.A., McKinley I.G. and Smellie, J.A.T., 1984. The potential of natural analogues in assessing systems for the deep disposal of high-level radioactive waste. NAGRA (Swiss Natl. Coop. Disposal Radioactive Waste), Wettingen, Tech. Rep. Ser., NTB 84-41, 103 pp.

Golian, C., 1991. Interpreting the uranium series activity ratio development in different rock mineral phases. In: P. Duerden (Editor), Alligator Rivers Analogue Project Progress Report. ANSTO (Aust. Nucl. Sci. Technol. Org.), Lucas Heights, N.S.W., pp. 71–80.

Hooker, P.G., MacKenzie, A.B., Scott, R.D., McKinley, I.G. and West, J.M., 1985. A study of long-term (10^3–10^4 y) elemental migration in saturated clays and sediments, III. BGS (Br. Geol. Surv.), Keyworth, FLPU (Rep. Fluid Processes Res. Group) 85-9, 76 pp.

Ivanovich, M., 1991. Aspects of uranium/thorium series disequilibrium applications to radionuclide migration studies. Radiochim. Acta, 52/53: 257–268.

Jackson, R.E. and Inch, K.J., 1989. The in-situ adsorption of Sr-90 in a sand aquifer at the Chalk River Nuclear Laboratories. J. Contam. Hydrol., 4: 27–50.

Krishnaswami, S., Graustein, W.C., Turekian, K.K. and Dowel, J.F., 1982. Radium, thorium and lead isotopes in groundwaters: application to the in-situ determination of absorption–desorption rate constants and retardation factors. Water Resour. Res., 18: 1663–1675.

Landström, O. and Tullborg, E.L., 1990. The influence of fracture mineral/groundwater interaction on the mobility of U, Th, REE and other trace elements. SKB (Swed. Nucl. Fuel & Waste Manage.), Stockholm, Tech. Rep. 90-37, 71 pp.

Laul, J.C., Smith, M.R. and Hubbard, N., 1985. Behaviour of natural uranium, thorium and radium isotopes in the Wolfcamp brine aquifers, Palo Duro Basin, Texas. Sci. Basis. Nucl. Waste Manage., 8: 475–482.

MacKenzie, A.B., Scott, R.D., Ridgeway, I.M., McKinley, I.G. and West, J.M., 1984. A study of long-term (10^3–10^4 y) elemental migration in saturated clays and sediments, II. BGS (Br. Geol. Surv.), Keyworth, FLPU (Rep. Fluid Processes Res. Group) 84-11, 37 pp.

MacKenzie, A.B., Shimmield, T.M., Scott, R.D., Davideon, G.M. and Hooker, P.J., 1990. Chloride, bromide and iodide distributions in Loch Lommond sediment interstitial water. UK-DOE (U.K. Dep. Environ.), London, Rep. DOE/RW/90/010, 24 pp.

Mangold, D.C. and Tsang, C.F, 1991. A summary of subsurface hydrological and hydrochemical models. Rev. Geophys. 29: 51–79.

McKinley, I.G., 1982. Prediction of radionuclide retardation during groundwater transport from laboratory sorption data. Proc. Symp. on Environmental Migration of Long-lived Radionuclides. IAEA (Int. At. Energy Agency) , Vienna, pp. 147–152.

McKinley, I.G., 1990. Applying natural analogues in predictive performance assessment. In: A. Saltelli, D.A. Stanners and M. D'Alessandro (Editors), Risk Analysis in Nuclear Waste Management. Kluwer, Dordrecht, pp. 359–396.

McKinley, I.G. and Alexander, W.R., 1992. Constraints on the applicability of "in-situ" K_d values. J. Environ. Radiochem., 15: 19–34.

McKinley, I.G. and West, J.M., 1987. Radionuclide retardation in the near- and far-field of a HLW repository. in: D.G. Brookins (Editor), The Geological Disposal of High Level Radioactive Wastes. Theophrastus, Athens, pp. 445–458.

Murakami, T., Yanase, N. and Isobe, H., 1990. Separation of mineral species for application of the sequential extraction procedure. In: P. Duerden (Editor), Alligator Rivers Analogue Project Progress Report. ANSTO (Aust. Nucl. Sci. Technol. Org.), Lucas Heights, N.S.W., pp. 207–214.

Smellie, J.A.T., MacKenzie, A.B. and Scott, R.D., 1986. An analogue validation study of natural radionuclide migration in crystalline rocks using U-series disequilibrium studies. In: N.A. Chapman and J.A.T. Smellie (Guest-Editors), Natural Analogues to the Conditions around a Final Repository for High-level Radioactive Waste. Chem. Geol., 55: 233–254 (special issue).

Smith, P.A., 1990. Modelling of a diffusion–sorption experiment by linear and nonlinear sorption isotherms. Nucl. Technol., 92: 363–373.

Yanase, N. and Isobe, H., 1991. Activity ratios of U-238, U-234 and Th-230 between minerals by sequential extraction procedures. In: P. Duerden (Editor), Alligator Rivers Analogue Project Progress Report. ANSTO (Aust. Nucl. Sci. Technol. Org.), Lucas Heights, N.S.W., pp. 119–134.

Journal of Contaminant Hydrology, 13 (1993) 261–262
Elsevier Science Publishers B.V., Amsterdam

Response to McKinley and Alexander (1993)

R.E. Jackson

INTERA Inc., 6850 Austin Blvd., Suite 300, Austin, TX 78731, USA

(Accepted for publication January 8, 1993)

McKinley and Alexander (1993 in this issue) have indicated that my measurements of ^{90}Sr partitioning in a sand aquifer at the Chalk River Nuclear Laboratories (CRNL) may be due not just to adsorption, as claimed in Jackson and Inch (1989), but also to precipitation of mineral phases. McKinley and Alexander state:

> "In many cases, in situ K_d-values have been obtained by simply measuring the trace-element concentrations in both the rock and associated pore water (e.g., Jackson and Inch, 1989). This totally ignores the fact that such measurement cannot distinguish between sorption and precipitation and produce data of no relevance to radionuclide retardation ..."

However, Jackson and Inch (1989, p.35) state explicitly:

> "Since the CRNL ground waters are undersaturated with respect to $SrCO_3$, $SrSO_4$ and $CaCO_3$ mineral phases, Jackson and Inch (1983) concluded that the retardation of ^{90}Sr must be due to adsorption and not precipitation."

The groundwater chemistry data presented in Jackson and Inch (1989, table 1) do not include a complete analysis of major ions and this perhaps suggested to McKinley and Alexander that precipitation had been ignored. This incomplete analysis permitted the small volume of interstitial water obtained from centrifuging cores to be used for analysis of those cations which might compete with ^{90}Sr for sorption sites, thus meeting a principal objective of the paper. Insufficient sample was available to analyze the various anions and thus determine equilibrium with respect to potential host minerals.

However, as is very clearly indicated in Jackson and Inch (1989, pp. 33–39), the ^{90}Sr plume at CRNL had been subjected to a detailed hydrogeochemical analysis beforehand (Jackson et al., 1980; Pickens et al., 1981; Jackson and Patterson, 1982; Jackson and Inch, 1983; Inch and Killey, 1987). This previous work was the basis for our statement eliminating ^{90}Sr precipitation from consideration within that plume. The water chemistry presented in our table 1 is consistent with this interpretation. Although not mentioned by Jackson and

0169-7722/93/$06.00

Inch (1989), the additional possibility of coprecipitation of ^{90}Sr by ferric hydroxide was also dismissed because of their undersaturation in the aquifer (see Jackson and Patterson, 1982).

Jackson and Inch (1989) summarizes results from a series of reports on the mechanisms of ^{90}Sr partitioning and transport in a sand aquifer composed of granitic minerals. As such, those interested in the performance assessment of nuclear waste repositories in granitic rocks may find the series of interest.

REFERENCES

Inch, K.J. and Killey, R.W.D., 1987. Surface area and radionuclide sorption in contaminated aquifers. Water Pollut. Res. J. Can., 22: 85–98.

Jackson, R.E. and Inch, K.J., 1983. Partitioning of strontium-90 among aqueous and mineral species in a contaminated aquifer. Environ. Sci. Technol., 17: 231–237.

Jackson, R.E. and Inch, K.J., 1989. The in-situ adsorption of ^{90}Sr in a sand aquifer at the Chalk River Nuclear Laboratories. J. Contam. Hydrol., 4: 27–50.

Jackson, R.E. and Patterson, R.J., 1982. Interpretation of pH and Eh trends in a fluvial sand aquifer system. Water Resour. Res., 18: 1255–1268.

Jackson, R.E., Inch, K.J., Patterson, R.J., Lyon, K., Spoel, T., Merritt, W.F. and Risto, B.A., 1980. Adsorption of radionuclides in a fluvial-sand aquifer: measurement of the distribution coefficients K_d-Sr and K_d-Cs and identification of mineral adsorbents. In: R.A. Baker (Editor), Contaminants and Sediments, Vol. 1, Ch. 14. Ann Arbor Science Publishers, Ann Arbor, MI, pp. 311–329.

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: Realistic application of natural analogue studies. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 249–259 (this special issue).

Pickens, J.F., Jackson, R.E., Inch, K.J. and Merritt, W.F., 1981. Measurement of distribution coefficients using a radial injection dual-tracer test. Water Resour. Res., 17: 529–544.

Journal of Contaminant Hydrology, 13 (1993) 263–266
Elsevier Science Publishers B.V., Amsterdam

Response to McKinley and Alexander (1993)

M. Ivanovich

AEA Environment and Energy, Harwell Laboratory, Harwell, Oxon OX11 ORA, UK

(Accepted for publication January 8, 1993)

In all the published models attempting to describe radionuclide transport in the geosphere the migration rate depends on the groundwater velocity and the radionuclide retardation factor which in turn depends on the distribution coefficients and the effective porosity (Chapman and McKinley, 1987). Distribution coefficients used in performance associated models have been and are being measured in the laboratory for a variety of radionuclides, groundwaters and rocks but doubts have been expressed on the extent to which laboratory data reflect the behaviour of natural geochemical systems for a number of reasons such as K_d dependence on Eh, pH, groundwater chemistry, properties of accessible minerals, kinetics of geochemical processes, and presence of colloids in the system. Uranium and thorium series radionuclides are uniquely suited to the study of retardation processes because several isotopes of the same element continuously enter groundwaters and because the supply rate of many of these radionuclides can be estimated with adequate accuracy. Several approaches involving the concept of U/Th series radioactive disequilibrium were illustrated in the invited paper by Ivanovich (1991) given at the Migration 1989 meeting. This is one of the papers singled out by McKinley and Alexander (1993) for their criticism. I welcome this opportunity to respond.

The gist of McKinley and Alexander's (1993) paper is that K_d (or R_d) concept has been "greatly abused" or "misunderstood" by many authors who are attempting to offer alternative means of measuring K_d-values using natural systems for subsequent use in performance assessment models used to predict radionuclide transport in the far field of a radioactive waste repository situated in geological formation at depth. They offer a rather one-sided critique of a number of papers published recently in which the authors allegedly offer wrongly, alternative K_d's for use in performance assessment.

In Ivanovich (1991), one of the papers singled out by McKinley and Alexander (1993) for criticism, I attempted to illustrate a number of points in radionuclide transport studies for which natural decay series could be useful to performance assessment needs but at no point have I advocated that the

0169-7722/93/$06.00

so-called effective R_d's should be used in performance assessment modelling as legitimate substitutes for the laboratory generated data. On the contrary, in my paper I tried to draw attention to the following three points:

(1) I cautioned against indiscriminate use of batch experiments carried out with freshly crushed rock not only because it opened new sorption sites for radionuclides to adsorb onto, but also because such work ignores the crucial role of surface minerals in rock–water interactions in real systems over geological timescales.

(2) I illustrated the use of natural decay series radionuclides in studies attempting to understand the radionuclide distribution (partitioning) between the fluid and solid phases. In particular, I emphasised that surface minerals are by far the most important part of the solid phase taking part in the rock–water exchange processes and, that the bulk of the rock does not participate actively on the short to medium timescales. (This is true for both crystalline and sedimentary rocks of low to medium permeability.)

(3) I also showed that natural colloids could act, in certain circumstances, as the third phase in the rock–water systems which would require a three-phase treatment of radionuclide transport in performance assessment modelling.

To illustrate item (2) above I only had a few papers/reports which had been published during the 3-year period before. From one of these (Ivanovich et al., 1988) I quoted some derived data for Bradwell (Essex, U.K.) and Fulbeck (Lincolnshire, U.K.) argillaceous rocks to which McKinley and Alexander (1993) refer to in their paper.

In these "early" days R_d's were calculated for both U and Th isotopes, and I agree that this simplistic approach is not entirely valid for Th isotopes because they are subject to low solubility limits and precipitation will dominate relative to adsorption. I have shown this to be correct for the case of the Lower Merseyside (Liverpool, U.K.) sandstone aquifer by applying an explicit rock–water interaction model which distinguishes adsorption from precipitation and takes explicitly into account recoil effects (Ivanovich et al., 1992; paper given in Jerez de la Frontera, Migration 1991 meeting). However, in the case of U isotopes, which are much more soluble than Th isotopes, precipitation is often less important than adsorption [also shown by Ivanovich et al. (1992)] and provided the relevant solid and liquid phases are in isotopic equilibrium ($^{234}U/^{238}U$ activity ratios in the two phases are the same or similar) then this simplistic approach is valid.

Unfortunately, McKinley and Alexander (1993) base their case on the summary data quoted in the invited paper (Ivanovich, 1991) and not on the original. If they took the trouble to look into the raw data set given in full in the original report (tables 8–10) they would have had no problem in recognising that the $^{234}U/^{238}U$ activity ratios in the "secondary phases" for both core

materials are very similar to ratios in respective pore waters, justifying our conclusions that the two phases were in isotopic equilibrium with respect to U isotopes at least.

There are a number of reasons why such data are not always 100% reliable. This too was discussed in Ivanovich et al. (1988) but I shall give two reasons here:

(1) The pore-water data may not reflect the real state of disequilibrium in the fluid phase because the method of squeezing pore water from ferruginous limestone (Fulbeck) in contact with atmosphere [the method used by the British Geological Survey (BGS) at the time to produce these precious samples] may have mobilised some daughter radionuclides (e.g., ^{234}U) preferentially, yielding artificially higher activity ratios than the true ones.

(2) The leaching methods used to separate solid "secondary phases" may have not been appropriate, resulting in anomalous phase definition.

Because of these uncertainties we never suggested that these R_d's should be used in performance assessment modelling in preference to batch experiment K_d's but, instead, we suggested that they should be used in support of data obtained in the short-term experiments.

In collaboration with BGS we have investigated item (2) uncertainties in great detail on other solids since, using Mössbauer spectroscopy, α-radiography, differential X-ray diffractometry and many other petrologic and mineralogic methods in order to identify the leached mineral phases and, in order to establish the relationship/association between the measured radionuclides and removed phases. This work has not quite been written up (several Nirex Ltd. reports in preparation) but will be available early in 1993 subsequent to a peer review procedure. What I can say at this stage though, is that we have a great deal more confidence in our choice of reagents now than we did five years ago when the work Ivanovich (1991) referred to was carried out. However, this subsequent work has also shown that the "efficiency" of various reagents depends a great deal on the porosity and "geometry" of the rock fabric (i.e. on accessibility of various secondary phases to the reagents). This explains artifacts which occasionally appear in such data sets.

In conclusion, I can say that McKinley and Alexander (1993) do have a partial case for criticising the work referred to in Ivanovich' (1991) invited paper. However, in their effort to get a very simple message across they have indulged themselves in a rather unbalanced tirade in which they have chosen only one of several points to illustrate their critique failing to acknowledge any points in which the invited paper actually agrees with their thesis. Their paper is also unbalanced by making no effort to illustrate "the approved approaches" in the use of natural analogues for decay series. Instead, they just list the "good" papers and offer no general discussion to show how these papers differ fundamentally in their approach from the "bad" papers. To have done that it would have made their jottings really valuable to other workers in this field. In short, their paper is still an ill-tempered text designed to embarrass rather than to educate or to engage in a deep and useful discussion. Thus, I am not convinced that their text represents a genuine effort to promote an impartial debate on the subject.

ACKNOWLEDGEMENTS

I am grateful to Professor Ghislain de Marsily for encouraging me strongly to respond with the above paper.

REFERENCES

Chapman, N.A. and McKinley, I.G., 1987. The Geological Disposal of Nuclear Waste. Wiley, New York, NY, 280 pp.

Ivanovich, M., 1991. Aspects of uranium/thorium series disequilibrium applications to radionuclide migration studies. Radiochim. Acta, 52/53: 257–268.

Ivanovich, M., Longworth, G., Wilkins, M.A., Hasler, S.E. and Lloyd, M.J., 1988. Measurement of effective K_d factors for the long-lived uranium and thorium isotopes in samples of London Clay (Bradwell) and Mudrock (Fulbeck). At. Energy Auth., Harwell Lab., Nirex, Rep. NSS-R117, 35 pp.

Ivanovich, M., Tellam, J.H., Longworth, G. and Monaghan, J.D., 1992. Rock/water interaction timescales involving U, Th and Ra isotopes in a Permo-Triassic sandstone. Radiochim. Acta, 58/59: 423–432.

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: realistic application of natural analogue studies. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 249–259 (this special issue).

Journal of Contaminant Hydrology, 13 (1993) 267–268
Elsevier Science Publishers B.V., Amsterdam

Response to McKinley and Alexander (1993)

Ove Landström[a] and Eva-Lena Tullborg[b]

[a]*Studsvik AB, S-611 82 Nyköping, Sweden*
[b]*Terralogica AB, Box 140, S-440 06 Gråbo, Sweden*

(Accepted for publication January 8, 1993)

The study by Landström and Tullborg (1990) referred to by McKinley and Alexander (1993 in this issue) presents Th, U, rare-earth element and other trace-element contents in fracture coatings (drillcore samples) from open water-conducting fractures (identified by geophysical loggings), and in *corresponding* groundwater. In two cases the groundwater was sampled in a 3-m section between double packers, and in one case using a single packer arrangement enclosing a 34-m section at the end of a borehole. However, for this particular section, geophysical logging confirmed the two analysed fractures to be the *only* water-conducting fractures.

Fracture coatings from open water-conducting fractures in other boreholes, where no corresponding groundwater was analysed, were also included in the study. The minerals of the fracture fillings were identified by X-ray diffractometry. Trace-element analyses were also carried out on rock types representative of the fracture wall rocks.

We treated the fracture filling–wall rock system in the same way as a weathering profile and thus applied the "immobile element method" (cf., e.g., Nesbitt, 1979), in order to determine the gain and loss of an element in the fracture coating, relative to the composition of the unaffected wall rock. This net supply (or removal) of an element is the result of several processes affecting the coating during its entire "lifetime", and may include elements transported by hydrothermal fluids as well as low-temperature water. Moreover, the supplied elements are reversibly sorbed as well as irreversibly incorporated in the mineral lattice by, for example, coprecipitation.

The ratio between the *net supply* of an element in the fracture coating and the concentration of the element in the *corresponding* groundwater was compared with laboratory determined K_d's (Landström and Tullborg, 1990, 1991). The laboratory K_d's were one to two orders of magnitude lower, but the *main point* is that the *trend is the same*. This is surprising since our distribution factors include trace elements contributed to the fracture filling (sorbed and incorporated in the lattice) during varying conditions over a long period of time. We named the distribution factor "in situ K_d"; a provisional term but obviously not adequate. We agree with the terminology for different distribution factors proposed by McKinley and Alexander (1992).

For some of the fracture fillings with different mineral and elemental composition, but with no corresponding groundwater available, average concentration values of the three analysed groundwaters (which were fairly similar in composition) were used. Although not correct in a strict sense, this allowed us to compare the distribution factor trends for quite different fracture coatings.

Based on our results, work in progress aim more specifically to determine the fraction of reversibly sorbed elements on natural fracture coatings, and will include mineral separation as well as conventional batch K_d experiments for comparison. The work will also focus on retardation of trace elements by coprecipitation during formation of low-temperature fracture minerals like carbonates and Fe-oxyhydroxide, since our results indicate that these processes are important when considering retardation of radionuclides.

It is not sufficient to base conclusions on radionuclide retention entirely on laboratory measurements since, for example, neglecting slow processes may lead to the use of incorrect sorption coefficients. Or worse, conditions which cause unexpected lowering of the sorption uptake on mineral surfaces may be overlooked. Therefore, converging results from laboratory experiments, in situ migration experiments, and studies of natural undisturbed systems are the best guarantee that adequate data are used.

REFERENCES

Landström, O. and Tullborg, E-L., 1990. The influence of fracture mineral/groundwater interaction on the mobility of U, Th, REE and other trace elements. SKB (Swed. Nucl. Fuel & Waste Manage.) Tech. Rep. TR 90-37, 71 pp.

Landström, O. and Tullborg, E.-L., 1991. Part I: Results of mineralogical studies and trace element analyses (U, Th and REE) of fracture coatings, groundwaters and rock samples. In: Hydrogeochemical Studies of Fracture Minerals from Water Conducting Fractures and Deep Groundwaters at Äspö. SKB (Swed. Nucl. Fuel & Waste Manage.) Äspö Hard Rock Lab. Progr. Re. 25-90-01, 60 pp.

McKinley, I.G. and Alexander, W.R., 1992. Contraints on the applicability of "in-situ" K_d values. J. Environ. Radiochem., 15: 19–34.

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: Realistic application of natural analogue studies. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 249–259 (this special issue).

Nesbitt, H.W., 1979. Mobility and fractionation of REE during weathering of a granodiorite. Nature (London), 279: 206–210.

Journal of Contaminant Hydrology, 13 (1993) 269–270
Elsevier Science Publishers B.V., Amsterdam

Response to McKinley and Alexander (1993)

L.H. Brush

Sandia National Laboratories, Division 6345, Albuquerque, NM 87185, USA

(Accepted for publication January 8, 1993)

McKinley and Alexander (1993 in this issue) criticized in situ K_d-values for Ra, Th, U, and Zr summarized by Brush (1991) as "worthless" because they were obtained by the "bulk-rock analysis method", which ignores the "matrix component" of the radionuclide of interest and "cannot distinguish between sorption and precipitation and produce data of no relevance to radionuclide retardation". In situ K_d's are, at least in some cases, subject to the concerns raised by McKinley and Alexander. Because the number of pages allocated for my paper was severely limited, I was unable to provide any details on the methods used to calculate in situ K_d's or on the experimental procedures used to determine K_d's in the laboratory studies that provided most of the data summarized in that paper. Unfortunately, McKinley made no effort to obtain such details, despite the fact that he was present when I visited NAGRA a few weeks prior to his presentation at Migration '91.

In the case of the in situ K_d's for Ra and Th summarized by Brush (1991), these concerns are minor. Modeling of solid-phase and pore-water data from surficial (zone of excess ^{230}Th) North Equatorial Pacific sediments by Cochran and Krishnaswami (1980) implies that ^{230}Th is present mainly on particle surfaces as a result of scavenging from the overlying water column. "Matrix" (detrital) ^{230}Th constitutes a small percentage (~ 3%) of the total ^{230}Th present in these surficial sediments. In the same environment, estimates of the K_d for Ra based on modeling of solid-phase and pore-water ^{226}Ra profiles may be subject to errors resulting from recoil injection of ^{226}Ra into the particles upon decay of ^{230}Th. They may also be subject to errors arising from precipitation of ^{226}Ra-bearing authigenic phases. However, Cochran and Krishnaswami (1980) also carried out laboratory desorption experiments which yielded results in good agreement with their model-derived K_d's for ^{226}Ra. This implies that very little ^{226}Ra resides within the particles or is present in precipitated phases.

In the case of in situ K_d's for U, the maximum estimate among those summarized by Brush (1991) is "particularly worrying" to McKinley and Alexander because it is "nonconservative from a safety assessment viewpoint" and "may lead to overprediction of contaminant retardation". This K_d, calculated from solid-phase (Colley, 1989) and pore-water data (Santschi et al., 1988) from eastern North Atlantic sediments is clearly not subject to significant errors resulting from the presence of undifferentiated detrital U because the quantity of immobilized U greatly exceeds that of detrital U at fossil redox fronts. However, it may fail to "distinguish between sorption and precipitation". Nevertheless, persistence of solid-phase U concentration maxima associated with fossil redox fronts for as logn as 750 kyr (Colley, 1989) implies that these sediments do provide a very effective barrier for U under these conditions, regardless of the form in which it is present on mineral surfaces.

In the case of in situ K_d's for Zr, I cannot respond to the criticisms of McKinley and Alexander in the absence of details regarding the procedures by which Duursma and Bosch (1970) calculated these K_d's. However, unlike McKinley and Alexander, I do not assume that they did so incorrectly merely because I lack such information!

Both in situ and laboratory K_d's are subject to concerns and must be determined in a manner that addresses these concerns. Nevertheless, in situ K_d's provide a powerful tool with which to check long-term predictions based on the results of laboratory studies.

REFERENCES

Brush, L.H., 1991. Summary of laboratory investigations of radionuclide migration through deep-sea sediments. Radioact. Waste Manage. Nucl. Fuel Cycle, 15: 133–143.

Cochran, J.K. and Krishnaswami, S., 1980. Radium, thorium, uranium, and 210-Pb in deep-sea sediments and sediment pore waters from the North Equatorial Pacific. Am. J. Sci., 280: 849–889.

Colley, S., 1989. Uranium redistribution in distal turbidites emplaced in pelagic conditions the Great Meteor east area, Madeira Abyssal Plan. In R.T.E. Schüttenhelm, G.A. Auffret, D.E. Buckley, R.E. Cranston, C.N. Murray, L.E. Shaphard and A.E. Spijkstra (Editors), Geoscience Investigations of Two North Atlantic Abyssal Plains: The ESOPE International Expedition, Vol. II. Comm. Eur. Commun., Joint Res. Cent., Luxembourg, CEC EUR 12330, pp. 939–948.

Duursma, E.K. and Bosch, G., 1970. Theoretical experimental, and field studies concerning diffusion of radioisotopes in sediments and suspended particles of the sea. Neth. J. Sea Res., 4: 395–469.

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: Realistic application of natural analogue studies. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 249–259 (this special issue).

Santschi, P.H., Bajo, C., Mantovani, M., Orciuolo, D., Cranston, R.E. and Bruno, J., 1988. Uranium in pore waters from North Atlantic (Great Meteor east and southern Nares Abyssal Plain) sediments. Nature (London), 331: 155–157.

Journal of Contaminant Hydrology, 13 (1993) 271–275
Elsevier Science Publishers B.V., Amsterdam

Comments on responses to our paper "Assessment of radionuclide retardation: Uses and abuses of natural analogues"

Ian G. McKinley[a] and W. Russell Alexander[b]

[a]*NAGRA, Hardstrasse 73, CH-5430 Wettingen, Switzerland*
[b]*RWIG, University of Berne, Balzerstrasse 1, CH-3012 Berne, Switzerland*

(Accepted for publication January 8, 1993)

The tone of our paper may be harsh, but we feel that it is important that a growing trend to over-interpret limited field measurements be nipped in the bud. This is particularly critical when such measurements could be used incorrectly in the analysis of different options for the disposal of radioactive (or any other toxic) waste.

An essential point is that there appears to be no disagreement about our definition of sorption or the importance of distinguishing between sorption and precipitation in transport models. The four replies to our paper (McKinley and Alexander, 1993 in this issue) basically either make the case that the ratios measured were, in fact, rigorous "K_d's" of the type we define or, alternatively, that the ratios measured were never intended to be used in transport calculations.

Jackson certainly has the strongest case for the former, as the ^{90}Sr which he studied comes from a well-defined source and hence has no "matrix" component. We still feel that discounting possible precipitation on the basis of calculated saturation indices (Jackson and Inch, 1983) for pure minerals is dangerous due to uncertainties in the data bases used (not very critical for this particular case) and the critical rôle played by coprecipitation in controlling the solubility of trace elements at concentrations well below those expected on the basis of "pure phases". Coprecipitation can be especially important when significant concentrations of Fe-oxyhydroxides are available (e.g., Bruno et al., 1991), which is the case for the aquifer examined in this study. Jackson's own data (Jackson and Inch, 1989), indeed, show that early estimates of ~80% of ^{90}Sr being exchangeable with $SrCl_2$ have been revised to 35% and he quotes Killey and Munch (1987) stating that

> "over 50% (of ^{90}Sr) was released by a treatment that partially dissolves the oxide coatings".

Given this key rôle of Fe–Al–Mn-oxides, it is strange that Jackson comments that the

> "additional possibility of co-precipitation by ferric hydroxide was dismissed because of their undersaturation in the aquifer".

Indeed, Jackson and Inch (1983) refer to the weathering of biotite as a source of sorbent clays — a process which also produces Fe(III)–Al-oxides.

The key aspect, essentially, is whether Jackson's "specific adsorption" on materials such as Fe-oxyhydroxides can be represented by a K_d or whether it could be a coprecipitation process, which must be represented by an effective solubility (see fig. 1 of our paper). In our opinion, Jackson's own data showing lack of exchange reversibility, extraction of "sorbed" Sr by "treatment with the acidified reducing agent" (Jackson and Inch, 1983) and "sorption" processes requiring "7–9 yr to reach 95% of equilibrium" argue very strongly for the latter and thus call the basis for his transport model into question.

The brevity of the paper by Brush (1991) is irrelevant to our criticisms of his conclusions as we are familiar with most (if not all) of the source literature. In any case, Brush's arguments are less clear and are based on a variety of general geochemical observations and comparison with "model-derived K_d's" without addressing the key isssue of whether sorption can be adequately distinguished from coprecipitation. Taking the "particularly worrying" case of U, Brush makes much of the work of Santschi et al. (1988) and Colley (1989). The fact that the solid-phase studies

> "fail to distinguish between sorption and precipitation",

acknowledged by Brush, is damming in this context — it may well be that U has not moved for 0.75 Myr but, in order to use this information to mathematically model the consequences of nuclear waste disposal, it is essential to be able to distinguish between these processes. Indeed, the paper by Santschi referenced was singled out for criticism in an earlier paper (McKinley and Alexander, 1992) due to their statement of (Santschi et al., 1988, p.155):

> "solubility control of U(IV) by an adsorbed phase"

which is a classic example of confusion of fundamentally different processes! Discussion with co-authors of both pieces of work (J. Bruno, J. Thompson) make it clear that some kind of coprecipitation was a likely explanation of the observations and hence the diffusion modelling used in both these studies is fundamentally flawed and any "K_d" values derived are really worthless.

Unlike Brush, we are also familiar with Duursma's classical work. Most of Duursma's data are derived from laboratory experiments and his "in situ" studies involved field diffusion experiments with ^{36}Cl. He actually notes that

> "conditions during the sorption experiment are therefore different from those in situ".

For the particular case of Zr, Duursma clearly states that these

> "distibution coefficients ... would be partly due to precipitation on the sediment particle surfaces"

and that precipitation was, indeed, observed in his supporting laboratory experiments (Duursma and Bosch, 1970, pp. 439–440; Duursma and Eisma, 1973, p.287).

Landstrom and Tullborg's response makes it clear that their approach is much more based on mass balances than determination of sorption per se. They reinforce our arguments that any ratios obtained, even if they do not have significant matrix components (which is not proven), often contain contributions from coprecipitation and hence cannot simply be treated as K_d's. While we agree with Landstrom and Tullborg's comments on the interplay between laboratory and field data, unambiguous nomenclature is clearly a prerequisite for any synthetic analysis.

Ivanovich appears to accept that his reported technique for determination of in situ K_d's is flawed but states that

> "at no point have I advocated that the so-called effective R_d's should be used in performance assessment as legitimate substitutions for the laboratory generated data!"

Ivanovich has a very short memory (cf. Ivanovich, 1991, p.264):

> "The approach described above should give more realistic and site-specific retardation information than laboratory derived K_d values currently used in transport asessment modelling"

referring to in situ K_d's including the set discussed in our paper. The same paper concludes with reference to the leaching studies (p.267):

> "Therefore, in the absence of colloids as a third phase of a rock/water system, studying individual mineral phases can yield more realistic distribution parameters, R_d and therefore retardation factors required by safety assessment modelling than short-term laboratory experiments are likely to."

Be that as it may, even if caveats on the use of K_d's were stated, re-expressing these numbers as retardation factors, as he has done many times (e.g., Ivanovich et al., 1988), betrays an ignorance of the limits of applicability of the ratios measured (discussed in detail by McKinley and Alexander, 1992).

In terms of Ivanovich's defense of his U data, it should be emphasised that similar ratios of ^{234}U/^{238}U for "secondary phases" and associated pore waters are necessary, but not sufficient, to show that sorption is the process occurring. Ivanovich refers to his original report (Ivanovich et al., 1988), but this is full of evidence that, even here, the U data cannot be interpreted in terms of sorption alone: he quotes K_d-values for ^{234}U and ^{238}U of 10^5 and 10^4 mL g^{-1}, respectively, clearly indicating that his approach is also incorrect for U.

We are pleased to hear that Ivanovich has finally accepted our criticisms of his phase separation methods and look forward to seeing better definition of the phases he analyses. We were, however, not alone in being unconvinced by the model which he presented at Jerez, but cannot comment further until we see it in print.

From the responses to our paper, it is obvious that critical differences between sorption and precipitation in terms of how they are represented in transport models are not recognised by many of those whose work shows clearly that much more than simple, reversible sorption immobilises or retards trace elements in natural systems. The responses do, indeed, make an excellent case for the critical rôle of coprecipitation — probably mainly with Fe-oxyhydroxides — especially in near-surface environments.

It should be emphasised that the papers which we discussed in our review were merely a representative sample of a much larger body of literature which, at best, represents poor use of nomenclature and, at worst, sloppy methodology and bad science. We appreciate Professor G. de Marsily providing this opportunity to extend the basic points raised in our article to a more open dialogue and hope that the ghost of easy in situ K_d's has finally been laid to rest!

REFERENCES

Bruno, J., Cross, J.E., Eikenberg, J., McKinley, I.G., Read, D., Sandino, A. and Sellin, P., 1991. Testing of geochemical models in the Poços de Caldas analogue study. NAGRA (Swiss Natl. Coop. Disposal Radioactive Waste), Wettingen, NTB 90-29/SKB TR 90-20/ UK-DOE WR 90-051, 75 pp.

Brush, L.H., 1991. Summary of laboratory investigations of radionuclide migration through deep-sea sediments. Rad. Waste Manage. Nucl. Fuel Cycle, 15: 133–143.

Colley, S., 1989. Uranium redistribution in distral turbidites emplaced in pelagic conditions, the Great Meteor East Area, Madeira Abayssal Plain. In: R.T.E. Schültenhelm, G.A. Auffret, D.E. Buckley, R.E. Cranson, C.N. Murray, L.E. Shephard and A.E. Spijkstra (Editors), Geoscience Investigations of Two North Atlantic Abyssal Plains, the ESOPE International Expedition, Vol. II, CEC (Comm. Eur. Commun.), Luxembourg, EUR 12330 EN, pp. 938–948.

Duursma, E.K. and Bosch, C.J., 1970. Theoretical, experimental and field studies concerning diffusion of radioisotopes in sediments and suspended particles of the sea, Part B: Methodology and experiments. Neth. J. Sea Res., 4: 395-469

Duursma, E.K. and Eisma, D., 1973. Theoretical, experimental and field studies concerning reaction of radioisotopes with sediments and suspended particles of the sea, Part C: Application to field studies. Neth. J. Sea Res., 4: 265-324.

Ivanovich, M., 1991. Aspects of uranium/thorium series disequilibrium applications to radionuclide migration studies. Radiochim. Acta, 52/53: 257–268.

Ivanovich, M., Longworth, G., Wilkins, M.A., Hasler, S.E. and Lloyd, M.J., 1988. Measurement of effective K_d factors for the long-lived uranium and thorium isotopes in samples of London Clay (Bradwell) and Mudrock (Fulbeck), U.K. Nirex Ltd., Harwell, Rep. NSS-R117, 35 pp.

Jackson, R.E. and Inch, K.J., 1983. Partitioning of strontium-90 among aqueous and mineral species in a contaminated aquifer. Environ. Sci. Technol., 17: 231–237.

Jackson, R.E. and Inch, K.J., 1989. The in-situ adsorption of ^{90}Sr in a sand aquifer at the Chalk River nuclear laboratories. J. Contam. Hydrol., 4: 27-50.

Killey, R.W.D and Munch, J.H., 1987. Radiostrontium migration from a 1953–54 liquid release to a sand aquifer. Water Pollut. Res. J. Con., 22: 107–128.

McKinley, I.G. and Alexander, W.R., 1992. Constraints on the applicability of "in-situ distributon coefficient" values. J. Environ. Radioact., 15: 19–34.

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: Uses and abuses of natural analogues. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 249–259 (this special issue).

Santschi, P.H., Bajo, C., Mantovani, M., Orciudo, D., Cranson, R.E. and Bruno, J., 1988. Uranium in pore waters from North Atlantic (GME and Southern Naves Abyssal Plain) sediments. Nature (London), 331: 155-157.