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Hydrologic Transport Section
Geosciences and Systems Performance Branch
Division of High-Level Waste Management
Office of Nuclear Material Safety and Safeguards
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Dear Dave:

Enclosed is the final version of our letter report that summarizes our work on hydrogeochemical modeling. We have attached copies of the diagrams that were discussed during the recent program review. Receipt of this letter report should complete our responsibilities in this area. Please call me if you have any questions.

Sincerely,

Gary K. Jacobs

Gary K. Jacobs
Geochemistry Group Leader
Geosciences Section
Environmental Sciences Division

enclosure

cc: A. D. Kelmers
V. S. Tripathi

B0287
NH14 1/1

LETTER REPORT LR-287-84

TITLE: Simulation of Groundwater-Transport-Dynamics of Chemically Reactive Radionuclides

AUTHORS: V. S. Tripathi, G. T. Yeh and G. K. Jacobs

PROJECT TITLE: Technical Assistance in Geochemistry (B0287-8)

PROJECT MANAGER: A. D. Kelmers

ACTIVITY NUMBER: ORNL #41 88 54 92 4 / NRC #50 19 03 01

SUMMARY

The K_d-based approaches predict monotonically decreasing concentrations of radionuclides away from a source; chemical interactions, however, can make this prediction incorrect by producing peaks and/or troughs in radionuclide concentration profiles. Simulations employing a process-level comprehensive model illustrate several important trends in radionuclide concentrations along the transport path that cannot be predicted by traditional K_d-based approaches. These include development of secondary concentration zones (in the aquifer), of concentrations greater than the concentrations released at the source, and development of *dissolved concentration peaks* that are greater in value than the incoming radionuclide concentrations! The computed "effective K_d" values change over more than six orders of magnitude for small changes in chemistry. The process-level comprehensive (and scientifically better-defensible) models, despite their greater data needs, must be favorably viewed against the "easy-to-apply" K_d-based models especially since the latter models have *never* made accurate prediction of transport of radionuclides in any natural system.

INTRODUCTION

This letter report summarizes the highlights of investigations into the currently used methodologies for simulating/predicting transport of radionuclides in groundwater. The methods used for simulation of radionuclide transport are essential for estimation of

radionuclide retardation during aqueous transport in near-surface environments (e.g., soil and groundwater). Reliable methods for prediction of radionuclide transport are also needed to predict the effects of changing hydrologic and/or geochemical system variables (caused by anthropogenic, natural, or a combination of factors) on transport.

A survey of the recent hydrologic literature indicates that virtually all publications dealing with radionuclide transport employ a retardation factor or the K_d approach. The two quantities are interrelated, and both depend on the fundamental under-lying assumption that the transport of radionuclides can be dealt with as though *all* of the element, in question, exists as a single species. Many additional assumptions are made in the use of K_d-based models (Leckie and Tripathi, 1985). For this study, it is important to note that the use of the K_d concept implies that a given K_d value is *invariant* with changes in chemical compositions of the system; this limitation, of course, can be overcome, at least in principle, by employing a series of K_d values commensurate with (evolving or changing) chemical composition of the system. Several "key" radionuclides of importance to the geochemistry of high-level nuclear waste isolation such as Pu, Np and Am exist in multiple oxidation states each of which may form several of numerous possible aqueous complexes and minerals depending on the chemical composition of the system. The radionuclides that undergo oxidation-reduction, complexation, dissolution-precipitation and adsorption-sorption are referred to as *reactive radionuclides* in this study in contrast to other radio-elements such as Cs and I whose chemical interactions are far less complicated. In view of the importance of reactive radionuclides to the geochemistry of high-level nuclear waste isolation, the study was aimed at examining the impact of chemical interactions on their transport-dynamics in hypothetical oversimplified groundwater systems. The study comprised geochemical and hydrogeochemical computer simulations of radionuclide transport and geochemical computations to elucidate the changes in speciation and partitioning of radionuclides in response to changes in solution/system composition.

OBJECTIVES

The major objectives of the study included:

- Examination of the impact of K_d's assumptions on the computed profile of radionuclide concentrations in groundwater.

- Evaluation of the transport of reactive radionuclides in hypothetical simple groundwater systems using a model (HYDROGEOCHEM) that permits explicit accounting of various chemical processes affecting the chemistry of radionuclides in question.

- Examination of the data needs of various approaches for reliable simulation of radionuclide transport.

ISSUES

The key issues that were examined in this study included the following:

- Can the use of the K_d-based computations always be conservative (i.e. overestimate) in predicting the dissolved radionuclide concentrations along the transport path and the cumulative release at a certain distance away from the "source?"

- What sort of variability in effective K_d of reactive radionuclides can occur in response to small chemical changes in system composition?

- Can the aqueous concentration of radionuclides away from the "source" be greater than their concentrations near the "source?"

- Can adsorption lead to the formation of secondary concentrations (analogous to sedimentary ore deposits) of radionuclides away from the "source?"

- What are the data needs of the K_d-based and the process-level approaches to modeling radionuclide transport?

SIMULATIONS, ANALYSES, AND DISCUSSIONS

Simulations of varying chemical and computational complexities were conducted on the Cray and Vax computers. Major results are presented and analyzed.

K_d-based Simulations:

A small number of K_d-based computations were conducted with FEMWASTE, a model developed at ORNL. The problems included transport of solutes with varying K_d values. As expected, increasing K_d values produced a marked increase in solute retardation. All simulations with single K_d values produced *monotonically decreasing solute concentrations* along transport path; this result is a mathematical reality. While a 0 K_d is always conservative for cumulative release computation, the same claim cannot be made for small but non-zero K_d values, at least, in so far as the prediction of concentration profiles is concerned (see the variation in effective K_d values below).

Comprehensive (Process-level) Simulations of Radionuclide Transport:

A large number of runs were made with HYDROGEOCHEM, another model developed at ORNL. HYDROGEOCHEM permits simulation of individual chemical processes such as complexation, oxidation-reduction, adsorption-desorption, and dissolution-precipitation.

Prior to proceeding further, it should be emphasized that the purpose of this project was *not* to compile and utilize the best available thermodynamic properties for reactions involving radionuclides and major ions. Instead, the project utilized readily available complexation/adsorption data and focused on demonstrating and analyzing the impact of considering process-level interactions in radionuclide transport simulations in contrast to the K_d-based approaches wherein the effect of all reactions for each element is lumped into a single value. The advantage of the project strategy is simple — the proof-of-the-principle analysis as to whether the K_d approach may suffice need not wait until we have a perfect understanding of chemical processes and perfect data. Consequently, we analyzed the impact and relative significance of various chemical processes on radionuclide-transport-dynamics without worrying about whether we had accurate thermodynamic values. In other words, we assume that with a different set of thermodynamic data, the relative

significance of difference processes may change (e.g. adsorption may become more or less important in controlling dissolved concentration), however, the conclusion as to whether or not we can lump all chemical interactions into a single parameter (K_d) for *reactive* radionuclides will not change.

A Representative Simulation: The results of a simulation that was constructed to minimize the intra-system chemical variability is presented. The transport of UO_2^{2+}, NpO_2^{+} and TcO_4^{-} in a 1-D column was considered; chemical interactions included hydroxide, carbonate and sulfate complexation, and adsorption of uranium and neptunium. The pH was held constant within a narrow range (7.6 to 7.9). The initial sulfate concentration was 10^{-4}M; the adsorption surface area (a model solid — goethite) varied from 10^{-4} to 10^{-2}M; CO_3 was 0.0001M. The initial concentration of uranium, neptunium, and technetium was 10^{-8}, 10^{-16}, and 10^{-16}M respectively. The concentration of radionuclides entering the column was held constant at 10^{-6}, 10^{-10}, and 10^{-9}M for uranium, neptunium, and technetium respectively.

The entire simulation was conducted for a period of 500 days. For the first 200 days the system was "static" in its chemical composition with the exception that uranium, neptunium and technetium were entering the column at much higher concentrations than the initial values; uranium(VI) and neptunium(V) were adsorbing upon entering the column onto the model adsorbent. The continued adsorption for two hundred days created a uranium and neptunium rich region in the adsorbent-rich zone of the column. To examine, the impact of desorption, a pulse of 0.01M CO3 was introduced in the column; the pulse slowly decreased in concentration to 0.001M at 500 days. The impact of carbonate was dramatic and quantitatively different for uranium and neptunium reflecting the differences in the "strength" of their carbonate complexes and in their adsorption reactions. Specifically, uranium which adsorbed more strongly but also has strong carbonate complexes underwent substantial desorption; its dissolved concentration increased 40x times incoming value, and its "effective K_d" varied over 6 orders of magnitude. This simulation demonstrates 1) that secondary formation of high concentrations of radionuclides is geochemically feasible, 2) that an increase in the concentration of complexing ligands (carbonate, for example) can lead to even higher dissolved uranium concentrations away from the source than near the source, and 3) that large variations occur in K_d values in response to geochemical changes. It can be argued that the results (development of high radionuclide concentration zone due to adsorption and of high dissolved concentration due to desorption) are due to the assumption of instantaneous

equilibrium in these simulations. It is important to remember, however, that the results were obtained in these computations within a short period of 500 days, a time scale negligible in comparison to geologic events and the groundwater flow velocity in natural systems, and that in natural systems, the time available for these reactions will be on the order of hundreds to thousands of years! The longer times will permit greater buildup due to adsorption, and thus more material will be available for desorption upon changes in system composition. Finally, the predictions of this simulation are documented in the geologic history of sedimentary uranium ore deposits; these uranium deposits are well known to have repeatedly formed and disappeared in response to geochemical changes.

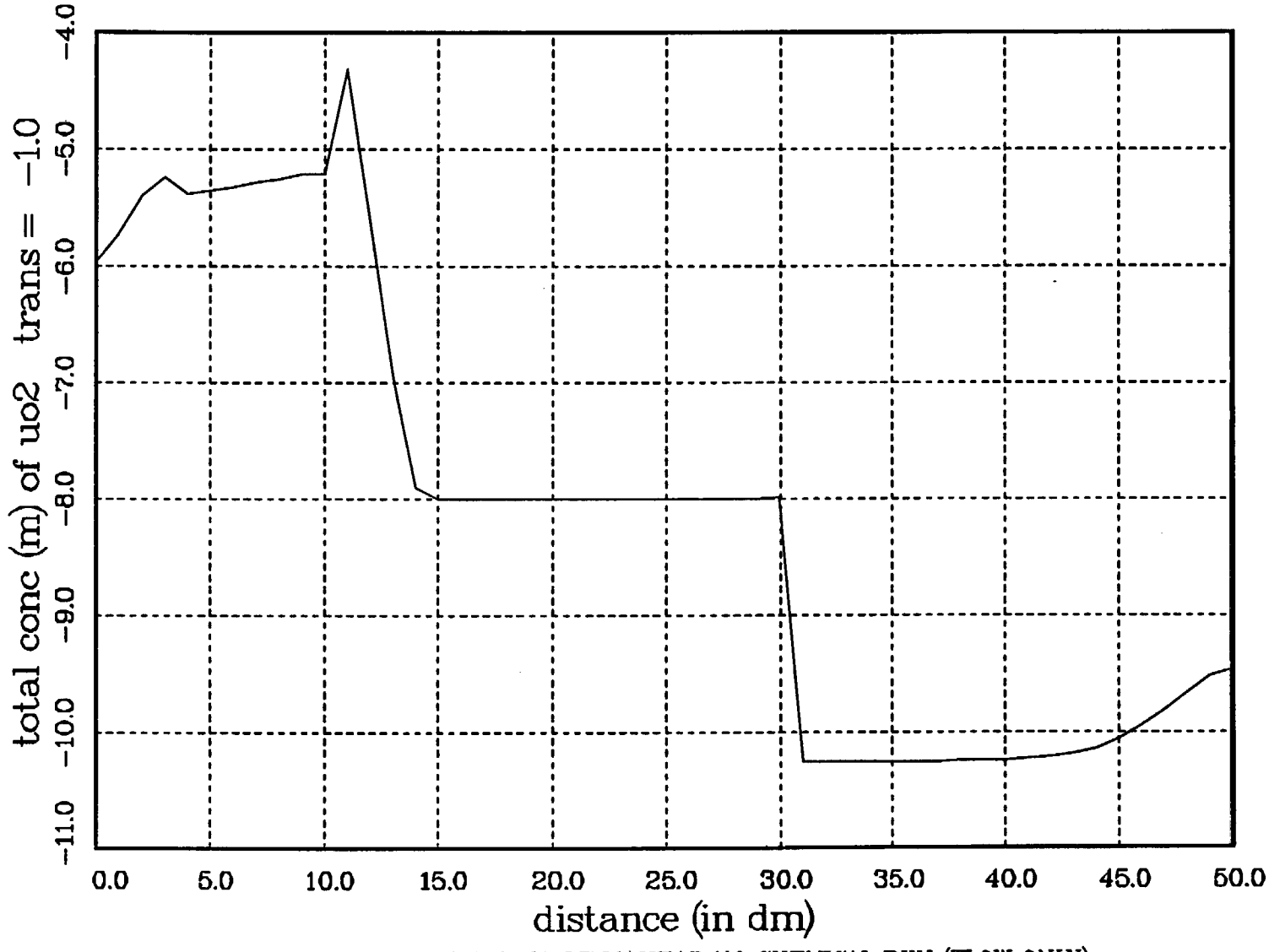
The behavior exhibited by neptunium is similar to that of uranium with some important differences. Since $NpO2^+$ adsorbs less strongly and its carbonate complexes are weaker, its concentration increase due to adsorption was less pronounced, and so was the concentration peak due to desorption. Technetium, on the other hand, was transported with water (without any retardation) since at the Eh values considered in this simulation, its adsorption is not known to occur.

Data Needs of the Kd-based and Process-level Approaches:

This is a very important component of any comparison of models. A rigorous technical analysis is beyond the scope of this report. Some observations will be presented, however. The more complex and "realistic" a model, the greater are its data needs, and therefore, the process-level comprehensive models require much more information about the system than the K_d-based models. The process-level models work or don't work depending on whether (and how well) we understand the underlying processes and the system, and whether we can provide accurate enough model inputs specific to the system under study. Furthermore, processes-level models are better-defensible in as much as they are built on the *best current* scientific and technical understanding. K_d-based models, on the other hand, are much simpler and less expensive to "apply", however, they have never proven to predict transport of *reactive* radionuclides in any natural system! This historical observation coupled with the fact that their underlying assumptions are invalid for reactive radionuclides such as Pu, Np, Tc, and Am argue in favor of generating information and understanding for the process-level comprehensive models.

REFERENCE

Leckie, J.O. and Tripathi, V.S., 1985, Effect of changing geochemical parameters on the distribution coefficient Kd. Keynote paper for the session on speciation and methodology, 5th International Conference on Heavy Metals in Environment, Athens, Greece. Proceedings of the conference, 2, 369-371, CEP Consultants Ltd., Edinburgh, UK, 586 p.



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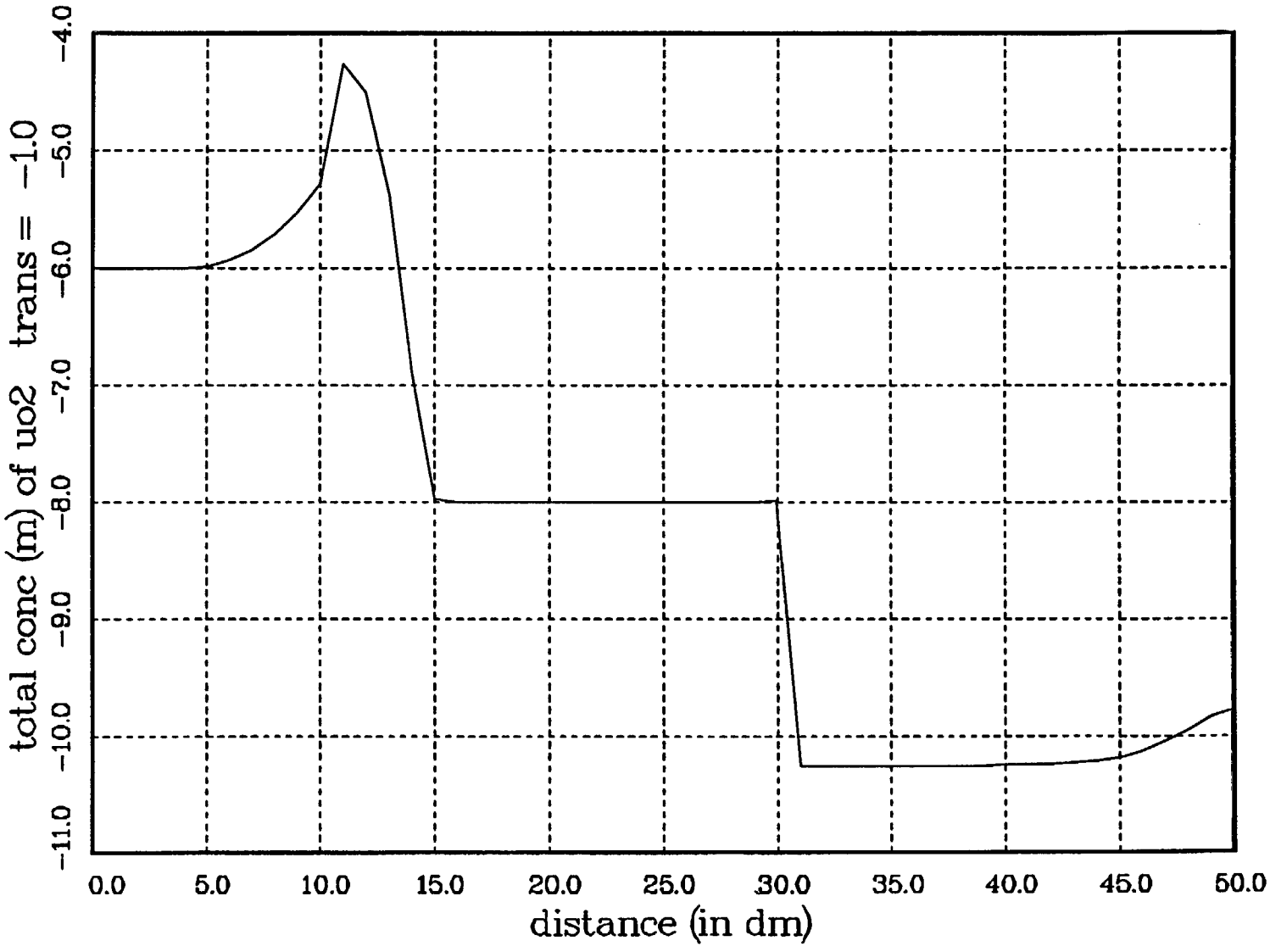

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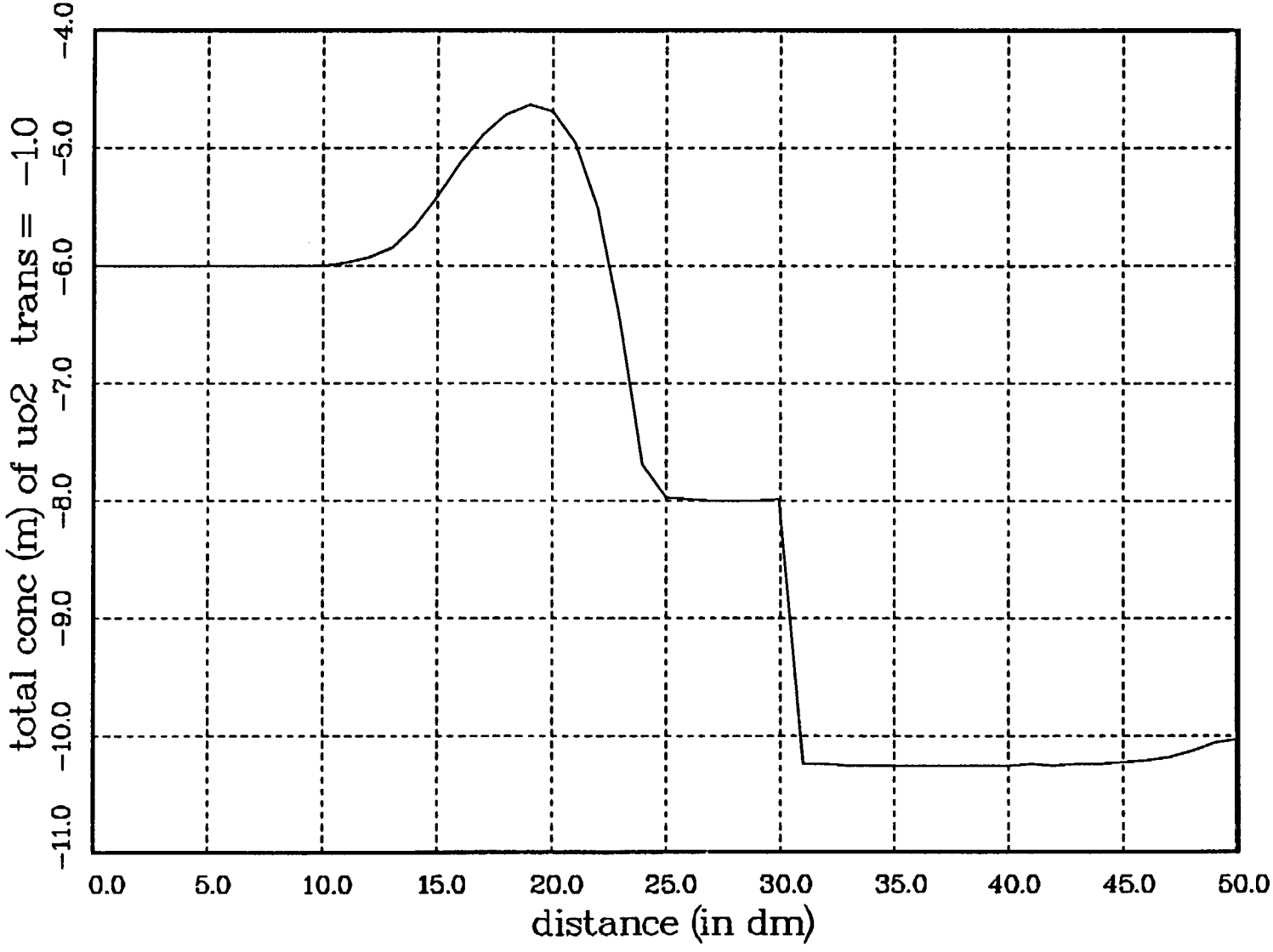

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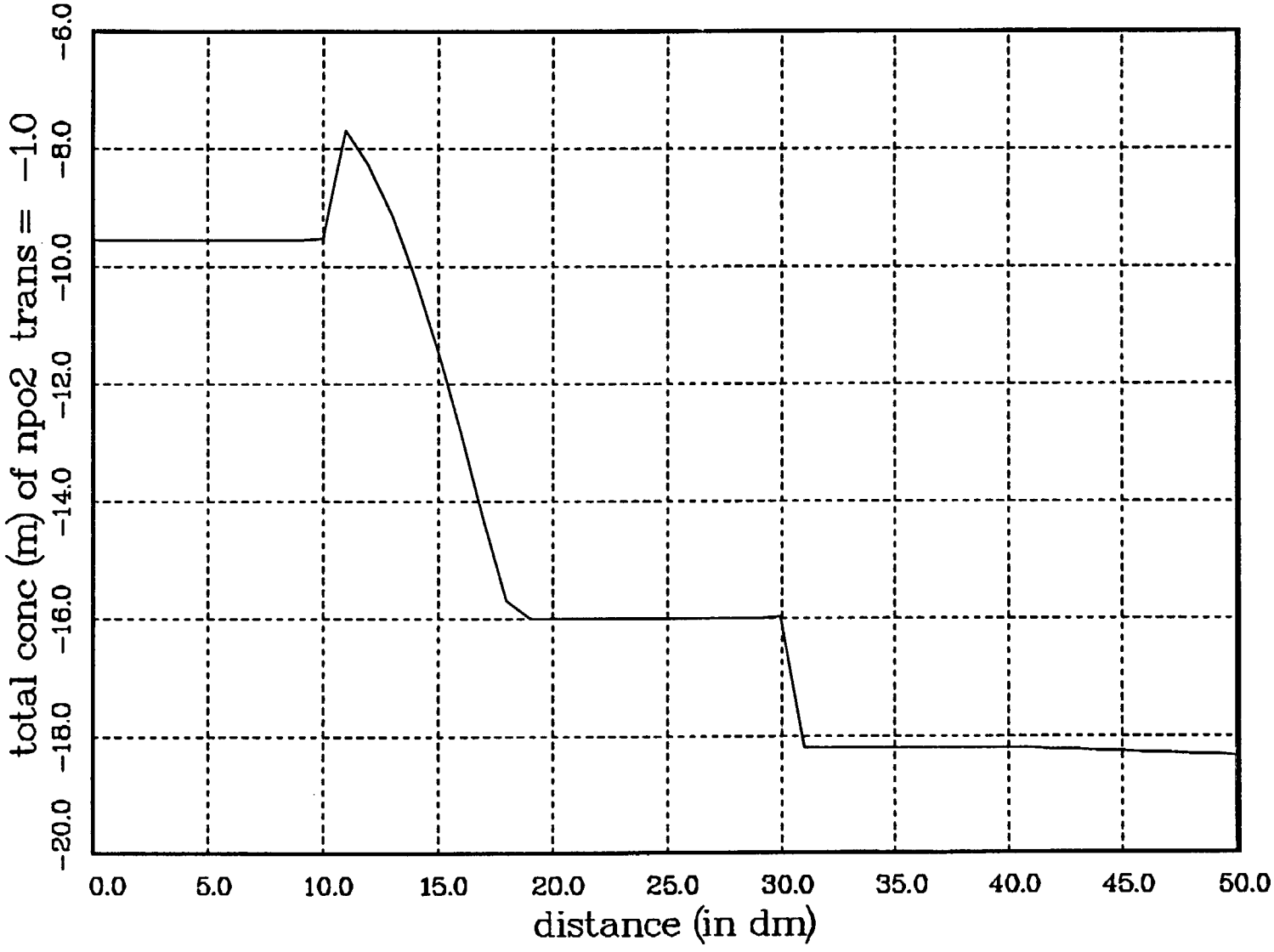

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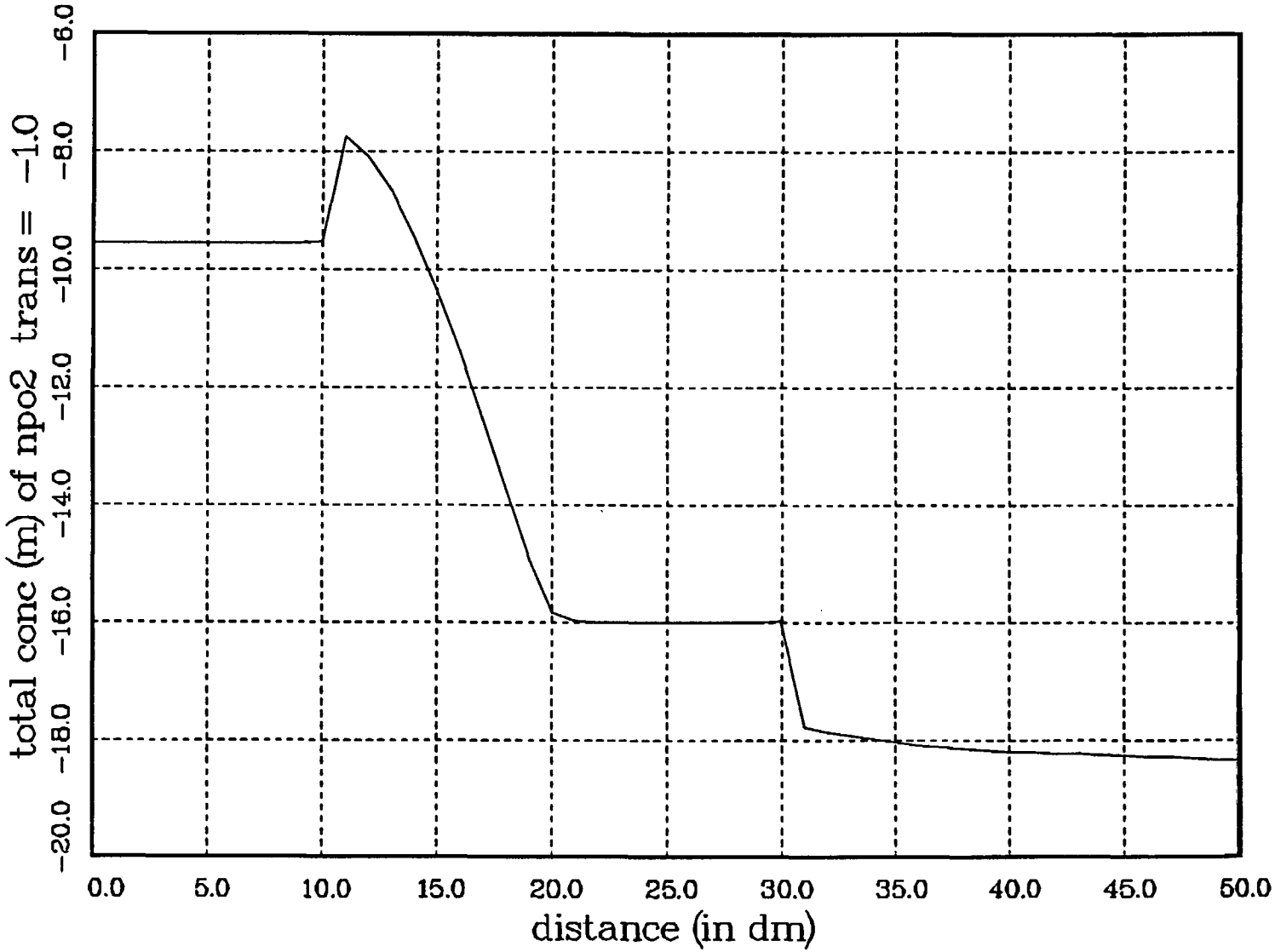

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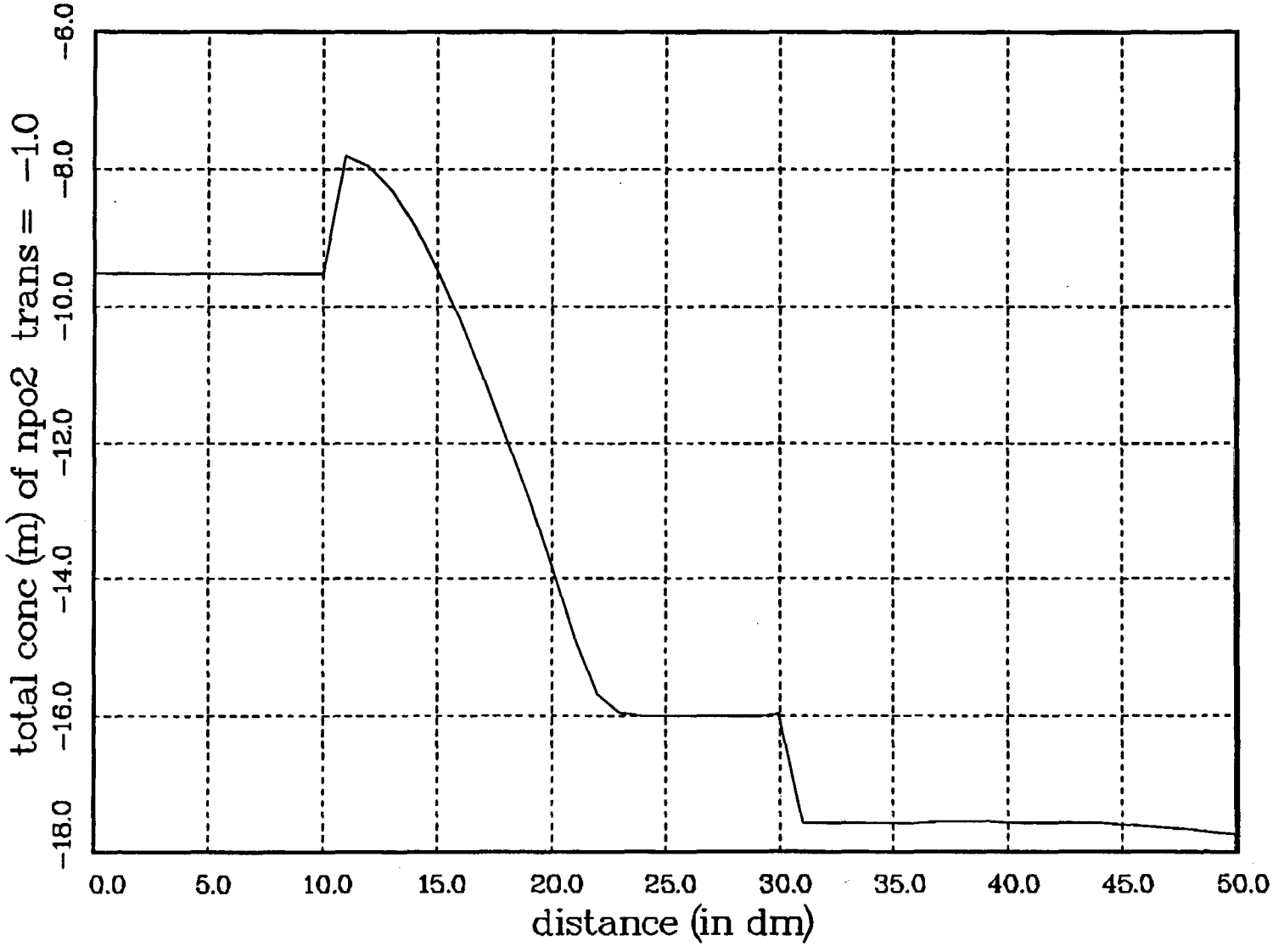

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