



Project Summary

Investigations of Coupled Geochemical and Transport Modeling for the Hazardous Waste Identification Rule

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Research to define both allowable metal concentrations in waste streams for landfill disposal and allowable landfill leachate compositions is being conducted by the U.S. Environmental Protection Agency. Leachate interaction with the subsurface may reduce or increase the impact of disposed metals on water quality. For regulatory purposes, it is important to develop models that encompass the full spectrum of landfill leachate migration scenarios possible in the United States. The calculations presented here were performed to establish reasonable high-end exposure scenarios.

The Chemical Transport Model was used to perform calculations to illustrate the interaction between landfill leachate and the subsurface. The major inorganic constituents of both the ground water and the landfill leachate are included in aqueous speciation/solubility calculations. Transport is described by a 1-D advection/dispersion equation. Cadmium was selected as an example metal for the calculations, and its adsorption onto ferric hydroxide is described by a surface complexation model.

Preliminary results showed that the continual influx of an acidic (pH = 5.9) landfill leachate into the subsurface may deplete the acid buffering capacity of alkaline soil and ground water (pH = 8.0) within 20 to 30 years. Changes in solution pH led to changes in aqueous speciation and metal adsorption. In the simulations performed, cadmium desorbed as pH decreased, leading to the migration of a Cd front

through the subsurface with higher Cd concentrations than those in the initial landfill leachate. Additional calculations will be required to determine whether changes in landfill leachate composition over the lifetime of the landfill or changes in the subsurface redox environment due to leachate migration will significantly affect the model results.

This Project Summary was developed by the National Exposure Research Laboratory's Ecosystems Research Division, Athens GA, to announce key findings of the research project that is fully documented in a separate report (see Project Report ordering information at back).

Synopsis of Report

The objectives of the Hazardous Waste Identification Rule (HWIR) are to define allowable constituent concentrations in waste streams for landfill disposal and to define allowable landfill leachate concentrations. A methodology for organic constituents has been developed in which a ground water chemical transport code is used to determine the dilution attenuation factor (DAF), or the ratio of the leachate concentration at a landfill to the concentration at a receptor well, for each constituent. Using the maximum allowable concentration level (MCL) at the receptor well, one can back-calculate the allowable concentration in the leachate. A distribution of DAFs representing the range of possible outcomes at landfills nationwide can be calculated by applying the transport code in a Monte Carlo mode.

Generating appropriate DAFs for metal constituents in waste streams is more dif-

difficult than generating DAFs for organics due to variations in metal behavior with changes in solution and soil chemistry. In the HWIR methodology, the chemistry and transport of metals from the landfill through the vadose and saturated zones to a potential receptor well is simulated with the use of a loosely coupled, deterministic transport and chemistry model. This report reviews the assumptions made in the HWIR methodology for metals, summarizes the compositional data available for landfill leachates, and explores (through the use of an aqueous speciation/solubility code and a one-dimensional coupled reaction/transport code) the "conservative nature" of the HWIR assumptions (i.e., do the HWIR assumptions provide conservative estimates of potential contamination at receptor wells).

In the HWIR methodology, geochemical reaction is coupled with transport through the use of sorption isotherms for several metal contaminants (beryllium, cadmium, chromium, mercury, nickel, and lead). Four master variables—ground water pH, organic matter from the landfill leachate, iron oxide adsorbent concentration, and natural organic matter—are considered to play significant roles in the behavior of metals in the subsurface environment. Each of these four master variables is assigned three values (high, medium, and low) to generate a grid of geochemical environments that spans the conditions that might be observed in landfill scenarios. This grid is accessed by the transport code whenever geochemical parameters are required.

This study examines whether the four master variables selected for the HWIR methodology characterize the landfill

leachate and the soil matrix/ground water system sufficiently to predict metal contaminant transport in the subsurface. The HWIR assumptions regarding landfill leachate compositions, soil buffering capacity, redox reactions, competition between metals for adsorption sites, and sorption by clay minerals are reviewed. A major concern with the HWIR methodology is that the development of the geochemical model separately from the transport model in the "loosely coupled" code may not sufficiently characterize the interactions that arise as leachate is generated and introduced into the subsurface.

Coupled reaction/transport simulations were performed using the Chemical Transport Model (CTM) in order to demonstrate the importance of the leachate and soil compositions on the transport and transformation of metals. Five simple scenarios illustrate the effects of variable amorphous hydrous ferric oxide (HFO) concentrations, the presence of calcite, and competitive adsorption between a metal and other solutes.

CTM requires a path line length, average pore water velocity, and the dispersivity of a conservative tracer along the path line. These input parameters were calculated using the values representative of the 85 percentile reported in prior HWIR studies, so that the results are representative of 15% of the HWIR scenarios. A representative landfill leachate composition and an HWIR ground water composition at pH 8.0 are used. Cadmium is used as a representative HWIR metal.

Cadmium may be retarded by both adsorption and solubility reactions in the subsurface environment. The adsorption

model in CTM is a surface complexation model developed to calculate the adsorption behavior of selected aqueous constituents on amorphous hydrous ferric oxide. A thermodynamic database was adopted and acetate complexes from the MINTEQA2 database and phosphate and ammonium complexes were added. Cadmium adsorption to organic matter was not considered.

The simulations show that both HFO and calcite contribute to the acid-buffering capacity of soil. Competitive adsorption between Cd^{2+} and the major cations in the leachate and ground water decreases the concentration of sorbed Cd^{2+} , thereby increasing the concentration of Cd^{2+} that migrates downstream.

The simulations also illustrate that one reasonable high-end scenario arises when the continual influx of an acidic (pH = 5.9) landfill leachate into the subsurface depletes the acid buffering capacity of the soil and ground water (pH = 8.0). Changes in solution pH led to changes in aqueous speciation and metal adsorption. In the simulations performed, Cd desorbed as the pH of the subsurface decreased due to mixing with the infiltrating leachate. This led to the migration of a Cd front through the subsurface with higher Cd concentrations than those in the initial landfill leachate.

Additional calculations will be required to determine whether changes in landfill leachate composition over the lifetime of the landfill or changes in the subsurface redox environment due to leachate migration will significantly affect the model results.

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The complete report, entitled "Investigations of Coupled Geochemical and Transport Modeling for the Hazardous Waste Identification Rule," (Order No. PB97-121164; Cost: \$21.50, subject to change) will be available only from:

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