



## Project Summary

# Batch-Type Procedures For Estimating Soil Adsorption Of Chemicals

W.R. Roy, I.G. Krapac, S.F.J. Chou, and R.A. Griffin

This Technical Resource Document (TRD) contains laboratory procedures and guidelines for conducting experiments using batch-equilibrium techniques to study the adsorption by clays or soils of chemicals dissolved in solution (solutes). The procedures were designed for routine use, and can be used for developing data for constructing equilibrium adsorption isotherms. Procedures are given for inorganic and organic solutes as well as for volatile organic solutes. The scientific basis for each procedural step is discussed in detail. These procedures were based on scientific literature, and were developed and tested by the authors and cooperating laboratories. Examples are given to show application of major procedural steps and concepts. Several types of soil materials and solutes are featured, as well as the application of batch-adsorption data in calculations of solute movement through compacted landfill liners.

This TRD was submitted by the Illinois State Geological Survey in fulfillment of Cooperative Agreement CR810245 with the U.S. Environmental Protection Agency. It has been revised to address issues that were raised during the public comment period on the draft TRD entitled *Batch-Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals* (EPA/530-SW-87-006). The revised TRD also includes technical information that became available after the draft TRD was completed in May 1987.

*This Project Summary was developed by EPA's Risk Reduction Engineering*

*Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The capacity of geological materials to attenuate potential pollutants had been studied by many researchers. The batch-adsorption or static-equilibration technique has often been used in laboratory studies to assess the capacity of soils and soil components to remove chemical constituents from solution. Batch procedures vary considerably from one another in terms of experimental conditions and research objectives, and sometimes yield different results even when the same soils, solutes and concentrations are used.

The simplicity of the batch-adsorption technique accounts in part for its popularity. With this technique, an aqueous solution containing solutes of known composition and concentration(s) is mixed with a given mass of adsorbent for a given period of time. The solution is then separated from the adsorbent and chemically analyzed to determine changes in solute concentration. The amount of solute adsorbed by the adsorbent is assumed to be the difference between the initial concentration (before contact with the adsorbent) and the solute concentration after the mixing period. Although the approach is relatively simple, several experimental parameters can affect the adsorption of a given constituent. These parameters include: contact time between the solute and adsorbent, temperature, method of mixing, soil:solution ratio, adsorbent mois-



ture content, solution pH, hydrolysis, and the composition and concentration of other dissolved constituents in the solution. Dissolved organic carbon, volatility, photodegradation, biodegradation, and compound stability can also affect adsorption data associated with organic solutes.

In the past adsorption studies, the particular experimental conditions selected were probably appropriate for the specific system under study and for the intended use of the data. However, the diversity in experimental conditions can make comparisons of adsorption data between studies difficult. The U.S. EPA perceived a need to develop a well-documented, comprehensive source for conducting batch-adsorption determinations.

This (TRD) incorporates the experiences gained during interlaboratory testing programs and the interactions with the scientists and laboratories affiliated with American Society for Testing and Materials. It describes procedural steps for inorganic and organic solutes, and documents their scientific basis. Most of the procedural steps recommended here were tested in the authors' laboratory with a variety of soils, solutions containing several solutes, and aqueous extracts of actual wastes. Characteristics of the soils, clays, and wastes are described in the appendices of the full report.

## Discussion

A brief review of the physicochemical forces and mechanisms thought to be responsible for the adsorption of ions and molecules from solution is presented in Chapter 1. The effects of adsorbent preparation are discussed in Chapter 2. The process of preparing samples taken in the field for laboratory investigations can directly influence adsorption results. Adsorbent samples are usually dried so that they can be homogenized and stored until needed. Oven-drying of adsorbents is not an advisable technique to accelerate drying even though air-drying may take several days with large bulk samples. Air-drying minimizes physicochemical changes that may occur when drying and is the most practical approach at this time. Air-drying anaerobic soils and sediments requires special handling to prevent the relatively reduced materials from oxidizing if exposed to the atmosphere.

The effects of temperature on adsorption measurements are discussed in Chapter 3. Batch-adsorption determinations should be conducted under constant-temperature conditions, if available, or in rooms where the ambient temperature is fairly constant (e.g.,  $\pm 3^\circ\text{C}$ ). When batch

experiments are performed, the temperature of the solution should be recorded and treated as a potential variable that can influence the data, and therefore may be useful in the interpretation of the results. The stability of nonionic solutes is the subject of Chapter 4.

In conducting batch-adsorption tests, investigators must consider the physicochemical stability of the solute in solution. Processes such as photodegradation, hydrolysis, and/or microbial degradation can potentially contribute to a decrease in solute concentration concomitantly with adsorption, and these changes may even occur before the solution contacts the adsorbent. Procedures are given in this chapter that can be used as simple screening tests to identify potential solute-stability problems.

In Chapter 5 on the effects of pH on adsorption, the adsorption behavior of ionic and ionizable inorganic and organic solutes by soils and soil materials is discussed. In general, the adsorption of inorganic cations increases with increasing pH, and the adsorption of anions is generally enhanced in acidic environments, although some anionic solutes are adsorbed to a greater extent in alkaline systems. The adsorption behavior of neutral, non-polar hydrophobic organic solutes appear to be largely unaffected by the pH of the soil-water system. The potential influence of pH on the results generated by batch-adsorption procedures depends on the system under study. The equilibrium pH of the soil-solute mixtures should be determined before separating the solution from the soil or soil component suspension. The measurement should be given along with the adsorption data. The failure to measure and report pH data may render the adsorption data impossible to interpret in a meaningful way.

The ionic strength of the solution may have several direct and indirect effects on adsorption data (Chapter 6). The extent of these effects depends on the magnitude of the ionic strength and on the concentration, composition, and charge of the ionic constituents. The position taken in developing the batch-adsorption procedures was governed by the philosophy that they should be simple and designed primarily for routine use. Thus, the use of a background electrolyte was rejected in anticipation that the inherent ionic strength of the solutions will be influenced by the chemical constituents occurring in the leachate or extract, and those derived from soluble constituents in the particular clay or soil under investigation. The electrical conductivity (EC) of the equilibrated soil-

solution should be measured so that the ionic strength of the solution can be calculated. The failure to measure and report EC data and/or ionic strength can make adsorption data difficult to interpret.

In the chapter on phase separation (Chapter 7), a search of the literature indicated that very few researchers have used a filtration technique to separate the liquid and solid phases before analyzing the liquid phase in batch-adsorption studies. This is probably due to the potential of the filter membranes to retain significant quantities of the solute, particularly organic compounds. Solid and liquid phases should be separated by centrifugation unless the investigator can clearly demonstrate that the filtration technique does not significantly affect the results.

In theory, the mechanical device used to mix the solid-liquid mixture during the equilibration interval should have no effect on the equilibrium distribution of solutes and adsorbates (Chapter 8). However, studies in the TRD show that the mixing method can influence the resulting adsorption data. For all adsorption experiments, National Bureau of Standards (NBS) rotary extractor or its equivalent should be used during each step necessary to develop an adsorption isotherm, i.e., determining a soil:solution ratio (Chapter 9), equilibration time (Chapter 13), and the adsorption isotherms. Adsorption data generated with other mixing devices may be valid; however, these data should not be routinely accepted unless the investigator can document that the device used yields data comparable to those from an NBS rotary extractor or its equivalent. This recommendation will help standardize results between laboratories.

The term "soil to solution ratio" refers to the ratio of the mass of the adsorbent sample to the volume of liquid. To construct an adsorption isotherm, soil:solution ratios must be determined that will permit enough solute to be adsorbed to result in measurable, statistically significant differences in solution concentration. If the soil:solution ratio is low (i.e., too much adsorbent or too little solution), most of the solute may be adsorbed, forcing the investigator to attempt to measure small differences in concentration at very low solute concentrations. If the ratio is too high (i.e., not enough adsorbent for a given volume), the changes in the initial solute concentration may be very small, forcing the investigator to measure small differences in concentration between large amounts of solute. Unfortunately, with inorganic and polar organic compounds, a suitable soil:solution ratio cannot be de-

terminated a priori, and procedures for selecting a suitable ratio are given in Chapter 9.

Finding a suitable soil:solution ratio for ionic and polar solutes requires laboratory work, but a simple calculation can be used to estimate a suitable ratio for nonionic solutes, particularly hydrophobic organic species. This estimation technique requires a value for the organic carbon content of the adsorbent and for the organic carbon partition coefficient ( $K_{oc}$ ) of the solute.

In Chapter 11, the effects of the soil:solution ratio on adsorption data are discussed. The soil:solution ratio may be one of the most important experimental variables to consider when developing an adsorption isotherm and evaluating the data, particularly when comparing results from different investigators who used different ratios. Specific soil:solution ratios provided in Chapter 17 should be adopted as standard ratios for the construction of adsorption isotherms. Adherence to this recommendation will enable direct comparisons of adsorption data generated by different investigators.

Two experimental techniques are used to generate batch-adsorption data:

1. The constant soil:solution ratio method: mixing a batch of aqueous solutions—each solution containing progressively decreasing solute concentrations—with adsorbent, keeping the amount of adsorbent (by weight) constant in all solutions.
2. The variable soil:solution ratio method: mixing a batch of solutions, all containing the same solute concentra-

tion, with progressively increasing amounts of adsorbent.

The first technique presumably is based on a standard ratio selected from the procedures given in Chapters 9, 10, and 17. The second is similar to the technique used to select a soil:solution ratio for ionic solutes (Chapter 9). An isotherm produced by variable soil:solution ratios was considered to be more environmentally conservative.

Adsorption at the solid-liquid interface is a thermodynamic process, and adsorption measurements are taken when the system has equilibrated (Chapter 13). Adsorption is generally regarded as a fast reaction, and subsequent removal of solute from solution may be attributed to other processes. Adsorption processes at solid-liquid interfaces are often initially rapid; further reduction in solute concentration continues at a decreasing rate, asymptotically approaching a constant concentration. In some cases, equilibrium is never clearly attained. The ambiguity in the definition and measurement of equilibration times has been acknowledged as a major problem in adsorption studies. The EPA suggested that the equilibration time should be the minimum amount of time needed to establish a rate of change of the solute concentration in solution equal to or less than 5% per 24-hr interval. This definition is an operational definition of equilibrium and is equivalent to a steady state.

The selection and construction of adsorption isotherms is discussed in Chapters 14 and 15. An adsorption isotherm is a graphic representation showing the

amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration of the solute. This relationship is quantitatively defined by some type of partition function or adsorption isotherm equation that is statistically applied to generalize the data.

Chapter 16 covers the use of batch-adsorption data. Adsorption data are used in describing the partitioning of chemicals between soils and water, and have been used successfully as input parameters in models describing the movement of chemicals through soil to groundwater. This chapter is a brief introduction to possible applications of batch-adsorption data. An example to calculate solute movement through a compacted soil liner of a landfill is provided.

The procedures for the determination of the soil:solution ratio, equilibration time, and other parameters necessary for the construction of adsorption isotherms are contained in Chapter 17 and are written in the ASTM format. The rationale for these procedures, presented in previous chapters, should be studied before attempting to use them. Throughout this chapter, references are made to other parts of the TRD that elucidate topics relevant to a specific procedural step. The references cited include 169 publications that were consulted in the evolution of this TRD.

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The complete report, entitled "Batch-Type Procedures for Estimating Soil Adsorption of Chemicals," (Order No. PB92-146190/AS; Cost: \$26.00; subject to change) will be available only from:

National Technical Information Service  
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