



Project Summary

The Swelling Properties of Soil Organic Matter and Their Relation to Sorption of Non-Ionic Organic Compounds

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A method has been developed to measure the swelling properties of concentrated natural organic materials in various organic liquids, and has been applied to various peat, pollen, chitin and cellulose samples. The swelling of these macromolecular materials is the volumetric manifestation of bulk sorption, i.e., sorption by dissolution (or partitioning) of the sorbed liquids into the macromolecular solid phase. Direct evidence for the existence of this category of sorbed materials has been obtained for soil organic materials by the present research; swelling in liquids has long been known in coals and polymers.

Bulk sorbed molecules are thought to be inaccessible to direct biological attack, and may represent a continuing source of low-level, "rebound" contamination of groundwater at a polluted site following attempted pump-and-treat remediation. Equilibration of bulk sorbed molecules with liquid phases surrounding the particles is kinetically slow (diffusion limited) relative to sorption and fluid movement, and this sluggishness is probably responsible for some nonequilibrium sorption phenomena seen in soil column flow experiments.

Molecules with molar volumes greater than about $93 \text{ cm}^3 \text{ mol}^{-1}$ appear to be strongly excluded from sorption inside the soil organic materials studied in this work. In contrast, cellulose excluded molecules with molar volumes greater than $88 \text{ cm}^3 \text{ mol}^{-1}$.

Besides the size exclusion factor, the degree of swelling of soil organic materials in different liquids is controlled mainly by site-specific, generalized acid-base interactions between the sorbed molecules and the various acidic sites within soil organic materials. The swelling spectra observed for soil materials are complex, and completely unlike the simple Gaussian swelling spectra observed for polymers like rubber (cross-linked polyisoprene) and for some coals. In these latter materials the intermolecular forces are dominated by non-specific dispersion forces (van der Waals interactions), and can be adequately treated by simple equations (Flory-Huggins-Rehner theory) involving the solubility parameters of the liquid and the swelling substrate.

Swelling in morpholine appears to be a characteristic of soil organic materials containing free cellulose. Unfortunately, the cellulose within natural ligno-cellulosic plant debris apparently behaves differently from free cellulose, so that swelling alone does not provide a simple measure of humification in soils or peats. We speculate that the intimate association of lignin with the cellulose at the molecular level blocks access to the specific sites (alcoholic-OH groups) on the cellulose with which morpholine interacts most strongly. Free cellulose does, however, appear to be present in pollen intine membranes.

This Project Summary was developed by EPA's Robert S. Kerr Environmental



Research Laboratory, Ada, OK, 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 Swelling Phenomenon

Macromolecular substances swell when placed in contact with various fluids¹; the amount of swelling depends both on the nature of the fluid, and of the macromolecular material. Strongly cross-linked materials swell less than weakly cross-linked materials. Such swelling is a property of the insoluble macromolecular network itself, and it occurs even when all associated soluble materials have been removed by exhaustive solvent extraction.

Swelling is the dissolution of small molecules of more mobile substances into the solid. The macromolecules act as a solvent for these smaller molecules, and the swollen phase represents an unusual kind of solution. An alternate point of view is that swelling represents the solvation of internal macromolecular "surfaces" by the smaller fluid molecules.

The Connection Between Sorption and Swelling

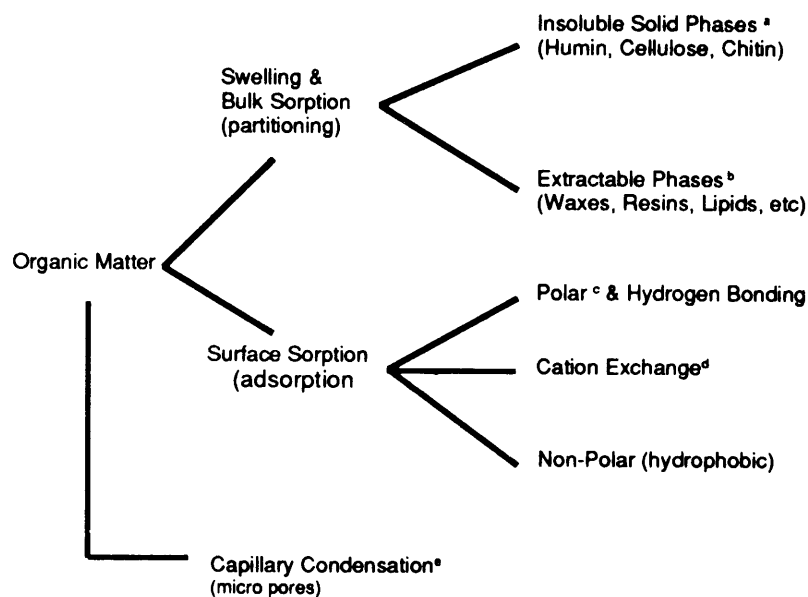
Swelling represents a volumetric manifestation of certain kinds of sorption involving *bulk sorption* (partitioning) into soil organic matter. The various categories of sorption in soil organic matter are detailed in the diagram below.

Bulk Sorption and Swelling

Swelling experiments measure the **maximum capacity for bulk sorption** of certain solvents that solid organic materials can hold while in contact with the pure solvent. This limiting capacity can be expressed if a variety of units, such as cm³ sorbed solvent per cm³ sorbent. Sorbed material in this form represents a potential source of residual contamination that is difficult to remove completely by any known process (e.g., solvent extraction, vacuum extraction, biodegradation, etc.) This residual contamination is considered to be of greatest importance for the smaller, more polar solvent molecules such as methanol. Some solid macromolecular soil organic materials (e.g., cellulose and chitin) can themselves be bio-

¹ Here we restrict the discussion to fluids with a single molecular constituent. When two constituents are present, a richer, more complex set of phenomena can occur, such as gel-collapse, phase transitions, where a swollen gel can suddenly decrease in volume when exposed to a fluid of different composition.

Sorption Categories in Natural Soil Organic Matter



^a Dissolution in these materials is accompanied by size exclusion. Also, within the solid macromolecular structures, different types of organic molecules will preferentially solvate various sites: polar, non-polar, hydrogen bonding, cation exchange, etc.

^b Dissolution of various sorbed molecules occurs without significant size exclusion. Naturally, too many "sorbed" molecules in the form of excess solvent will extract and mobilize these materials. Here we emphasize the role of native waxes, resins, etc., rather than that of anthropogenic residual separate-phase liquid contaminants which can act similarly.

^c Polar is used here only to denote a class of molecules. Various authors (for example, Fowkes, 1980) have shown that dipole-dipole interaction between polar molecules in a liquid (in contrast to the vapor phase) represent only a very tiny portion of the intermolecular interactions compared to donor-acceptor interactions.

^d Cation exchange sorption phenomena would include replacement of ionizable, acidic hydrogens by cationic organic species, but also polarization of some ligands by multi-charged, exchanged cations.

^e Some size exclusion effects probably operate here also.

degraded, and would presumably release materials sorbed in bulk as the macromolecular matrix is destroyed.

The extractable organic soil phases are also capable of bulk sorption (dissolution) of various hydrophobic chemicals. Unlike the insoluble solid phases, however, these materials are potentially capable of mobilization by the right mixtures of nonaqueous solvents. The sorbed species are probably also somewhat more accessible to re-adsorption measures, especially if they are sorbed into biodegradable lipid or wax fractions.

Surface Sorption

True surface sorption can be defined meaningfully for insoluble soil organic matter for **sufficiently large organic molecules that are effectively excluded from the macromolecular framework of**

humin and other macromolecules. This restriction to surface interaction is probably very important for many agrochemicals such as insecticides, fungicides and herbicides, which tend to be rather large molecules². Note, however, that the lower molecular weight, microbial metabolites of these chemicals may distribute themselves over the available sorption categories in a completely different way than the parent chemical.

Sorption in Micropores

The final category of sorbed material is that which resides in the micropores of the various solid organic materials without causing any volumetric increase. No doubt, some size exclusion effects oper-

² Large in this context means somewhat larger than the aromatic ring of benzene.

ate in this situation as well, but probably not as stringently as in the bulk sorption into macromolecular organic matter. The difference between certain gravimetric determinations of sorption and volumetric determinations of sorption (via swelling, see below) can indicate the magnitude of the sorption capacity in this form. In many ways, this is the least understood of the categories in the diagram. Diffusion in and out of micropores also could produce some of the non-equilibrium effects seen in column studies.

Operational Definition of Volumetric Swelling

The volumetric swelling³, Q_v , is defined as the ratio of the swollen volume to the unswollen volume of the sorbent; a value of unity⁴ indicates no swelling. The reciprocal of the volumetric swelling is equal to the volume fraction of macromolecular material in the swollen, solution phase. Thus, the volumetric swelling at equilibrium is related to the saturated solubility of the sorbed fluid in the swollen phase. Knowledge of appropriate densities, allows this volume-fraction solubility to be converted to the more usual gravimetric concentration units.

The volumetric swelling⁵ is the quantity determined experimentally in the present work. A swelling spectrum is obtained when the volumetric swelling for various solvents is plotted versus some pertinent solvent property, such as the conventionally chosen solubility parameter.

Experimental Procedures

Samples Studied

Michigan Peat

The sample of Michigan peat was commercial horticultural peat from the *Alpar

Peat Company of Ovid, Michigan (Clinto~County). The dark, muck peat is a predominately reed-sedge peat with some contributions from tamarack trees. The mined deposit is a layer approximately 8 to 10 feet in thickness in a region once used for farming.

Canadian Peat

The Canadian peat was a commercial horticultural peat with a light brown color and a distinctly fibric texture. Information on the origin of this material was unavailable. Both acid-washed and calcium-exchanged versions of this peat were studied.

Atoka Pine Duff

The Atoka material consisted of composted pine needles (*Pinus echinata*) that had collected in small pockets on a rocky slope located in Atoka County, Oklahoma (S20, T1S, R13E). The mineral constituents were in the form of fine, wind-blown, clay-sized dust.

Pine Pollen (*Pinus echinata*) & Oak Pollen (*Quercus stellata*)

The samples of pine pollen and oak pollen were obtained from a commercial laboratory that supplies various species of pollen and mold spores to allergists.

Cellulose

The sample of cellulose was obtained from Aldrich Chemical Company, Inc. and was a powder of nominally 20 μ m average particle diameter. Data from the supplier showed an average assay of about 90% α -cellulose based on acid hydrolysis and an average residue on ignition ("ash") of about 0.05%.

Chitin (Crab Shell Chitin)

The sample of purified crab shell chitin was obtained from Sigma Chemical Company.

Solvents Used

The solvents used for swelling measurements are listed in Table I along with values for their solvent parameter and molar volume. All solvents were the best available commercial grades, and were used without further purification.

Summary of Swelling Measurement Method

The basic method has been described by Green *et al.*, 1984 for coal samples.

The adaption of this method to the present kind of sample is detailed in the full report. Spectra were taken in pairs and averaged to obtain the final spectra reproduced in this project summary.

Powdered organic matter was placed in small glass tubes and exposed to various liquid organic solvents. Centrifuging at a constant speed for a fixed time period was used to obtain reproducible compaction of the powders. Length measurements were made on the powder columns before and after wetting with each solvent, and the final swelling was computed as a ratio of lengths once equilibrium had been achieved. Samples were equilibrated at 30°C in a waterbath prior to swelling length measurements to avoid known kinetic difficulties near room temperature, especially in the swelling of cellulose.

Preparation and Processing of Samples

Air-Drying, Diminution of Particles and Sieving

The swelling experiment requires samples of finely powdered organic materials, relatively concentrated in their swelling components. Fibrous materials such as the Canadian peat cannot be readily "ground" to a fine powder, but can be chopped to a sufficiently small size with the blades in a blender so that a reasonable harvest of -100 mesh (i.e. less than 100 mesh) material can be obtained by sieving.

Soxhlet Extractions

Soxhlet extractions were conducted using a three-stage sequence of solvents consisting of 1-propanol, 1-propanol-toluene (28% propanol) mixture, and toluene. The purpose of this pre-swelling extraction procedure was two-fold:

1. to remove as much of the extractable fraction as possible so that the various swelling solvents applied to these organic materials would not dissolve any further materials from the samples, and
2. to remove hydrophobic, low-melting waxes from the particle surfaces so that the samples could be dried at 105°C without blocking access to the particle interiors for some of the more hydrophilic swelling solvents.

Unfortunately, some highly swelling solvents such as DMSO and the various amides dissolved considerable amounts of humic materials from some samples during the swelling determinations. In sev-

³ The volumetric swelling, Q_v , should not be confused with the volume change, $\Delta V_{swelling}$, associated with the swelling process:

solvent + solid sorbent \rightarrow swollen sorbent

The values for Q_v are positive values ≥ 1.0 except in the extremely unlikely situation where the $\Delta V_{swelling}$ is negative and exceeds the imbibed volume of solvent. Many values of $\Delta V_{swelling}$ are potentially negative, and they are usually not known because of the difficulty of determination. Usually $\Delta V_{swelling}$ values are some small percentage of the volume of imbibed liquid.

⁴ Apparent swelling values less than unity could occur if some material is extracted into solution by the applied solvent.

⁵ We note that swelling can also be determined gravimetrically. In these cases, the amount of sorbed material is determined gravimetrically, and converted to a volume basis using densities. Usually the gravimetrically determined swelling is larger than the volumetric quantity because it includes the filling of micropores without any associated swelling.

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Table 1. Solvents for Obtaining Swelling Spectra

Solvent	δ_s (MPa ^{1/2}) ^a	Molar Volume (cm ³ /mol) ^b
n-Pentane	14.3	116.3
n-Heptane	15.1	147.6
Methylcyclohexane	16.0	127.6
Cyclohexane	16.8	108.1
p-Xylene	18.0	123.3
Toluene	18.2	106.8
Ethyl Acetate	18.6	98.5
Benzene	18.8	89.4
Tetralin	19.4	137.1
Acetylacetone ^c	19.5	103.4
Chlorobenzene	19.6	102.6
Dichloromethane	19.8	64.5
Acetone	20.2	74.0
Carbon Disulfide	20.4	60.6
1,4-Dioxane	20.5	85.7
Nitrobenzene	20.5	103.4
3-Methyl-1-butanol	20.5	108.9
1-Octanol	21.1	158.4
Pyridine	21.9	80.9
Morpholine	22.1	87.5
N,N-Dimethylacetamide	22.1	93.0
1-Pentanol	22.3	108.8
Nitroethane	22.7	71.9
1-Butanol	23.3	91.9
2-Propanol	23.5	77.0
Acetonitrile	24.1	53.0
1-Propanol	24.3	75.2
Dimethylsulfoxide	24.5	70.9
N,N-Dimethylformamide	24.8	77.0
Nitromethane	26.0	53.7
Ethanol (99.9%)	26.0	58.7
Propylene Carbonate ^d	27.2	85.9
Methanol	29.6	40.7
1,2-Ethanediol	29.9	55.9
1,2-Propanediol	30.7	73.7
N-Methylformamide	32.9	58.4
Formamide	39.3	39.7
Water	47.9	18.1

^a The delta values tabulated here are mostly the simple solubility parameters of the liquids at 25°C tabulated by Barton, 1983; in a few instances where these were missing, the total solubility parameter, δ_s , from the same reference was used instead.

^b The values for the molar volume (cm³/mol) were in most cases computed from molecular weights (g/mol) and density (g/cm³) values for the liquids at 25°C tabulated by Barton, 1983. A few missing values were computed from similar data tabulated in standard handbooks elsewhere (e.g., Weast, 1984)

^c 2,4-Pentanedione

^d 1,2-Propanediol cyclic carbonate

eral instances these solvents gave supernatant solutions over the swollen solid material that were as dark as coffee.

Acid Washing and Cation Exchange

Acid washing with 0.1 M HCl solutions was performed when it was desired to have the acid form of the organic materials for study. Washing with 0.5 M CaCl₂ solution was performed when the calcium-exchanged version of the organic materials was needed; this was followed by water

washing to a chloride-free condition as determined by tests with aqueous AgNO₃ solution.

Vacuum Oven Drying

The drying treatment for all organic materials consisted of vacuum oven drying at 105°C for 24 hours at a few Torr pressure: **once** just before loading the powders in the swelling tubes, **and a second time** after loading in the tubes. After the second drying, the filled tubes were quickly capped with teflon caps to prevent uptake of moisture from the air.

Results

Swelling Spectra

The choice of solvent solubility parameter as the abscissa is traditional in plots of swelling, but solubility parameter, by itself, has no special predictive power for the swelling in these materials. What is seen instead, are spectra with large jumps in swelling for very small changes in solvent solubility parameter. These jumps in swelling are largely attributable to site-specific chemical interactions of the donor-acceptor type that lower the net free

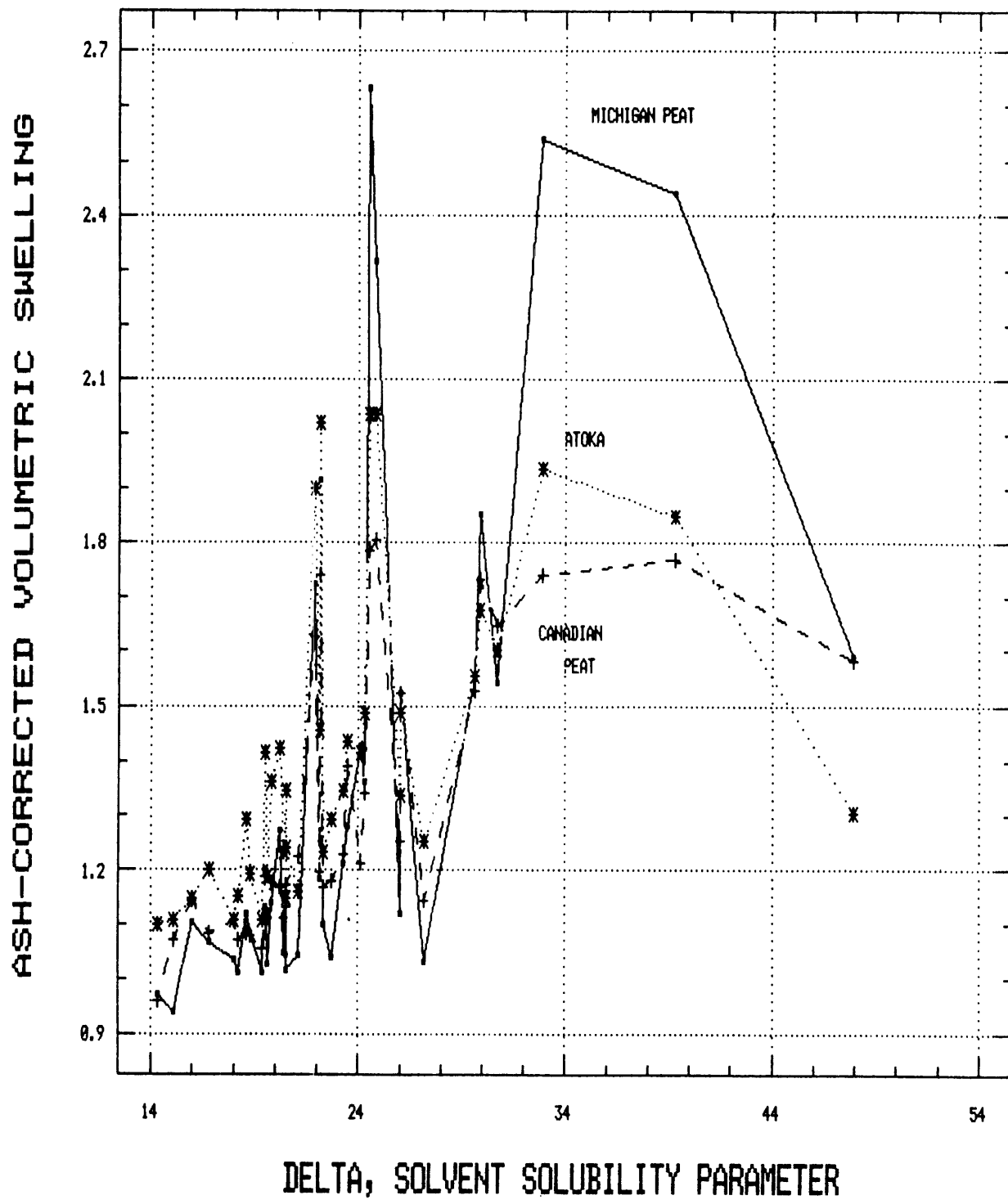


Figure 1. Ash-corrected swelling vs. δ_s peat-like materials. The swelling spectra for Michigan and Canadian peat and for the Atoka pine duff are compared in this figure after ash corrections.

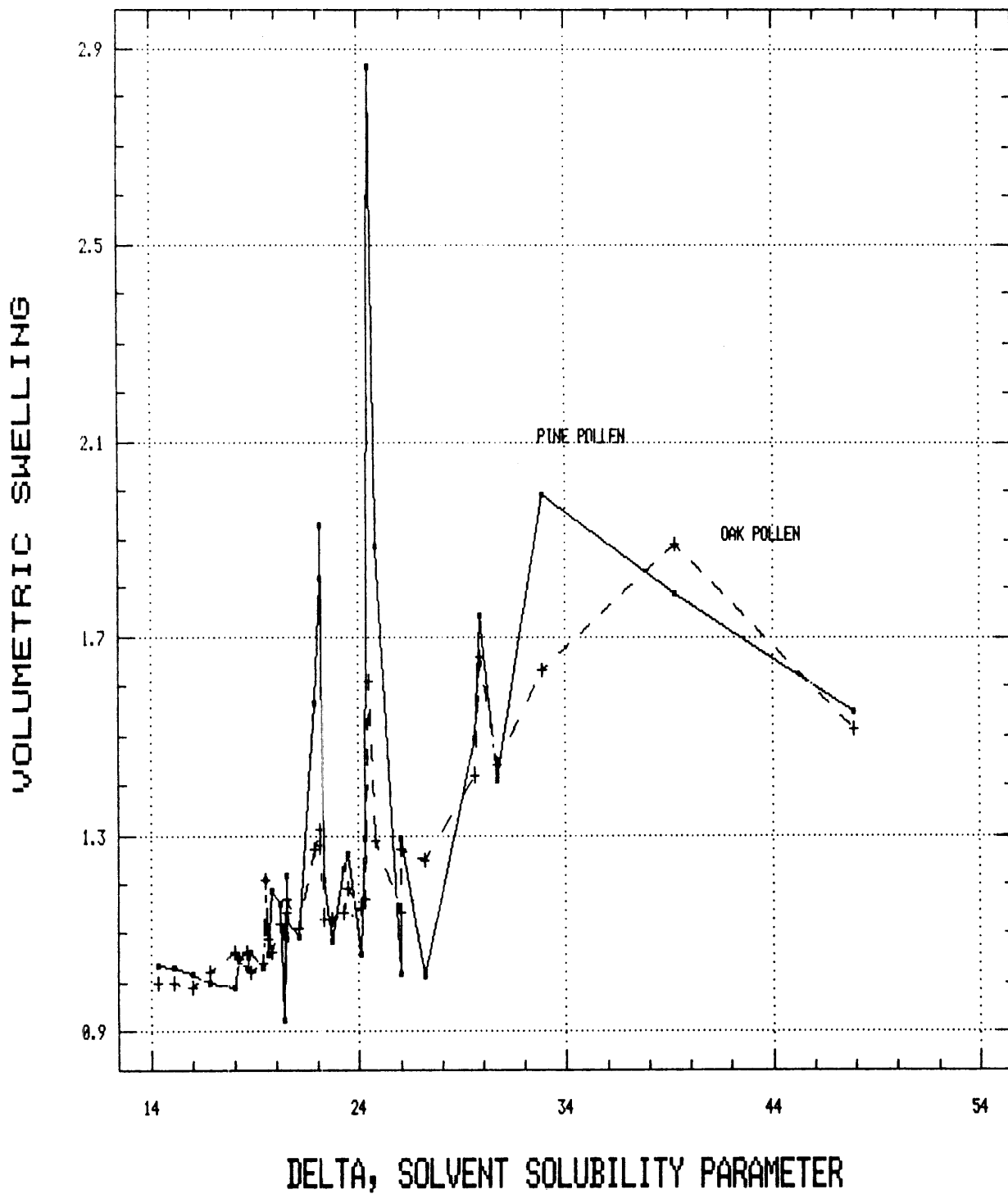


Figure 2. Swelling vs. δ_s , pine and oak pollen. The swelling spectra of pine pollen and oak pollen are compared in this plot. No ash corrections were applied to these data.

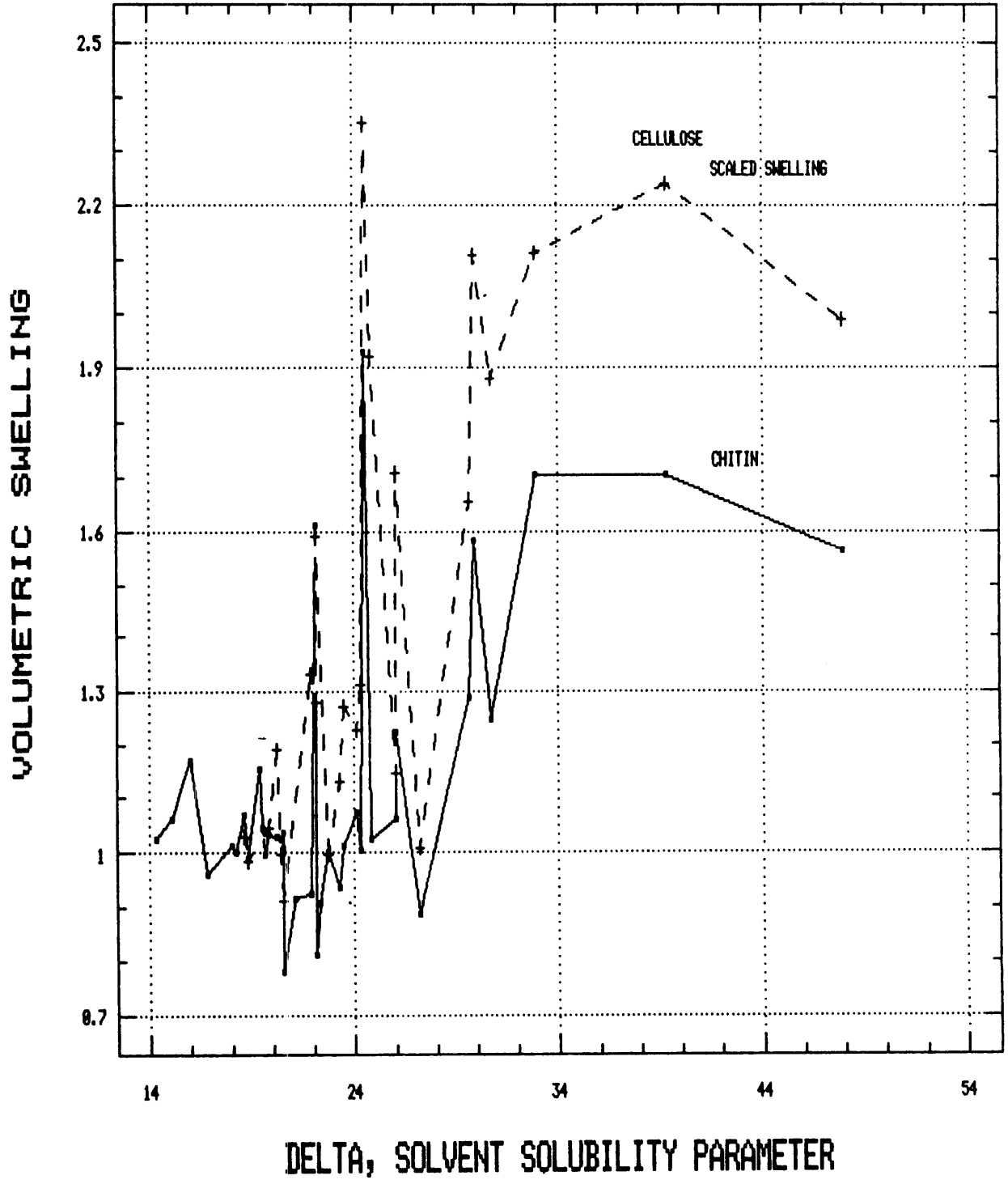


Figure 3. Swelling vs. δ_s , cellulose and chitin. This figure compares the swelling spectra for cellulose and chitin. The raw spectrum for cellulose was scaled by a constant factor so that the average background value of the swelling was shifted upwards to 1.0. No corrections for ash were applied to either spectrum.

energy of the swollen state for some swelling agents.

Representative swelling spectra for the major classes of materials studied in the present work (peat-like materials, pollens, and polysaccharides) are given in Figures 1, 2, and 3. Ash corrections for the peat-like materials were made under the assumption that the mineral matter was entirely an inert, non-swelling diluent. The spectrum for cellulose was scaled by a constant factor so that the average background value of the swelling was shifted upwards to 1.0.

Molecular Size-Exclusion Effects

The evidence for molecular size-exclusion is simple and direct. Figure 4 displays a graph of swelling values plotted against solvent molar volume for all materials except cellulose. The largest solvent still capable of significantly swelling these materials is N,N-dimethylacetamide with a molar volume of ca. $93 \text{ cm}^3 \text{ mol}^{-1}$. Many solvents with molar volumes less than this can swell these materials. For cellulose, the pattern is similar except that morpholine with a molar volume of ca. $87 \text{ cm}^3 \text{ mol}^{-1}$ represents the largest swelling solvent observed.

Consequences for Environmental Studies

It would be desirable in environmental studies of the fate and transport of organic contaminants in the subsurface to delineate all possible categories of sorption onto soil and aquifer materials in terms of capacity, equilibrium, energetics and kinetics. This is far from being accomplished even for the simplest of typical real systems.

The major application of the present work to real environmental questions centers on the direct demonstration of an additional category of sorbed substances that can occur in soil and aquifer systems. Some nonequilibrium partitioning effects seen in soil column experiments may well involve a diffusion-limited step between swollen organic particles and the external

fluid phase. We wonder, also about laboratory biodegradation studies using small molecules such as methanol as a carbon source. Here we would expect methanol to swell any soil organic matter that was present, and thus, add a slow diffusion step to the overall kinetics of the degradation process for methanol. In dilute systems, this would be complicated by competitive sorption phenomena involving water also.

The bulk-sorbed fraction inside macromolecular organic materials probably can serve as a source of hard-to-remove residual contamination in a pump and treat remediation; however, not all organic molecules can participate in bulk sorption into the solid organic matter. Size exclusion seems to limit the category to fairly small, polar molecules such as some alcohols and amides. If these species were present in a contaminating mixture, they also might serve as co-sorbents for other small molecules with less polar character, such as the smaller chlorinated hydrocarbons. **We do not expect most of the alkanes and aromatic species present in fuels to undergo significant bulk sorption into macromolecular organic materials in soils and aquifers.**

The present work with its emphasis on macromolecular materials does not, however, rule out the possible bulk sorption of hydrophobic organic molecules into the wax-resin-lipid fraction of soils, nor does it rule out significant sorption into micropores (i.e., capillary condensation). These sorption categories, extractable materials (bitumens) and microporosity, represent potentially important separate areas for further study, and may be responsible for much supposed "partitioning" of non-ionic organic contaminants.

Suggestion for Future Work

Since volume is only a partial constraint on molecular shape, it is to be expected that the volume boundary for swelling is a somewhat blurry barrier; some long rod-like molecules might retain some swelling ability though more globular molecules with similar donor-acceptor capabilities might

not. The magnitude of molecular exclusion has been partially delimited by the present work, but these limits really need to be challenged with further swelling studies using carefully chosen homologous series of compounds (e.g., substituted pyridines or sulfoxide) with similar donor-acceptor properties.

The present method of obtaining swelling measurements is fairly labor intensive, and, unfortunately, rather imprecise. Recently, various instrumental methods have become available for studying the particle-size distributions of powdered materials dispersed in liquids. It would be very worthwhile to explore the use of these instruments for obtaining swelling data on a given material from particle size distributions taken in different solvents. This should be relatively simple to do for powders consisting of a single substance like cellulose or chitin. The swelling of a heterogeneous mixture of insoluble organic materials might still be successfully analyzed by such methods, provided:

1. a series of solvents were used that affected the components differently, and
2. the size distribution functions for the different components were of relatively simple analytical types, such as lognormal or Gaussian.

References

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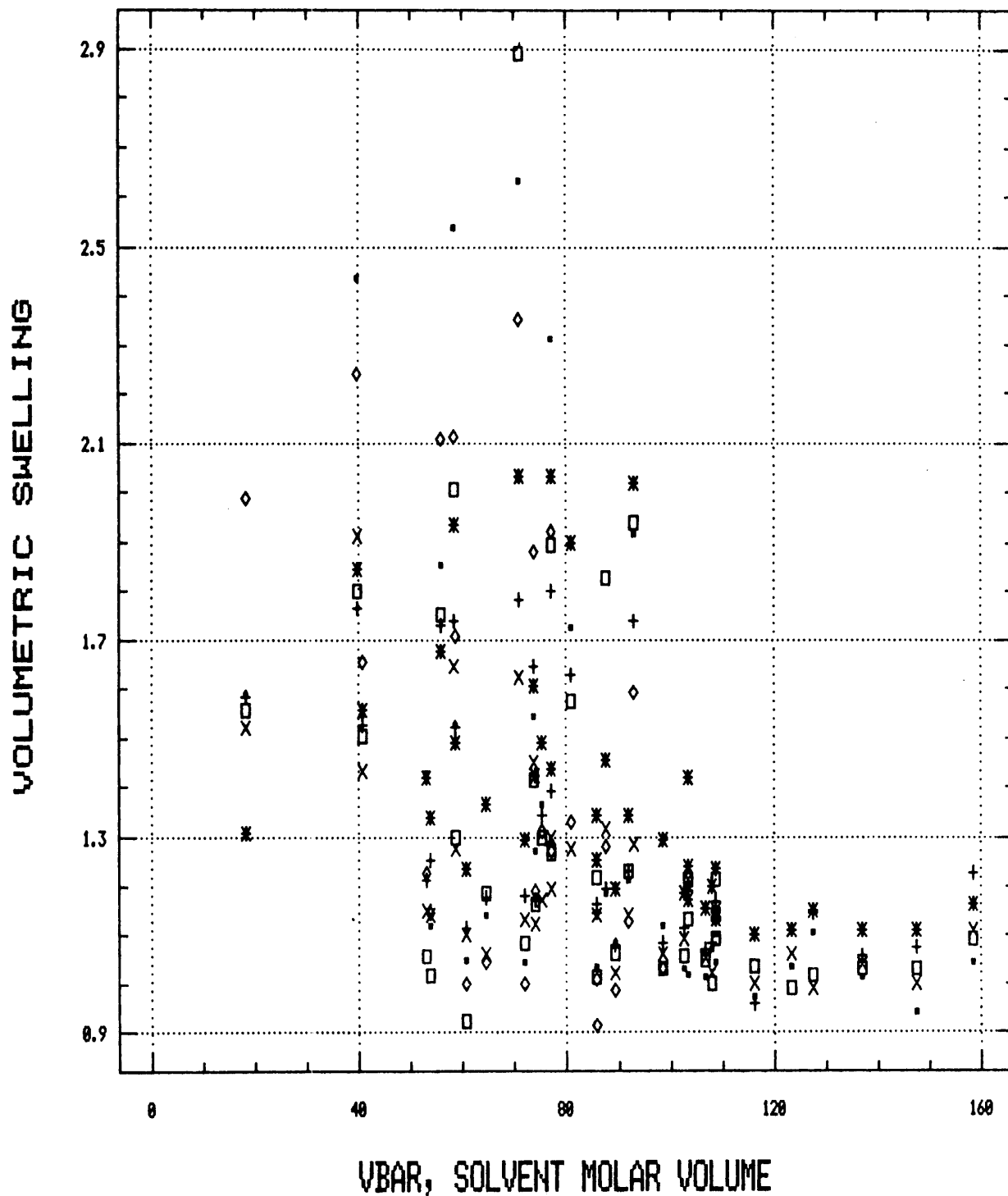


Figure 4. Swelling vs. solvent molar volume. Swelling for Michigan and Canadian peats, Ca-exchanged Canadian Peat, Atoka oak pollen and chitin are plotted versus solvent molar volume. The data exhibit an abrupt drop-off for solvents with volumes larger than *N,N*-dimethylacetamide (ca. 93 cm³ mol⁻¹). Above this rather fuzzy boundary, swellings tend to be near 1.0 plus some background imprecision.

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Roger Crosby is the EPA Project Officer (see below).

The complete report, entitled "The Swelling Properties of Soil Organic Matter and thier Relation to Sorption of Non-Ionic Organic Compounds," (Order No. PB91-217 406/ AS; Cost: \$23.00; subject to change) will be available only from:

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