Environ. Sci. Technol. **1986**, *20*, 502–508

Water Solubility Enhancement of Some Organic Pollutants and Pesticides by Dissolved Humic and Fulvic Acids

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■ Water solubility enhancements by dissolved humic and fulvic acids from soil and aquatic origins and by synthetic organic polymers have been determined for selected organic pollutants and pesticides (*p,p′*-DDT, 2,4,5,2′,5′-PCB, 2,4,4′-PCB, 1,2,3-trichlorobenzene, and lindane). Significant solubility enhancements of relatively water-insoluble solutes by dissolved organic matter (DOM) of soil and aquatic origins may be described in terms of a partition-like interaction of the the solutes with the microscopic organic environment of the high-molecular-weight DOM species; the apparent solute solubilities increase linearly with DOM concentration and show no competitive effect between solutes. With a given DOM sample, the solute partition coefficient (K_{dom}) increases with a decrease of solute solubility (S_w) or with an increase of the solute's octanol–water partition coefficient (K_{ow}). The K_{dom} values of solutes with soil-derived humic acid are approximately 4 times greater than with soil fulvic acid and 5–7 times greater than with aquatic humic and fulvic acids. The effectiveness of DOM in enhancing solute solubility appears to be largely controlled by the DOM molecular size and polarity. The relative inability of high-molecular-weight poly(acrylic acids) to enhance solute solubility is attributed to their high polarities and extended chain structures that do not permit the formation of a sizable intramolecular nonpolar environment.

Introduction

Water solubilities of organic pollutants and pesticides are among the most important physical properties controlling the transport and fate of the chemicals in aquatic systems. Their magnitudes determine not only the individual limiting loads in water but also such partition constants as the soil sorption coefficients (*1–8*) and bioconcentration factors (*9–12*). Whereas the solubility of a solute in "pure water" may be regarded as an unambiguous physical constant, the apparent solubility and the physical state of a solute in water containing coexisting solutes (or impurities) are both susceptible to modification by interactions with cosolutes. Such modifications would consequently affect the behavior of the solute in natural waters.

Previous studies indicate that low concentrations of dissolved and/or suspended particulate-bound natural organic matter in water can significantly enhance the solubility and stability of many "hydrophobic" organic compounds (*13–25*), notably DDT and some PCBs. Whereas the effect with the particulate-bound organic matter can be accounted for by solute partitioning (*24*) analogous to the effect with soil/sediment organic matter (*1, 8*), the mechanism of solubility enhancement by dissolved organic matter (DOM) has not been well-understood (*18–20*). From a fundamental point of view and from results of previous studies, one would expect that large solubility enhancements by dissolved cosolutes in relatively dilute solutions would be largely restricted to those solutes that are themselves extremely insoluble in water. It is unlikely, for example, that a dilute concentration of a cosolute could produce a significant solubility enhancement for a solute of comparable or greater water solubility.

Given that the solubility enhancement is most striking for the least soluble organic solutes, one may consider which of the cosolute properties are most important. In principle a cosolute can produce an enhancing effect on solute solubility either by changing the solvency of the medium or by direct solute interaction either by adsorption or by partitioning (solubilization). It seems unlikely that cosolutes such as natural organic matter (i.e., humic substances) at relatively low concentrations would have a strong impact on water solvency; it is also questionable that they should exhibit specific interaction with nonionic organic solutes (such as DDT and PCBs) in aqueous solution, since the hydrophilic functional groups of humic molecules would be more effectively associated with water.

In view of the fact that humic substances are relatively high-molecular-weight species containing nonpolar organic moieties, we speculate that a partition-like interaction of the solute with the "microscopic organic environment" of dissolved humic molecules would be a reasonable explanation for solute solubility enhancement. However, the effectiveness of such a partition-like interaction from the standpoint of the cosolute (DOM) would depend on the size and polarity of the cosolute; i.e., the cosolute molecule must be sufficiently large and possess a sizable intramolecular nonpolar environment to promote solute partitioning. One would therefore not expect a low concentration of a small-sized organic cosolute to produce significant solubility enhancements regardless of its polarity. For the solute, the important properties for solubility enhancement are very low solubility in water and significant compatibility with the organic phase.

If one assumes that a partition–like interaction with dissolved high-molecular-weight organic matter is responsible for solute water solubility enhancement, the magnitude of this effect for an organic solute with respect to a specific DOM can be expressed as

$$S_w^* = S_w + XC_0 \tag{1}$$

where S_w^* is the apparent solute solubility in water containing DOM (as cosolute) at concentration X (in gram per milliliter of water), S_w is the solubility in pure water, and C_0 expresses the mass of solute partitioned into a unit mass of DOM. The quantity C_0 can be related to S_w and a newly defined solute partition coefficient between DOM and pure water (K_{dom}) to give

$$K_{\mathrm{dom}} = C_0/S_w \tag{2}$$

Combining eq 1 and 2 gives

$$S_w^* = S_w(1 + XK_{\mathrm{dom}}) \tag{3}$$

Alternatively, if parameters X and C_0 in eq 1 are expressed in terms of organic carbon content of the DOM, one obtains

$$S_w^* = S_w(1 + XK_{\mathrm{doc}}) \tag{4}$$

where K_{doc} is the corresponding organic-carbon-based partition coefficient.

By eq 3 or 4, the apparent solute solubility (S_w^*) would be greater than the solubility in pure water (S_w), if the magnitude of XK_{dom} (or XK_{doc}) is significant (*23, 24*). The

https://doi.org/10.1021/es00147a010

Table I. Ash-Free Elemental Analysis of Soil and Stream Organic Matter Extracts (in % on Moisture-Free Basis)

organic matter extract	C	H	O	N	S	P	total	ash
Sanhedron soil humic acid (SSHA)	58.03	3.64	33.59	3.26	0.47	0.10	99.09	1.19
Sanhedron soil fulvic acid (SSFA)	48.71	4.36	43.35	2.77	0.81	0.59	100.59	2.25
Suwannee River humic acid (SRHA)	54.22	4.14	39.00	1.21	0.82	0.01	99.40	3.18
Suwannee River fulvic acid (SRFA)	53.78	4.24	40.28	0.65	0.60	0.01	99.56	0.68

value of X can be determined or is known by design. The magnitude of the partition coefficient, K_{dom} (or K_{doc}), depends on the type of DOM and the solute. The K_{dom} value for a solute with a given DOM can be obtained from a plot of S_w^* vs. X, which should yield a straight line, with slope equal to $S_w K_{dom}$ and intercept equal to S_w. By carrying out the same calculations for different solute–DOM pairs, one can determine the effect on K_{dom} of a solute by different types of DOMs and the influence of solute solubility on K_{dom} with a given DOM. Since soil humic and fulvic acids are known to be compositionally different (based on elemental analysis), it is of interest to investigate the relative K_{dom} values for a group of organic pollutants and pesticides with these two acids as DOMs. Similarly, the effects with aquatic humic and fulvic acids and other well-defined small and macromolecular organic acids would be of both environmental and theoretical interest.

In the present study, the magnitudes and variations of K_{dom} values were determined for some environmentally significant solutes (DDT, PCBs, lindane, and 1,2,3-trichlorobenzene) with some soil and stream humic and fulvic acids as cosolutes (DOMs). Similar experiments had been carried out to evaluate the effect of small organic acids (phenylacetic acid) and high-molecular-weight synthetic acids (poly(acrylic acid)) on the solubility of the selected solutes. To distinguish between the effects of "dissolved" and "particulate-bound" organic matter, low-ash humic and fulvic acids were employed in this work. The experiments consisted of measuring the apparent solubility of selected organic solutes in water containing varying amounts of dissolved humic acids, fulvic acids, and other cosolutes over the range that may possibly be encountered in aquatic systems. The present experimental design, similar to a method used by Carter and Suffet (*20*), is relatively simple and straightforward in comparison with the dialysis method (*19–21*) and reverse-phase separation method (*21*) used in similar studies.

Experimental Section

Test solutes (*p,p'*-DDT, 2,4,5,2',5'-PCB, 2,4,4'-PCB, lindane, and 1,2,3-trichlorobenzene) and phenylacetic acid and poly(acrylic acid) (as cosolutes) were reagent grade or analytical standards purchased from commercial sources (Aldrich and Analabs) and were used as received. *n*-Hexane, used for standards preparation and sample extraction, was supplied as a reagent grade solvent for organic residue analysis (Baker). Deionized water obtained from a Sybron/Barnstead Nanopure II water treatment system was used for preparation of the solution.

All humic and fulvic acids (DOMs) used as cosolutes were originally in the hydrogen-saturated, freeze-dried form. Soil humic and fulvic acids were obtained from the surface (Al) horizon of the Sanhedron soil series by alkaline extraction of the soil, followed by established fractionation and purification procedures (*26*). The soil sample was collected in the Mattole River Valley in Mendocino County of northern California. The Sanhedron soil humic acid (SSHA) and Sanhedron soil fulvic acid (SSFA) were representative of most humic and fulvic acids from surface soils of the United States based on extensive characterization (R. L. Malcolm, U.S. Geological Survey, unpublished results). Complete solubilization of SSHA in the hydrogen-saturated form was accomplished by hydrating the lyophilized sample in dilute sodium hydroxide (pH 9–10) with subsequent hydrogen saturation by passing the solution through a column of hydrogen-saturated exchange resin (Bio-Rad AD-50W-X8, 20–50 mesh). The resulting SSHA solution had a pH of 4.0 and was essentially sodium-free (<0.03 mg of Na/L) based on atomic absorption analysis. The concentration of SSHA was confirmed by dissolved organic carbon (DOC) analysis. Hydrogen-saturated SSHA visually appeared to be in true solution at concentrations up to 200 mg/L. After centrifugation at high speed (2987*g*), a minute amount of precipitate was observed in experimental blanks of SSHA below a pH of 6.0 when the SSHA concentration exceeded 50 mg/L. To prevent any slight precipitation at high SSHA concentrations and for experimental consistency, all experimental solutions were adjusted to pH 6.5. The initial pH of SSFA solution was 3.9 at a SSFA concentration of 100 mg/L. Although the SSFA remained in solution above a pH of 3.9 at concentrations in excess of 100 mg/L, the pH of SSFA solutions was also adjusted to 6.5 in order to allow a direct comparison of the solubility enhancement data derived with the SSHA.

The Suwannee River humic acid (SRHA) and Suwannee River fulvic acid (SRFA) were concentrated from the Suwannee River near Fargo, GA, by the XAD-8 resin techniques, fractionated into humic and fulvic acids at pH 1.0, and purified by the method of Thurman and Malcolm (*27*). The pH of the SRHA solution ranged from approximately 4.1 at a concentration of 91 mg/L to 5.5 at 9.0 mg/L, and the pH of the SRFA solution varied from about 3.9 at a concentration of 94 mg/L to 5.7 at 9.4 mg/L. Solution pH was not adjusted for most of the experiments with SRHA and SRFA, since they remained completely soluble at all concentrations. However, the pH of these two solutions was also raised to 6.5 in a study of DDT solubility enhancement in order to assess the effect of pH over this range.

Elemental analyses of the SSHA, SSFA, SRHA, and SRFA as shown in Table I were performed by Huffman Laboratories, Wheatridge, CO. Concentrations of the humic and fulvic acids presented in Figures 1–4 have been corrected for the ash and moisture content of the lyophilized samples.

Solutions containing phenylacetic acid and poly(acrylic acid) as cosolutes were prepared without pH adjustment. The pH of the solution of poly(acrylic acid) having an average MW of 90 000 ranged from about 4.4 at a concentration of 100 mg/L to 5.3 at 10 mg/L, while the pH of the solution of the same compound with an average MW of 2000 ranged from approximately 4.1 in a 100 mg/L solution to 4.7 for a 10 mg/L solution. The pH of phenylacetic acid solutions ranged from 3.7 at 720 mg/L to 4.1 at 100 mg/L.

A series of concentrations, ranging from 0 to 100 mg/L, were prepared for each of the cosolutes (SSHA, SSFA, SRHA, SRFA, and poly(acrylic acid)). Concentrations of phenylacetic acid were extended to more than 600 mg/L

Table II. Water Solubilities (S_w) of Selected Organic Solutes

compd	S_w, mg/L from literature	ref	S_w, mg/L this study
p,p'-DDT	5.5×10^{-3} (25 °C)	28	5.4×10^{-3} (24 °C)
2,4,5,2',5'-PCB	1.0×10^{-2} (24 °C)	10	1.1×10^{-2} (25 °C)
2,4,4'-PCB	0.115 (20 °C)	8	0.116 (25 °C)
1,2,3-trichlorobenzene	16.3 (23 °C)	12	18.0 (25 °C)
lindane	7.80 (25 °C)	28	7.87 (24 °C)

in order to facilitate an accurate assessment of solubility enhancement.

Solutions containing cosolutes were placed in 25-mL Corex centrifuge tubes with Teflon-lined screw caps, and the test compound was subsequently added to each tube in amounts slightly more than required to saturate the solution. In addition, binary solute solutions of 2,4,4'-PCB and 2,4,5,2',5'-PCB with SSHA as cosolute were prepared by adding an excess amount of each solute to water containing SSHA. Generally, duplicate samples were prepared for each concentration of cosolute. These samples were then equilibrated at 24 ± 1 °C for 12–18 h on a reciprocating shaker; this equilibration time was sufficient to establish solubility equilibrium. Instead of filtering the solution (*20*), samples were subsequently centrifuged at 24 ± 1 °C at 5000 rpm (2987*g*) for 1 h to separate the excess solute. Undissolved solute particles adhering to the meniscus were aspirated from the surface, and glass walls previously in contact with solution were carefully cleaned with tissue paper. Samples were then recentrifuged and the cleaning repeated. Subsequently, a 2-mL aliquot of the supernatant was carefully withdrawn with a volumetric pipet and extracted with an equal amount of hexane for a subsequent determination of the apparent solute solubility. The recovery efficiency for this extraction procedure was shown to be greater than 95% for all solutes tested.

Determination of DDT and the PCBs was carried out by gas chromatography using a (^{63}Ni) EC detector, and a 2-m, $^1/_4$-in.-i.d. glass column packed with a 3% OV-1 liquid phase on 100/200 Supelcoport. Lindane and trichlorobenzene were analyzed with a flame ionization detector, using the same packed column.

Results

Figure 1A (top) shows the dependence of the apparent water solubilities (S_w^*) of *p,p'*-DDT, 2,4,5,2',5'-PCB and 2,4,4'-PCB as single solutes on the concentration of Sanhedron soil humic acid (SSHA) in water, with the SSHA concentration extending from 0 to 94 ppm (mg/L). The values shown represent averages of duplicate determinations, and the error bars indicate the range of variation. A similar plot for lindane and 1,2,3-trichlorobenzene in water containing SSHA is given in Figure 1B (bottom). Included in Figure 1A are the solubility-enhancement data of 2,4,5,2',5'-PCB and 2,4,4'-PCB as binary solutes with SSHA. Solubilities of the compounds in pure water (S_w) are given in Table II.

Figure 1A shows a linear increase of S_w^* with increasing concentration of dissolved SSHA for *p,p'*-DDT, 2,4,5,2',5'-PCB, and 2,4,4'-PCB. The observed solubility-enhancement factor (S_w^*/S_w) at given SSHA concentrations for the three compounds follows the order of *p,p'*-DDT > 2,4,5,2',5'-PCB > 2,4,4'-PCB. In the binary solute system of 2,4,5,2',5'-PCB and 2,4,4'-PCB, the enhancement for each solute is virtually the same as found in single-solute systems; i.e., no interfering effect is observed between the two solutes. For lindane and 1,2,3-trichlorobenzene with SSHA (Figure 1B), no discernible solubility enhancement was detected over the range of SSHA concentration imposed. Note, however, the large difference in ordinate scales between parts A and B of Figure 1.

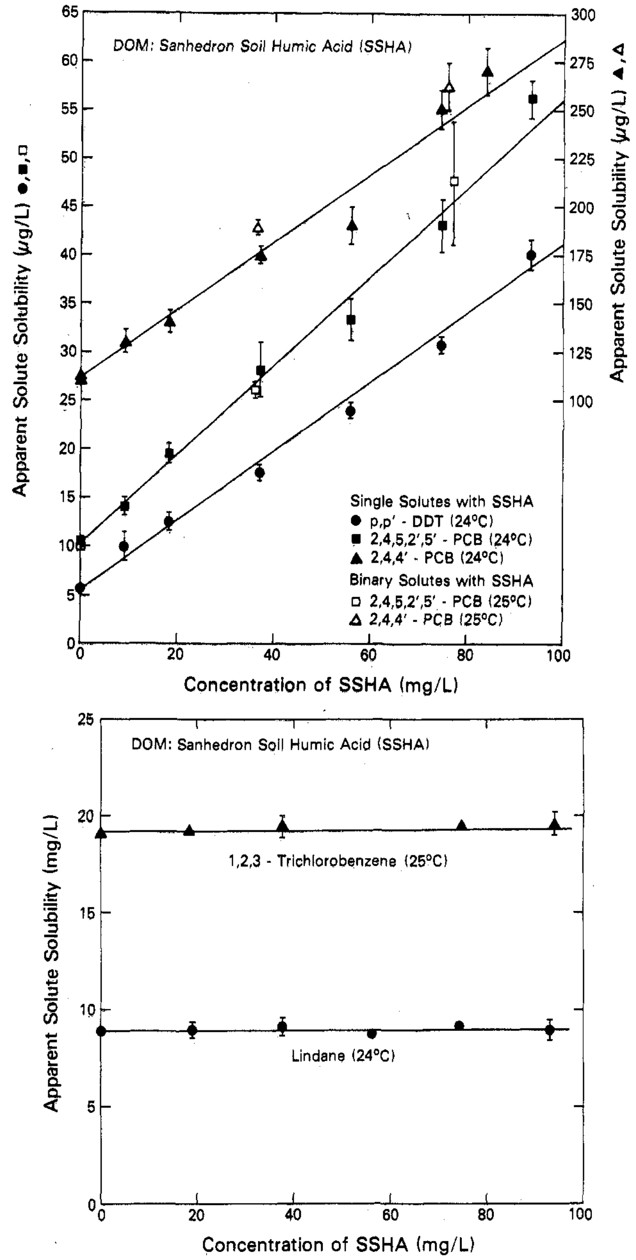

Figure 1. (A, top) Dependence of the apparent water solubility of *p,p'*-DDT, 2,4,5,2',5'-PCB, and 2,4,4'-PCB on the concentration of SSHA. (B, bottom) Dependence of the apparent water solubility of lindane and 1,2,3-trichlorobenzene on the concentration of SSHA.

Figure 2 shows the dependence of the apparent water solubility of *p,p'*-DDT, 2,4,5,2',5'-PCB, and 2,4,4'-PCB on the concentration of dissolved Sanhedron soil fulvic acid (SSFA), with the SSFA concentration extending over the same range as the SSHA shown in Figure 1A, B. The observed enhancements of the three compounds with SSFA are all about fourfold less than with SSHA. Again, no noticeable water solubility enhancement was found for lindane and 1,2,3-trichlorobenzene with SSFA.

Figures 3 and 4 show, respectively, the water solubility enhancements of the same three compounds by Suwannee River humic acid (SRHA) and Suwannee River fulvic acid (SRFA) at the original solution pH of 4.0–5.7. The en-

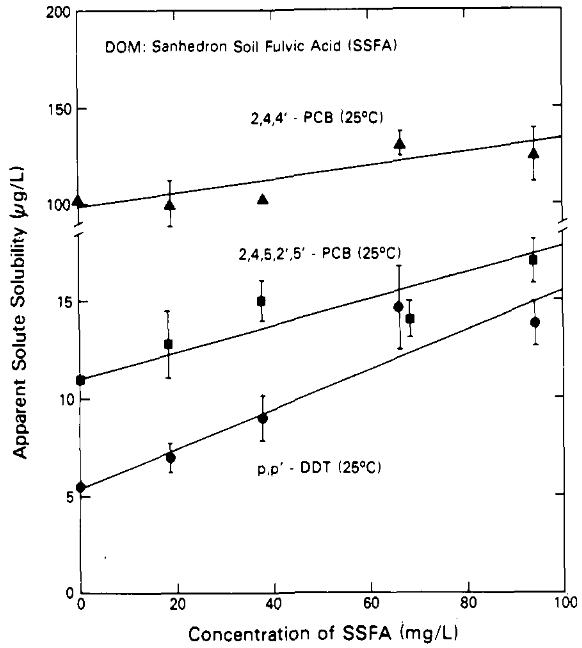

Figure 2. Dependence of the apparent water solubility of *p*,*p*′-DDT, 2,4,5,2′,5′-PCB, and 2,4,4′-PCB on the concentration of SSFA.

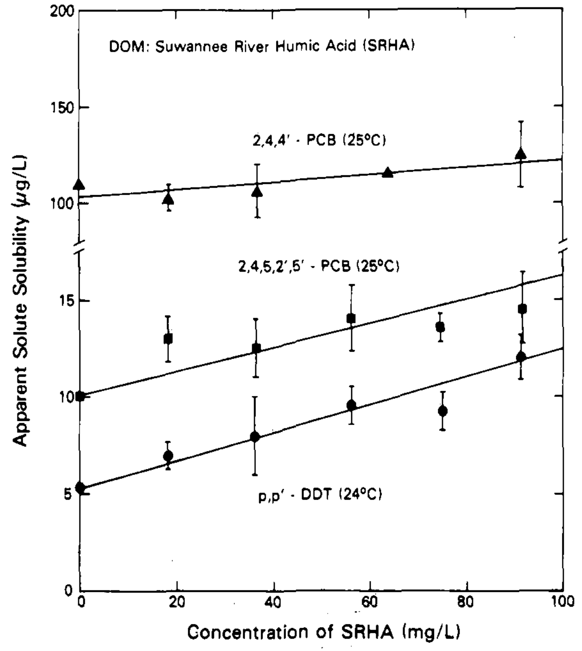

Figure 3. Dependence of the apparent water solubility of *p*,*p*′-DDT, 2,4,5,2′,5′-PCB, and 2,4,4′-PCB on the concentration of SRHA.

hancement of DDT solubility by SRHA and SRFA at an adjusted pH of 6.5 was not significantly different from that of the unbuffered solutions, and therefore, was not included in Figures 3 and 4. The result indicates that the enhancement by SRHA and SRFA is not strongly sensitive to pH over the stated range. No noticeable solubility enhancements were observed for lindane and 1,2,3-trichlorobenzene, with the concentration of SRHA or SRFA extending to about 90 mg/L. SRHA and SRFA show virtually identical effects on the solubility enhancements of *p*,*p*′-DDT, 2,4,5,2′,5′-PCB, and 2,4,4′-PCB, about 5–7 times less than with SSHA.

Figure 5 shows the effect of phenylacetic acid as cosolute on the apparent water solubility of *p*,*p*′-DDT, lindane, and 1,2,3-trichlorobenzene, with the concentration of phenylacetic acid exceeding 600 mg/L. DDT shows slight enhancement, whereas lindane and 1,2,3-trichlorobenzene

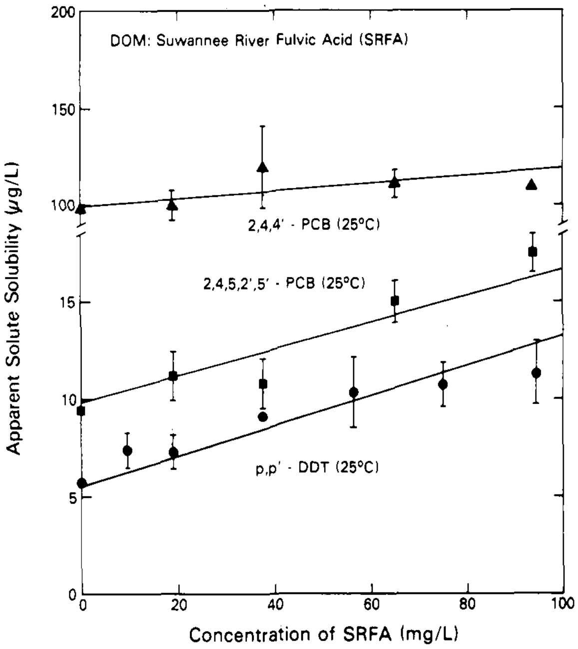

Figure 4. Dependence of the apparent water solubility of *p*,*p*′-DDT, 2,4,5,2′,5′-PCB, and 2,4,4′-PCB on the concentration of SRFA.

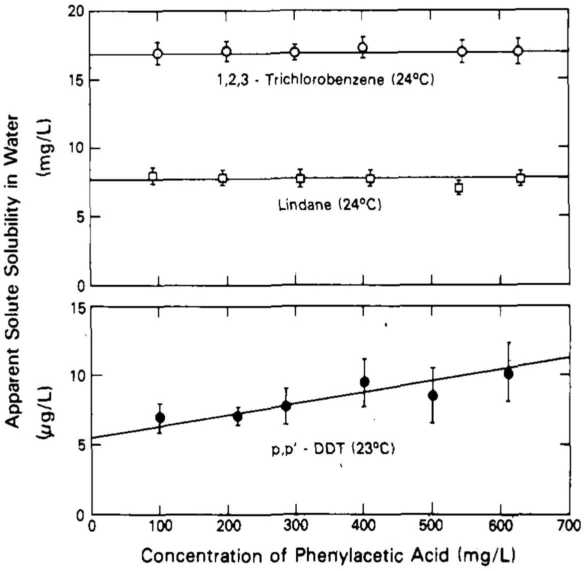

Figure 5. Effect of phenylacetic acid on the water solubility of *p*,*p*′-DDT, lindane, and 1,2,3-trichlorobenzene.

show no obvious effects. The magnitude of DDT solubility enhancement per unit mass of phenylacetic acid is much smaller than with the humic or fulvic acids.

Figure 6 shows the effect of poly(acrylic acid) (MW = 2000) (or rather its absence) on the solubility of *p*,*p*′-DDT, 2,4,5,2′,5′-PCB, 2,4,4′-PCB, and 1,2,3-trichlorobenzene. In addition (data not shown), a higher molecular weight poly(acrylic acid) (MW = 90 000) also exhibited no effect on DDT solubility.

Discussion

A comparison of the results from Figures 1–6 indicates that SSHA is most effective in enhancing solute solubility and that DDT is most sensitive to dissolved organic substances. The linear relation between S_w^* and cosolute concentration, the decrease of solubility enhancement with increasing solute solubility in pure water, and the lack of interference in solubility enhancement between binary solutes are in keeping with the postulate that a partition-like interaction between the solute and humic/fulvic

Table III. Comparison of log K_{dom}/log K_{doc} Values of Selected Organic Solutes with SSHA, SSFA, SRHA, and SRFA and with Respective Solute Octanol-Water Partition Coefficients (log K_{ow})

		log K_{dom}/log K_{doc}			
compd	log K_{ow}[a]	SSHA	SSFA	SRHA	SRFA
p,p′-DDT	6.36	4.82/5.06	4.27/4.58	4.12/4.39	4.13/4.40
2,4,5,2′,5′-PCB	6.11	4.63/4.87	3.81/4.12	3.80/4.07	3.83/4.10
2,4,4′-PCB	5.62	4.16/4.40	3.58/3.89	3.27/3.54	3.30/3.57
1,2,3-trichlorobenzene[b]	4.14	~2.8/3.0	~2.0/2.3	~1.7/2.0	~1.7/2.0
lindane[b]	3.70	~2.5/2.7	~1.5/1.8	~1.2/1.5	~1.2/1.5

[a] Values from ref 12 and 36. [b] Approximate log K_{dom}/log K_{doc} values for 1,2,3-trichlorobenzene and lindane are obtained by linear extrapolations of the log K_{dom}/K_{doc} against the log K_{ow} of p,p′-DDT, 2,4,5,2′,5′-PCB, and 2,4,4′-PCB.

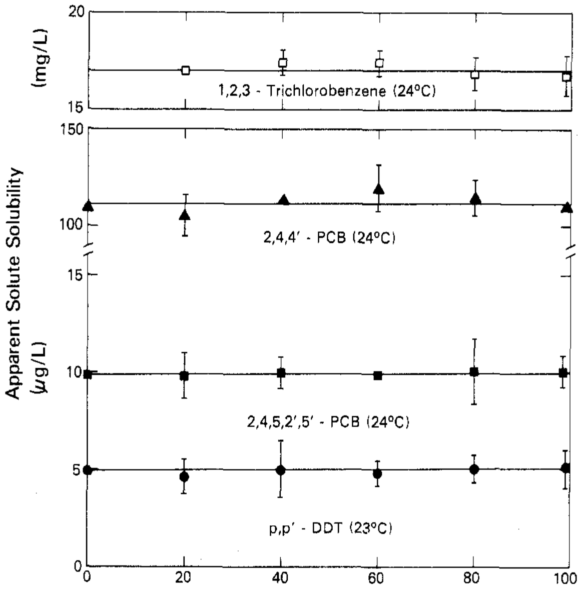

Figure 6. Effect of poly(acrylic acid) (MW = 2000) on the water solubility of p,p′-DDT, 2,4,5,2′,5′-PCB, 2,4,4′-PCB, and 1,2,3-trichlorobenzene.

acids is responsible for the solubility enhancement. That small organic cosolutes such as phenylacetic acid are unable to produce the same kind of effect as humic and fulvic acids is consistent with this hypothesis, in which the size of the cosolute is a critical factor. The much smaller enhancement effect with small-sized phenylacetic acid molecules may quite possibly result from changes in the solvency of water, much like the effect of a mixed solvent. In situations where the solubility enhancement is caused by specific interactions, one would expect such an effect to be more related to the acidity or polarity of the cosolute, and therefore, phenylacetic acid should be a strong enhancer. The proposed hypothesis is further supported by the low enhancement effect of SSFA relative to SSHA, whereas SSFA is a smaller molecule but a stronger acid.

The relatively large solubility enhancements for DDT and 2,4,5,2′,5′-PCB with SSHA suggest that the enhancing SSHA must have a substantially larger molar volume (or molecular weight) than those of the solutes. Although the molecular weights of soil humic acids may depend on the source of soil samples and on the procedure used to extract them from soils, the generally accepted values are 2000–20 000 (*29*). Based on these values and elemental analysis data, dissolved soil humic acids may be assumed to provide a sufficiently large intramolecular nonpolar organic environment for promoting a partition-like interaction with relatively nonpolar organic solutes. The kind of partition interaction that is here envisioned for a cosolute of high molecular weight is mechanistically similar to the solubilization effect of relatively water-insoluble organic solutes by micelles (*30–34*), in which a microscopic organic phase is formed through aggregation of surfactant monomers.

As indicated earlier, the fact that the solubility enhancement is strongest for such solutes as DDT or 2,4,5,2′,5′-PCB is attributable to their low water solubilities. Therefore, 2,4,4′-PCB, having a higher water solubility, shows less enhancement, and relatively highly water-soluble solutes such as lindane and 1,2,3-trichlorobenzene exhibit negligible enhancement over the same range of humic acid concentration. Since the water solubility (for solid solutes, the supercooled liquid solubility) is closely correlated to the corresponding octanol–water partition coefficient in an inverse manner (*35*, *36*), the log K_{dom} values calculated according to eq 3 are essentially linear with respective log K_{ow} values (Table III).

Whereas the size of the cosolute is essential to solute solubility enhancement by a partition-like interaction, the polarity and molecular configuration of the cosolute also appears to be important. Poly(acrylic acid) (with MW = 2000 and 90 000) as a linear polyelectrolyte shows no enhancement effect despite that its carbon (50%), oxygen (44.4%), and hydrogen (5.6%) contents are quite comparable to those with SSFA. The inability of poly(acrylic acid) to enhance solute solubility may be related to the frequent and orderly attachment of hydrophilic (carboxyl) groups to the carbon chain and to an extended chain structure, which do not permit the formation of a sizable intramolecular nonpolar environment.

The smaller enhancement effects with soil fulvic acid (SSFA), aquatic humic acid (SRHA), and aquatic fulvic acid (SRFA) relative to soil humic acid (SSHA) may be attributed in part to increasing polarity of SSFA, SRHA, and SRFA relative to SSHA, as manifested by their high oxygen-to-carbon ratios. Among SSHA, SSFA, SRHA, and SRFA there is a good correlation between solubility-enhancement effects and elemental analysis data. The lower enhancement effects of SSFA, SRHA, and SRFA could also result in part from their smaller molecular sizes compared to SSHA. Commonly accepted molecular weights for soil fulvic acids are 1000–5000 (*37*, *38*), and the values for aquatic humic acids and fulvic acids are 1000–10 000 and 750–2000, respectively (*39*, *40*). While, according to these data, the molecular weight of aquatic fulvic acid is significantly lower than those of aquatic humic acid and soil fulvic acid, the solubility-enhancement effects of SRFA, SRHA, and SSFA are relatively comparable. Thus, the sizes of SSFA, SRHA, and SRFA do not appear to be the primary factor reducing their solubility-enhancement effects. Moreover, the partition effect with polar cosolutes should generally be weak because of their inability to provide a strong nonpolar organic environment. The reduced solubility-enhancement effects of SSFA, SRHA, and SRFA relative to SSHA appear to result more from the polarity than from the size of these cosolutes. However, this point should be substantiated by further studies.

The dependence of K_{dom} on S_w (or K_{ow}) and on the type of cosolute as described is consistent with results previously observed on the behavior of some organic solutes in systems containing dissolved or particuate-bound natural organic matter. For example, our DDT solubility data with SSHA are comparable to the results reported by Carter and Suffet (*19, 20*) on the effect of dissolved sediment humic acids on DDT solubility, although their humic acid samples contain significant amounts of ash (9.8–28.8%). The dependence of the sediment–water sorption coefficient on sediment concentration (*19, 22–24*) and the occurrence of an isotherm "hysteresis" (*24*) as noted for highly water-insoluble solutes are largely a result of the water solubility enhancement of the solutes by dissolved and suspended particulate organic matter, as illustrated by Gschwend and Wu (*24*) in the sorption of 2,4,5,2′,5′-PCB and 2,3,4,5,6,2′,5′-PCB by lake and river sediment samples. As may be expected from the present study, the effect of DOM (up to 100 mg/L) on solute solubility should be minimal for solutes of markedly greater solubility, such as lindane and 1,2,3-trichlorobenzene. Caron et al. (*25*) show that dissolved sediment humic acid (at DOC = 6.95 mg/L) exerts little effect on the sediment–water sorption coefficient of lindane, while reducing the sorption coefficient of DDT by a factor of 4, in agreement with our data of DDT and lindane with SSHA.

Finally, we compare the calculated partition coefficients for solutes in dissolved organic matter (K_{dom}) with the corresponding coefficients in bulk soil organic matter (K_{om}) for estimating the relative efficiency of dissolved and bulk organic matter in concentrating organic solutes, although this comparison should be regarded as semiquantitative because the K_{om} values vary somewhat among soils (*3, 7, 23*). Considering DDT and 2,4,4′-PCB as examples, the observed log K_{om} values of about 5.2 ± 0.1 for DDT (*1, 3*) and 4.4 for 2,4,4′-PCB (*8*) indicate that the bulk organic matter is roughly 10 times more efficient than aquatic humic acid and fulvic acid extracts (SRHA and SRFA) and 6–8 times more efficient than the soil fulvic acid extract (SSFA) in concentrating the solutes. While these data are not in agreement with the findings by Means and Wijayaratne (*41*) that the estuarine colloidal material is 10–35 times more efficient than bulk soil organic matter in concentrating atrazine and linuron, their data appear to be complicated by experimental procedures. Based on the results of DDT and 2,4,4′-PCB, the bulk organic matter is only moderately more efficient than the soil humic acid extract (SSHA), by about a factor of 2, in concentrating the solutes. The approximate agreement between SSHA K_{dom} and soil K_{om} suggests that the size of the extracted soil humic acid should not be a critical limiting factor to solute partitioning and that the polarity of the soil humic acid should be comparable to the overall polarity of the soil organic matter, which is comprised of fulvic acid, humic acid, and humin in order of decreasing polarity. That dissolved aquatic humic and fulvic acids are relatively ineffective as compared to the bulk organic matter in concentrating organic solutes can be attributed to their high polarity and possibly to their smaller organic environment, making the partition interaction less favorable for the solutes.

In summary, water solubility enhancements of relatively insoluble organic solutes by dissolved high-molecular-weight organic matter can be accounted for by a partition-like interaction of the solute with dissolved organic matter. The extent of solubility enhancement depends on the type of solute and on the concentration and source of DOM (in which the DOM size, polarity, and molecular configuration are considered to be the important factors). The calculated partition coefficient (K_{dom}) increases with a decrease of solute water solubility (or with an increase of its octanol–water partition coefficient) and with a decrease of the polarity of the dissolved organic matter as illustrated by the elemental analysis data. The K_{dom} values for given solutes with soil humic acids are about 4 times greater than the values with soil fulvic acids and 5–7 times greater than the values with aquatic humic and fulvic acids. With DOM $\leq$ 100 mg/L, the effect of DOM on solute solubility is minimal for relatively water-soluble solutes such as lindane and 1,2,3-trichlorobenzene. The effect becomes significant for highly insoluble solutes even at moderate DOM concentrations, in which the extent of the solubility enhancement depends on the nature of DOM.

Registry No. Poly(acrylic acid), 9003-01-4; 2,4,4′-PCB, 7012-37-5; *p,p′*-DDT, 50-29-3; 2,4,5,2′,5′-PCB, 37680-73-2; 1,2,3-trichlorobenzene, 87-61-6; lindane, 58-89-9.

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Received for review August 8, 1985. Accepted November 22, 1985. Any use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Depth Profiles for Hydrocarbons and Polycyclic Aromatic Hydrocarbons in Soil beneath Waste Disposal Pits from Natural Gas Production

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■ Soil samples were obtained at four depths from 0 to 121 cm below unlined earthen waste pits associated with production, processing, and distribution of natural gas in the San Juan basin of northwest New Mexico. Sample extracts were analyzed by using capillary gas chromatography and gas chromatography/mass spectrometry for polycyclic aromatic hydrocarbons (PAH) to characterize potential for contamination of shallow groundwater. All soils contained complex mixtures of over 60–100 resolved hydrocarbons with carbons numbering from 10 to 45. Extracts were prefractionated for PAH quantification, due to complexity and concentration of interfering hydrocarbons. Over 30 PAH and alkylated PAH at total concentrations of 30–683 mg/kg were detected in soil samples. While concentration profiles for two-ring PAH showed a 20-fold decrease with depth at the produced water pit, less striking reductions were seen with the same compounds at the dehydrator and pipeline drip pits. Moreover, three- and four-ring PAH showed no appreciable variation with depth in any pit. Contamination of shallow groundwater at depths of 1–2 m in flood plains of river valleys in New Mexico from wastes in unlined earthen pits is possible and likely.

Introduction

Throughout production, processing, and distribution of natural gas, aqueous and hydrocarbon wastes can be generated in large volumes (*1–3*). Such wastes include brine (or produced) water from in-field separators, blow-down liquids from wellheads, condensate from inside pipelines, fluids from regeneration of dehydration and sweetening units, and discharge water from hydrostatic testing (DWHT) of pipelines. A common practice nationwide for disposal of these wastes is use of either surface impoundment pits, for containing wastes, or reinjection procedures. In northwest New Mexico and elsewhere in the U.S. Southwest, earthen waste pits are constructed often without a clay or synthetic lining that retards movement of wastes into nearby soil and shallow groundwater. Since natural gas wells and associated waste pits are often found in flood plains of river valleys in New Mexico, and since groundwater can be found at depths as shallow as 1.8 m in the same areas, mobility of organic compounds from waste pits through these soils should be known for prediction of impact on groundwater quality. However, suitable models and supporting studies on mobility of hydrocarbons and polycycic aromatic hydrocarbons (PAH) in complex aqueous mixtures through these soils are unavailable.

Wastes that are generated during natural gas production are highly complex mixtures of hydrocarbons and PAH. For example, in samples of produced water from wells located in the San Juan basin of northwest New Mexico, concentrations of hydrocarbons in the aqueous portion of wastes were 200 μg/L to 235 mg/L while in the same produced waters over 50 PAH were found at total concentrations of 130 μg/L to 25 mg/L (*1*). Volatile organic compounds were also present in these wastes, and benzene was detected at 10–50 mg/L in the same produced water. Volumes of these wastes can be large; in New Mexico in 1982, over 24 billion liters of water were generated from 31 172 natural gas wells (*4*). Some of these wastes are stored in unlined earthen waste (brine) pits in northwest New Mexico and elsewhere.

Condensation of hydrocarbon impurities with molecular weights greater than hexane in pipelines leads to formation of liquids that result in reduced efficiency of gas flow (5). Such condensate is usually removed from pipelines in geographically low regions, and liquids are placed in earthen waste (drip) pits. These wastes can also be released to the environment in discharge water from hydrostatic testing of pipelines (*2, 6*). Few records are available to assess the total volume of either DWHT or condensate drippings, but the problem can be severe, as demonstrated in an exteme event where about 6000 L/day of condensate

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