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John Baham

Volatile hydrophobic compounds (HOCs) brought into soil and sediment systems represent a serious threat to the environment. Dissolved organic carbon (DOC) may exert an important influence over the total aqueous solubility and mobility of organic pollutants through their incorporation into micelles or the formation of soluble complexes. To date, however, it is not clear whether DOC interacts with nonionic volatile HOCs under natural conditions. Also, very little is known about the influence of DOC-type and other environmental parameters. A static headspace analysis technique was used in combination with gas chromatography to determine the extent of interactions between DOC and benzene, toluene, and chlorobenzene. Three different types of DOC were compared: a natural water-soluble extract (WSE) obtained from a Cumulic Humaquept (Labish Series), a commercial humic acid (HA), and a high purity fulvic acid (FA). In factorial experiments, the effect of type and concentration of DOC, solution pH, preparative treatment of DOC solutions, and hydrophobicity of HOCs was examined. DOC concentrations in the experiments ranged from 1.3 to 36.5 $\mathrm{mmol \cdot L^{-1}}$, the ionic background was made up by 0.10 *M* KCl, and the

temperature was held constant at 25 °C. The solution pH in different experiments was 4.0, 6.5, and 9.0. The acidity of classes of DOC functional groups, the influence of solution pH on the degree of DOC-protonation, and the maximum number of protons complexed per mol DOC were determined for WSE, HA, and FA through continuous potentiometric titrations. Basic solutions 9.36 mM in DOC were titrated with HCl under N_2 in a 0.1 M KCl ionic background at 25 °C. At DOC concentrations $\geq$ 9.3 mmol·L^{-1}, a small percentage of HOC molecules associated with DOC. However, no statistically significant linear relation between DOC concentration and DOC-HOC interaction was observed. Differences in the association of benzene, toluene, and chlorobenzene with DOC were inconsistent with different DOC-sources. Toluene exhibited a higher affinity for unfiltered and aged WSE- and HA-solutions when compared with freshly prepared, filtered solutions of the same materials. Most HOC molecules associated with DOC at pH 6.5. HA and FA showed a significantly greater affinity for HOCs than WSE. This reflects the acidic functional group properties of the three DOC-sources.

WSE displayed the greatest capacity to complex protons, although the FA and HA functional groups were more acidic. WSE, FA, and HA complexed a maximum number of 0.196, 0.158, and 0.136 mol H·mol^{-1} DOC, respectively. Formation functions of WSE, HA, and FA calculated from titration data were fitted to a chemical model through a non-linear least-squares minimization program in order to obtain conditional protonation constants (^{c}K) for classes of functional groups. Log ^{c}K values were 5.52 and 9.12 for WSE, 4.87

and 8.77 for FA, and 4.75, 7.62, and 9.39 for HA. These values were in agreement with protonation constants obtained through a graphical procedure. A comparison of the data obtained for WSE, HA, and FA from association and titration experiments shows that the capacity to complex protons and the affinity for HOCs are inversely related. The relatively high functional group content of WSE corresponds to a relatively low hydrophobicity, as expressed in the small extent of WSE-HOC interactions when compared with HA and FA.

Association of Hydrophobic Organic Compounds with Dissolved Soil Organic Carbon

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Redacted for Privacy

Head of Department of Soil Science

Redacted for Privacy

Dean of Graduate School

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GLOSSARY

α	Probability of type I error
α_1, α_2, α_3	Disribution coefficients
α_H	Degree of protonation
ANOVA	Analysis of variance
C_g	HOC concentration in the gas phase
C_H	Molar concentration of dissociable H in solution
C_ℓ	HOC concentration in the liquid phase
CV	Coefficient of variation
δn_H	Formation function
Δn_H	Normalized formation function
dg	"Determined graphically"
DOC	Dissolved organic carbon
EPICS	Equilibrium partitioning in closed systems
FA	Fulvic acid
γ	Activity coefficient
GC	Gas chromatograph; or: gas chromatographic
HA	Humic acid
H_c	Dimensionless Henry's law constant
HOC	Hydrophobic organic compound
HQW	High-quality water
HSA	Headspace analysis
^cK	Conditional protonation constant
K_1, K_2, K_3	Stepwise acidity constants

K_d	HOC-distribution coefficient between the DOC- and aqueous phase.
K_{ow}	Octanol-water partition coefficient
K_w	Ion-product of water
ls	"Determined using a least-squares routine"
m_{HOC}	Total mass of HOC
n	Number of replicates
r^2	Coefficient of determination
TOC	Total organic carbon
WSE	Water soluble extract
X	Number of mols of HOC associated with DOC
%*HDA*	Percent of HOC associated with DOC
I, *II*, *III*	Classes of acidic organic functional groups
[x]	Concentration of x in molar units
{x}	Activity of x

ASSOCIATION OF HYDROPHOBIC ORGANIC COMPOUNDS WITH DISSOLVED ORGANIC CARBON

Introduction

Groundwater contamination by a vast array of hydrocarbons through gasoline spills and leaking underground storage tanks has become a serious threat to the environment (Marley and Hoag, 1984; Patrick et al., 1985). Moreau (1984) reported that gasoline spills and petroleum contaminated wells represent by far the most severe environmental problem in the State of Maine. For Pennsylvania, Osgood (1974) reported the occurrence of more than 200 hydrocarbon spills within a period of 2.5 years, affecting the water needs of more than 800,000 people. The most troublesome constituents of petroleum products are volatile hydrophobic organic compounds (HOCs), such as benzene and toluene (Sanders and Manyard, 1968; Patrick et al., 1985). The estimated annual global loss of benzene and toluene into the environment is 4.3 and 6.2 million tons (Merian, 1983).

Once relatively water-soluble HOCs are introduced into soils or sediments, absorption to the solid matrix, vertical and horizontal movement with the groundwater, volatilization into the atmosphere, and biological degradation will determine their environmental fate (Marley and Hoag, 1984; Merian and Zander, 1982).

Research on the physical-chemical distribution and transport of HOCs in soil and sediment systems has focussed almost exclusively on the partitioning of HOCs between the aqueous and solid phase (Karickhoff et al., 1979; Karickhoff, 1980, 1981; Wilson et al., 1981; Rao et al., 1985; Wu and Gschwend, 1986; Woodburn et al., 1986). Only recently has it been realized that the association with dissolved organic carbon (DOC) may significantly enhance the aqueous solubility and environmental mobility of organic pollutants in the environment (Gjessing and Berglind, 1981; Carter and Suffet, 1982, 1983; Landrum et al., 1984; Garbarini and Lion, 1985; Haas and Kaplan, 1985; McCarthy and Jimenez, 1985; Chiou et al., 1986). When compared to the free species, DOC-associated HOCs are apparently less available for uptake by organisms (Boehm and Quinn, 1976) and adsorption by solids (Hassett and Anderson, 1982).

The generic term DOC refers to the water-soluble component of organic matter originating from terrestrial or aquatic sources, and represents a portion of humic substances. Humic substances are commonly divided into three operationally defined fractions: (i) humin, which is insoluble in water, (ii) humic acid, which is water soluble at a pH greater than about 2, and (iii) fulvic acid, which is water soluble under all pH conditions.

A chemical model for interactions between DOC and HOCs has been proposed recently by Wershaw (1986). He suggests that DOC in aqueous solutions forms micelles or membranes with a hydrophilic exterior and a hydrophobic interior. DOC-HOC association could then be explained as a simple partitioning of HOCs between aqueous and organic phase (Chiou et al., 1986). Other research (Ziechmann, 1972; Kress and Ziechmann, 1977) suggests the formation of charge-transfer complexes.

To date, very little is known about the significance of DOC on the environmental fate of nonionic volatile HOCs. This is especially true with respect to the influence of environmental conditions and different types of DOC on DOC-HOC interactions. Of particular interest are the acidic functional group properties of DOC. Since acidic functional groups contain most of the organically bound oxygen, the hydrophobicity of DOC should decrease with an increase in functional group content. DOC represents a complex mixture of partially protonated polyanions surrounded by counterions (Sposito and Holtzclaw, 1977). In such a system, the secondary and tertiary molecular structure will depend on the solution pH (Tanford, 1961; Sposito and Holtzclaw, 1977; Ghosh and Schnitzer, 1980). In turn, structure and aggregation of DOC molecules can be expected to bear an important influence on their interaction with HOCs.

The goal of this study was to determine whether a group of HOCs (benzene, toluene, and chlorobenzene) representative of petroleum products and industrial solvents associate with DOC at environmentally realistic concentrations. A water-soluble soil extract (WSE) was selected as natural DOC-source and compared with a commercial humic acid (HA) and a high-purity fulvic acid (FA). The effect of DOC concentration and preparative treatment of DOC solutions was investigated. The proton complexation characteristics of WSE, HA, and FA were determined through continuous potentiometric titrations and compared with their affinity for HOCs under different pH conditions.

Associative Interactions Between Dissolved Organic Carbon and Benzene, Toluene, and Chlorobenzene in Aqueous Solution

MICHAEL OCHS AND JOHN BAHAM*[1]

ABSTRACT

Volatile hydrophobic organic compounds (HOCs) represent a serious threat to terrestrial and aquatic environments. Their environmental fate may be influenced through hydrophobic interactions with dissolved organic carbon (DOC). A static gas chromatographic headspace analysis technique was used to determine the extend of associations of benzene, toluene, and chlorobenzene with three types of DOC. A water-soluble soil extract (WSE) was used as a source of DOC representative for natural environments. For comparisons, a commercially available humic acid (HA) and a high purity fulvic acid (FA) were used. The influence of DOC concentration, preparative treatment of the DOC solutions, pH, and hydrophobicity of the HOCs were examined.

DOC concentrations in the experiments ranged from 1.3 to 36.5 mmol $DOC \cdot L^{-1}$, the ionic background was made up by 0.10 *M* KCl, and the

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*Corresponding Author.

temperature was held constant at 25 °C. Experiments were performed at solution pH values of 4.0, 6.5, and 9.0.

No statistically significant linear relation between DOC concentration and DOC-HOC interaction was observed, but a small degree of association was noted at DOC concentrations ≥9.3 m*M*. Most HOC molecules associated with DOC at pH 6.5. HA and FA showed a significantly greater effect on HOCs than WSE. This result is related to the acidic functional group properties of the three DOC sources. Aged and unfiltered materials were found to behave more hydrophobically towards HOCs than freshly prepared, filtered DOC solutions.

Additional Index Words: humic substances, water-soluble soil extract, hydrophobic organic compounds, headspace analysis.

INTRODUCTION

The contamination of soils and groundwater by organic compounds has obtained much attention in the last decade. Within the diversity of organic chemicals, volatile nonionic hydrophobic organic compounds (HOCs) make up one of the more troublesome classes with respect to environmental control (Merian and Zander, 1982; Wilson et al., 1981; Harland et al., 1985). This class of organic compounds comprises many gasoline constituents, toluene and benzene being most important (Merian and Zander, 1982; Sanders and Manyard, 1968), and a variety of industrial solvents. Groundwater contamination by petroleum products through spills and leaking underground storage tanks has become a serious threat to the environment (Marley and Hoag, 1984; Moreau, 1984; Patrick et al., 1985). Once introduced into the soil or sediment environment, the major pathways of these chemicals will be absorption to the solid matrix, movement with the groundwater, and volatilization (Marley and Hoag, 1984; Bruggeman, 1982).

Research on the distribution and transport of HOCs in soil and sediment systems has focussed almost exclusively on the partitioning of HOCs between the aqueous and solid phase (e.g..: Karickhoff et al., 1979; Karickhoff, 1980, 1981; Wilson et al., 1981; Rao et al., 1985; Wu and Gschwend, 1986; Woodburn et al., 1986). Only recently has the mechanism of association with dissolved organic carbon (DOC) originating from terrestrial sources been recognized as an important pathway influencing the distribution of organic chemicals in the environment (Gjessing and Berglind, 1981; Carter and Suffet, 1982, 1983; Landrum et al., 1984; Garbarini and Lion, 1985; Haas and Kaplan, 1985; McCarthy and Jimenez, 1985; Chiou et al., 1986).

DOC is a generic term, which refers to the water-soluble component of terrestrial or aquatic organic matter, and represents a portion of humic substances. Humic substances are commonly divided into three operationally defined fractions fulvic acid (FA), humic acid (HA), and insoluble humin (e.g. Stevenson, 1982). DOC may exert an important control over the total solubility and mobility of HOCs through the formation of dissolved DOC-associated species of the HOCs. Linear partitioning of HOCs into DOC-micelles or -membranes (Wershaw, 1986) seems to be the most plausible mechanism to explain this process, but apparently complexation by individual DOC molecules (Ziechmann, 1972; Kress and Ziechmann, 1977) is also possible.

Most research concerned with the influence of DOC on the environmental fate of HOCs, however, has been carried out with relatively large molecules such as DDT or PCB's, which are characterized by a very low water solubility and octanol-water partition coefficients of 10^6 or higher.

Little is known about the behavior of nonionic volatile compounds which comprise the bulk of groundwater pollutants (Thurman, 1985a). This is especially true with regard to the influence of environmental conditions on DOC-HOC interaction. As pointed out by Carter and Suffet (1983), different humic materials may associate with HOCs to a different extent, but the reasons for this are not very clear yet. From the model discussed by Wershaw (1986) it can be concluded that the conformation and aggregation of DOC molecules determines their ability to hydrophobically interact with HOCs. In turn, secondary and tertiary structures of dissolved humic materials are influenced in a complex way by the proton and electrolyte concentration in the surrounding solution (Wershaw, 1973; Sposito and Holtzclaw, 1977; Ghosh and Schnitzer, 1980).

The goal of this study was to determine whether a group of HOCs (benzene, toluene, and chlorobenzene) representative of petroleum products and solvents associate with humic materials at DOC concentrations found in natural environments (Thurman, 1985b). The effect of DOC concentration, solution pH, and source or type of DOC on DOC-HOC interactions was also investigated.

METHODOLOGY

General Experimental Considerations

In the context of this research the term "dissolved organic carbon" (DOC) should be defined unequivocally. Only in a few studies concerning DOC-HOC interactions a clear distinction was made between dissolved and suspended (particulate) humic materials. Usually, DOC is defined in operational terms since it is difficult and not necessarily desirable to distinguish between "dissolved" and "colloidal" matter. The particle-size limit for dissolved materials employed by various researchers varied between 0.3 μm (McCarthy and Jimenez, 1985; Landrum et al., 1984) and 0.45 μm (Haas and Kaplan, 1985; Thurman, 1985b). In this work, high speed centrifugation (27000 *g*) combined with 0.2 μm membrane filtration was used as a criterion for DOC. As a basis for comparison, 0.6 μm-filtration was also used.

Likewise, the respective source, extraction method used, and purity are important parameters with respect to the chemical behavior of DOC. Malcolm (1976) and Malcolm and MacCarthy (1986) point out that commercially available HAs are rarely representative for either terrestrial or aquatic environments. However, these materials are most frequently used for experimentation. In this study, a simple water extract (WSE), a commercially available humic acid (HA), and a high purity fulvic acid (FA) were compared. The elemental composition of WSE, HA, and FA solutions is given in Table 1.

Most of the methods used to quantify the extent of DOC-HOC interactions are designed to physically separate free and DOC-associated HOC species in the liquid phase. The incomplete separation of these species (and adsorption of some HOCs to parts of the experimental apparatus) are a potential problem with this approach. This difficulty can be avoided using equilibrium partitioning in closed systems (EPICS), a static headspace analysis (HSA) method developed by Lincoff and Gossett (1984). EPICS also is free of equilibration and mass transfer problems frequently encountered with dynamic HSA-methods.

Table 1. Elemental composition of the three sources of dissolved organic carbon (DOC) employed in the association experiments.[+]

DOC	Elemental Constituents														Ash
	C	H	O	N	P	S	Ca	Mg	Fe	Mn	Cu	Zn	Al	B	%
	mmol·L^{-1}	mmol·mol^{-1} DOC													
HA	9.356 ± 0.008	---	---	13.4	<0.4	21.1	1.8	1.0	3.5	<0.06	0.05	<0.02	2.0	5.2	---
FA[‡]	9.356 ± 0.008	150	600	50.0	0.4	4.4	---	---	---	---	---	---	---	---	0.78
WSE	9.356 ± 0.008	---	---	56.0	30.4[§]	13.2	57.6	13.5	2.8	0.3	0.12	0.12	3.2	<1.1	---

[+] Analytical methods are described in the "Materials"-section.

[‡] Concentration values for FA are determined from the solid sample (ash-free basis); the FA dissolved completely in water. WSE and HA values are determined on dissolved samples.

[§] Total inorganic phosphate determined as Mo-blue.

Materials

Dissolved Organic Carbon

A water soluble extract (WSE) high in DOC (Inskeep, 1982) was obtained from the surface horizon of an agricultural soil (Cumulic Humaquept, Labish Series). The air-dried soil was extracted with high quality water (HQW, electric resistance > 17 MΩ) by shaking for 20 h in 250 mL polyethylene centrifuge bottles. (Solid:solution ratios of 1:10 and 1:1.8 were used depending on the DOC concentration needed). The slurries were centrifuged at 8000 *g* for 20 min in a temperature controlled centrifuge. Subsequently, the supernatants were decanted and filtered through qualitative filter paper (VWR grade 617). The filtrate was transferred to 50 mL polyethylene centrifuge tubes, centrifuged at 27000 *g* for 20 min, homogenized, and frozen in polyethylene bottles for storage. Prior to experiments, samples were thawed and then centrifuged at 27000 *g* for 20 min. The supernatants were then passed, under vacuum, successively through 0.6 μm and 0.2 μm polycarbonate membrane filters (Nucleopore Corp.) prewashed with HQW and a small amount of sample.

The water-soluble fraction of a humic acid (Aldrich Chemical Company, lot # 018 16 HH), and a soil fulvic acid (standard material obtained from the International Humic Substances Society [IHSS], Arvada, Colorado, U.S.A.) were dissolved by mixing 0.990 and 0.20 g, respectively, of the dry materials with 1 L HQW. The solutions were stirred for 5 h and then centrifuged for 20 min at 27000 *g*.
A significant amount of particulate HA remained after centrifugation,

whereas with FA no residue was noted. The samples were stored and prepared for experimentation in the exact same fashion as the WSE.

DOC concentrations were measured in duplicate for each extract with a TOC-analyzer (Oceanographic Instruments). Elemental analysis of WSE- and HA-samples was performed on a Jarrell-Ash ICAP-9000 inductively coupled plasma optical emission spectrometer, total N was determined through micro-Kjeldahl analysis. Elemental composition of the FA was obtained from the IHSS. Phosphate in the WSE and HA solutions was determined colorimetrically in four replicates as molybdenum blue (American Public Health Association, 1975).

Hydrophobic Organic Compounds

High purity benzene and toluene (assay = 99.9 %, 'Photrex' grade) were obtained from J.T.Baker Chemical Company, chlorobenzene with a purity of at least 99 % (Gold Label) was supplied by Aldrich Chemical Company. HOC stock solutions were prepared by rapidly delivering 342.00 ± 0.01 mg toluene, 302.04 ± 0.01 mg benzene, and 427.25 ± 0.01 mg chlorobenzene to 2.542 L, 2.492 L, and 2.490 L HQW, respectively. The amount of HOC delivered was determined gravimetrically with a Mettler H51AR analytical balance and the HOCs were dissolved by shaking the bottles for 16 h. All stock solutions were 1.512 ± 0.057 m*M* in the respective HOC. The initial airspace in the full bottles was less than 10 mL. The bottles were equipped with Teflon seals and stored in the dark.

Methods

EPICS

Originally, this method was designed for the measurement of Henry's constants for volatile organic compounds (Lincoff and Gossett, 1984). The basic experimental procedure includes two closed reaction vessels which contain the same amount of HOC, and liquid and gas volumes. The mass balance for a compound added to one of the systems is given by:

$$m_{HOC} = C_{\ell}V_{\ell} + C_gV_g \qquad \text{Eq. [1]}$$

where m_{HOC} is the total mass of hydrophobic organic compound added, C is the concentration of the HOC, and V_g and V_l are the total volumes the gas and liquid phase, respectively.

Henry's law constants can then be determined through the addition of equal masses of target compound to two bottles which contain different liquid volumes at constant temperature. The dimensionless Henry's law constant (H_c) is given as :

$$H_c = (V_{\ell 1}(C_{g1}/C_{g2}) - V_{\ell 2})/(V_{g2} - (C_{g1}/C_{g2})V_{g1}) \qquad \text{Eq. [2]}$$

where the 1 and 2 refer to system 1 and 2 (Lincoff and Gossett, 1984).

Activity coefficients can be obtained by adding the same amount of HOC to two identical bottles one of which contains a known quantity of an electrolyte. If the temperature is constant and the liquid and gas volumes are the same in both bottles (Gosset et al., 1985):

$$\gamma = (V_\ell/H_c)/((C_{g1}/C_{g2})\ (V_g + V_\ell/H_c) - V_g) \qquad \text{Eq. [3]}$$

In order to investigate DOC-HOC interactions, one of the systems contains a known amount of DOC in addition (Garbarini and Lion, 1985). It can be concluded from the chemical model discussed by Wershaw (1986) that DOC-associated HOC molecules do not undergo any exchange with the gaseous phase. Thus, the amount of HOC associated with DOC can be determined by measuring the HOC-concentration in the headspace of the two systems. The mass balance in the systems can be formulated as follows (Garbarini and Lion, 1985):

$$\begin{aligned} \text{System 1: } m_{HOC} &= C_{g1}\ V_g + C_{\ell 1}\ V_\ell && \text{Eq. [4]} \\ &= C_{g1}\ V_g + (C_{g1}/\gamma\ H_c)V_\ell \end{aligned}$$

$$\begin{aligned} \text{System 2: } m_{HOC} &= C_{g2}\ V_g + C_{\ell 2}\ V_\ell + X && \text{Eq. [5]} \\ &= C_{g2}\ V_g + (C_{g2}/\gamma\ H_c)V_\ell + X \end{aligned}$$

where system 1 and 2 refer to the bottles without and with DOC, respectively, and *X* is the number of mols HOC associated with DOC. It follows that

$$X = (C_{g1} - C_{g2})\ (V_g + (V_l/\gamma\ H_c)), \qquad \text{Eq. [6]}$$

and, combining Eq. [4] and [6], the amount of DOC-associated HOC in percent (%*HDA*) can be calculated as:

$$\%HDA = ((C_{g1} - C_{g2})100)/C_{g1} = (100\ X)/m_{HOC} \qquad \text{Eq. [7]}$$

The distribution coefficient K_d for the DOC-HOC association can be calculated as (Garbarini and Lion, 1985):

$$K_d = ((C_{g1}/C_{g2}) - 1)/(m_{DOC}/(V_\ell + H_c\ \gamma\ V_g)) \qquad \text{Eq. [8]}$$

The values V_g and V_ℓ are known and C_g can be determined for both systems through gas chromatographic headspace analysis (GC-HSA). If the detector response and C_g are linearly related, gas chromatographic peak areas may be substituted for C_g in equations [2], [3], [7], and [8]. Also, it should be pointed out that m_{HOC} has to be known only for reference. Values for H_c, γ, %*HDA*, and X can be determined without this knowledge since only relative measurements are taken. Lincoff and Gossett (1984) and Gossett (1987) noted that EPICS is most precise for compounds with values of H_c between approximately 0.1 and 1.

Experimental Procedures

All experiments were carried out in gas-tight crimp-seal reaction vials (Supelco, Inc.). The total volume of each labeled vial was determined gravimetrically to 0.01 ± 0.01 mL and sets of vials with uniform volumes (less than 0.1 mL difference between any two vials) were selected for each experiment. Keeping this in mind, sets of vials for experimentation were randomized so that a particular vial would be used both as system 1 ("standard-vial") and system 2 ("DOC-vial") in different experiments. Thus, a systematic effect of any possible sorption of HOCs to glass walls (Brownawell, 1986) could be ruled out. The vials were sealed with Teflon-lined rubber septa and aluminum crimp caps (Supelco, Inc.).

Total liquid volumes used in the experiments were 100 mL and 10 mL in the determination of H_C, 100 mL in the measurements of the activity coefficients, and 50 mL in the association experiments. Henry's constants were determined in HQW, activity coefficients were measured in different ionic media made up carefully with 1.00 ± 0.03 *M* KCl stock solution, and all association experiments were carried out in 0.100 ± 0.003 *M* KCl solution. Prior to experimentation, the pH of DOC solutions was adjusted with HCl and NaOH to 4.0, 6.5, or 9.0, using a Beckman combination electrode connected to a Beckman SelectIon 2000 ion analyzer. The electrode was calibrated using four buffers ranging between pH 4.00 ± 0.01 and 10.01 ± 0.03.

The reaction vials were prepared for analysis as follows: the desired volume of HQW was measured into the vials gravimetrically and aliquots of DOC and KCL stock solutions were added as necessary using volumetric glass pipets (CV = 0.03, n = 31; for a 4 mL pipet). An Oxford adjustable micropipettor (CV = 0.01, n = 31, at the 300 μL setting) was used to deliver 200 μL - 800 μL aliquots of HOC stock solutions. (It was determined that the resulting HOC concentrations of 6, 15, and 24 $\mu mol \cdot L^{-1}$ did not result in any statistical difference during the experiments. Therefore, data for all three concentrations were pooled to form six replicates for every data point) The vials were then capped immediately and equilibrated at ambient temperature (19-21 °C) for at least 15 h in the determinations of H_c and γ, and for at least 24 h in the association experiments. During this period, the vials were gently swirled by hand at three different times.

At least 4 h prior to sampling the headspace, the vials were placed in a 18 L waterbath (B.Braun) coupled with a Forma Scientific Inc. Model 70 countercooling unit and brought to thermal equilibrium at 25.000 ± 0.005 °C. A special rack was designed that allowed the vials to be uniformly immersed (only the top 1 cm protruded above the water surface). After each experiment, the serum vials were washed 6 times with HQW (vials that were used repeatedly were washed with concentrated nitric acid) and 3 times with methanol. Then the vials were heated overnight at 230 °C.

A 200 μL gas-tight syringe with a tapered needle, Teflon plunger, and push-button valve (Pressure-Lok Series A-2; Precision Sampling Corp.) was used to obtain 100 ± 5 μL headspace samples. Since the vials were sealed and sampled at different temperatures, the vapor phase samples were taken at vial-pressure, the syringe-valve was closed, the pressure of the sample was adjusted to the column-head pressure of the gas chromatograph, the syringe needle was inserted into the GC injection port, the valve was opened, and the sample immediately injected. Quantitative analysis of headspace samples was carried out on a Hewlett Packard 5890 A gas chromatograph equipped with a flame ionization detector and a 2.44 m by 3.2 mm stainless steel 60/80 Carbopack B/ 1% SP-1000 column (Supelco, Inc.). The instrument was interfaced with a Hewlett Packard 3393 A integrator, and operated isothermally at 200 °C for benzene and toluene, and 220 °C for chlorobenzene, respectively.

Design and Statistical Analysis of the Experiments

A factorial experimental design was planned and carried out. The factors for the experiments with WSE and their levels were: DOC concentrations of 0, 1.33, 4.0, and 9.33 m*M*, pH values of 4.0, 6.5, and 9.0, and log K_{OW} values of 2.13, 2.69, and 2.84 for benzene, toluene, and chlorobenzene, respectively. (log K_{OW} values are from Chiou et al., [1982]). Selected subsets of this design were repeated with FA and HA. Experiments with FA were performed using toluene at pH 6.5 and pH 9, HA was used in conjunction with all three HOCs at pH 9. Because of the limited quantity of the FA which could be obtained, only relatively few experiments could be carried out with this material.

For comparison, the following additional experiments were performed (with toluene only) using WSE, HA, and FA solutions treated as follows: (i) materials were centrifuged (20 min at 27000 *g*) and filtered through 0.6 μm membrane filters, (ii) materials were neither centrifuged or filtered, and (iii) unfiltered materials were aged in closed containers under ambient conditions for about four weeks. Further experimentation was carried out with WSE and HA at DOC concentrations up to 36.5 $\text{mmol}\cdot\text{L}^{-1}$.

Linear relations between DOC concentration and magnitude of DOC-HOC interaction were tested with linear regression. Regression models that included a constant were tested against models forced through the origin. Effects of different treatments, where every factor-level combination represents a treatment, were evaluated with two- and three-way ANOVA models. Where data sets were not balanced well enough (as was the case with some of the additional experiments mentioned above), treatments were compared using t-tests or orthogonal contrasts.

RESULTS AND DISCUSSION

The analysis of a series of HOC standard solutions demonstrated that the GC detector response was linear ($r^2 > 0.995$) for the HOCs used in the experiments. All regression lines passed through the origin, which justifies the substitution of integrated peak areas for C_{g1} and C_{g2} in Eq. [2], [3], [7], and [8]. This analysis also verifies the validity of Henry's law over the concentration range used in the experiments and the reliability of the HSA technique (Lincoff and Gossett, 1984).

The combined analytical error associated with the initial addition of HOCs to the vials and possible subsequent losses, small differences in the volumes of individual vials, headspace sampling and GC injection technique, and variations in the GC detector response was estimated by analyzing sets of vials ($n = 7 - 10$) at various times during the course of the experiment. The average CV for all HOCs was 0.057 ± 0.018.

Henry's Constants and Activity Coefficients

Dimensionless Henry's law constants (H_C) for benzene, toluene, and chlorobenzene at 25.000 ± 0.005 °C are given in Table 2. A limited number of literature values are available for comparison. Henry's constants determined by Mackay et al. (1979) using batch air stripping are about 19 % greater than the values determined in the present study, a value for toluene determined through EPICS (Garbarini and Lion, 1985) is about 15 % greater. No comparisons with Henry's constants estimated from solubility data are made, since available solubility data are generally not very reliable (Gossett, 1987). The relatively small Henry's constants reported here could possibly be the result of a systematic underestimation, but for several reasons these data are considered accurate. First, because of the long equilibration times possible with the EPICS procedure, an incomplete phase equilibration of the HOCs is avoided. Second, only relative measurements are taken with this method. Therefore, a possible loss of HOCs through volatilization or sorption to container

Table 2. Dimensionless Henry's law constants (H_c) in HQW and activity coefficients (γ) in 0.05 *M* KCl solution at 25°C.

HOC	H_c	n	γ	n
Benzene	0.182 ± 0.002	3	1.023 ± 0.006	2
Toluene	0.222 ± 0.006	9	1.024 ± 0.022	2
Chlorobenzene	0.120 ± 0.004	3	0.959 ± 0.020	2

walls will have no effect, provided the loss is of comparable magnitude for all reaction vials. Third, any systematic effect of container-specific artefacts can be ruled out since three to nine different pairs of vials were employed in the measurements and the variation between different pairs were very small (Table 2).

Activity coefficients (γ) were initially determined at 25.000 ± 0.005 °C in an ionic medium made up by 0.05 *M* KCl solution. HOC concentrations of different replicates covered the range of 4.6 to 23.5 $\mu mol \cdot L^{-1}$. In the subsequently performed association experiments, the ionic strength was held uniformly at a value of 0.1. Since a calculation of distribution coefficients for the HOCs became redundant because of the experimental results, measurements of γ were not repeated for the higher ionic strength.

Association Experiments

Effect of DOC Concentration, pH, and K_{OW} of the HOCs

The extent of the reaction between DOC and HOC showed no significant trend with time over a period of 23 h. The slope of a regression of time vs. HOC concentration in the headspace was not different from zero ($r^2 = 0.03$).

The data in Fig. 1 suggest that the interaction between HOCs and DOC probably occurs within 1.5 hours. Therefore, 24 h was a time period more than sufficient in order to reach chemical equilibrium and relatively short with respect to microbial growth. No turbidity which might be attributable to microbial growth was noted after

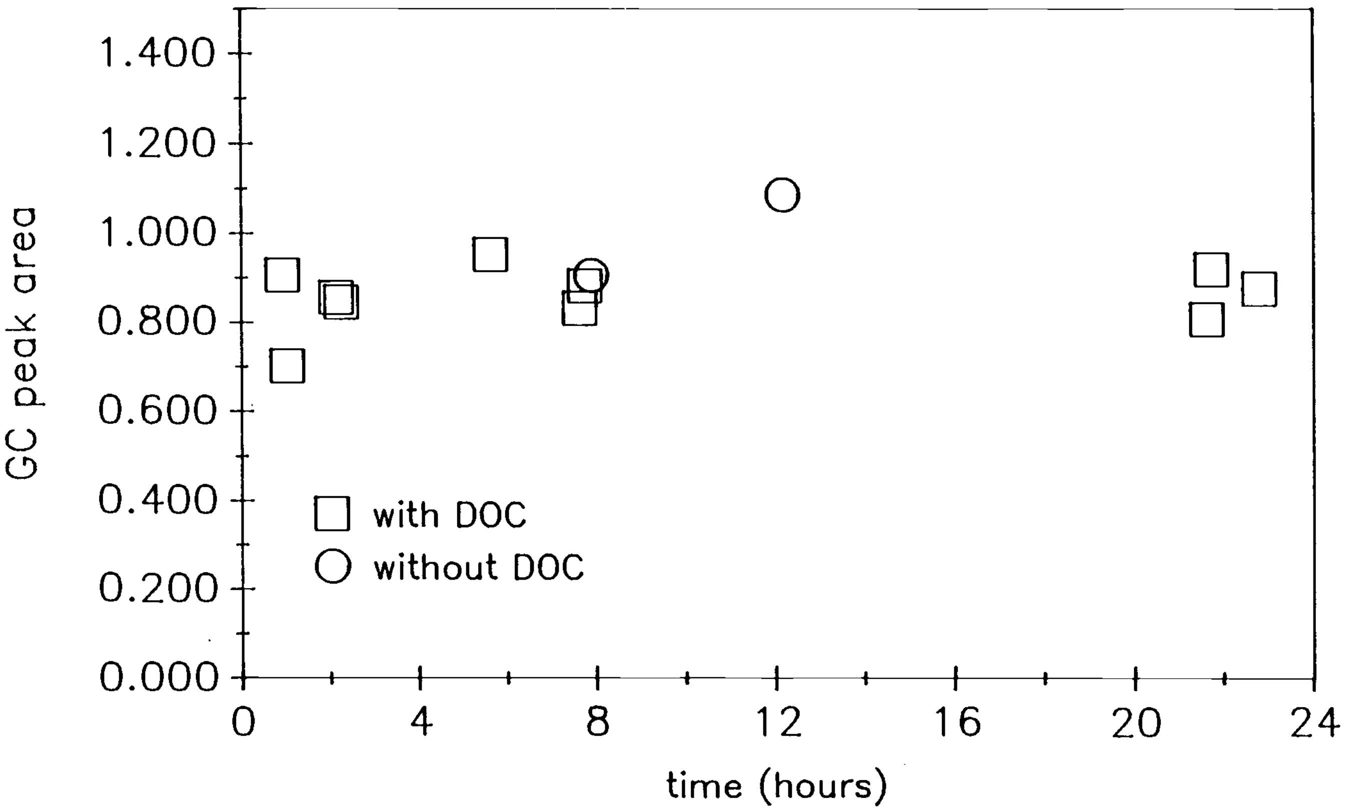

Fig. 1. EPICS headspace concentrations of toluene as measured over time. (DOC concentration was 1.3 mmol HA·L^{-1}, initial toluene concentration in the liquid phase was 15 μM, solution pH was 9).

experiments. Fig. 1 also shows that phase and temperature equilibration of HOC were completed within less than 1.5 h.

Regression analyses of %*HDA*-values obtained for WSE showed that at pH 9.0 all regression coefficients were not different from zero. At pH 6.5, regressions of all three HOCs showed small positive slopes (Fig. 2) which were statistically different from zero (t-test were significant at the 97 %-level for benzene and toluene, and at the 99.9 %-level for chlorobenzene, respectively). However, the coefficients of determination were very small (0.21 for benzene, 0.16 for toluene, and 0.45 for chlorobenzene, respectively). At pH 4, the slope of the regression lines for toluene and chlorobenzene was zero, a very small negative slope and a r^2 of 0.18 was obtained for benzene. In conjunction with the negative slope, the data in Table 3a suggest that this particular experimental subset may be an experimental outlier. The regression results show that no linear relationship between DOC concentration and %*HDA* can be claimed. The data also indicate that a very small positive effect might exist at pH 6.5. Results obtained for experimental subsets performed with FA and HA also show no significant correlation between DOC concentration and DOC-HOC association.

The means of all experiments carried out with standard DOC solutions (filtered through 0.2 μm filters) are given in Table 3. The pooled means of WSE, HA, and FA represent the relative difference in headspace concentration of HOCs between all vials with and without DOC. The standard errors of the total means for WSE, HA, and FA are relatively small. On the other hand, the analytical error was

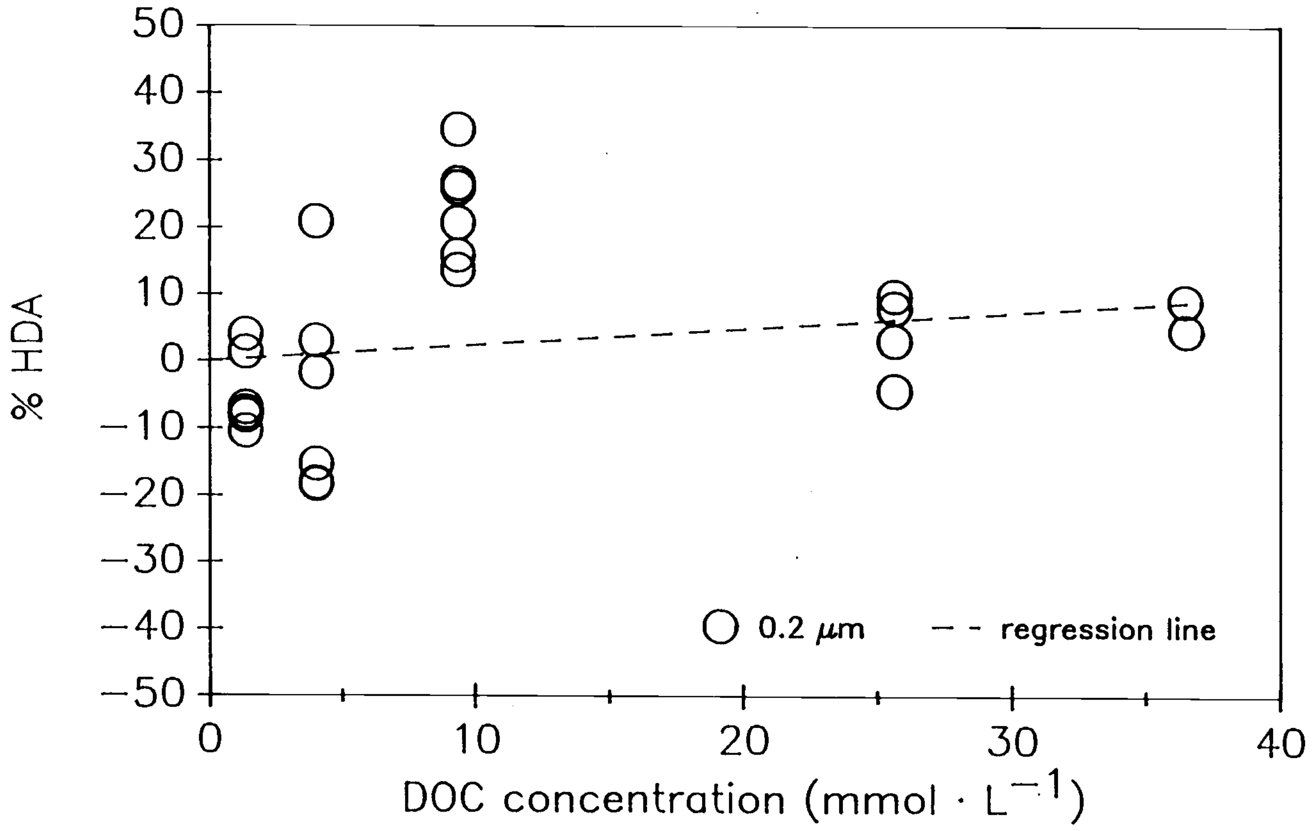

Fig. 2. %*HDA*-values for the association of toluene with WSE at pH 9

Table 3a. Mean values and standard errors of %*HDA* for experiments performed with WSE.

	pH 4		pH 6.5		pH 9		pooled	
HOC	%*HDA*	n	%*HDA*	n	%*HDA*	n	%*HDA*	n
	%		%		%		%	
Benzene†	-24.84 ± 4.94	18	2.57 ± 3.16	18	2.13 ± 4.35	18	-6.72 ± 2.97	54
Toluene‡	1.06 ± 1.68	23	4.57 ± 2.97	24	-3.40 ± 2.19	24	0.75 ± 1.40	71
Chloro-benzene†	-4.66 ± 2.87	18	6.92 ± 2.58	18	-4.74 ± 3.98	17	-0.75 ± 1.95	53
Pooled	-8.59 ± 2.33	59	4.86 ± 1.69	60	-2.10 ± 1.96	59	-1.96 ± 1.22	178

†Data were obtained at DOC concentrations of 1.3 - 9.3 mmol•L^{-1}.

‡Data were obtained at DOC concentrations of 1.3 - 36.5 mmol•L^{-1}.

Table 3b. Mean values and standard errors of %*HDA* for experiments performed with HA and FA solutions.

DOC	HOC	pH 6.5		pH 9		pooled	
		%*HDA*	n	%*HDA*	n	%*HDA*	n
		%		%		%	
HA[†]	Benzene	----	--	0.20 ± 1.43	24	---	--
	Toluene	----	--	2.59 ± 1.64	24	---	--
	Chlorobenzene	----	--	-6.00 ± 1.84	21	---	--
	pooled	----	--	-0.85 ± 1.12	69	---	--
FA[‡]	Toluene	3.51 ± 7.17	4	2.35 ± 1.46	4	2.93 ± 3.44	8

[†] Experiments were performed at DOC concentrations of 1.3 - 25.6 mmol•L^{-1}.

[‡] Experiments were performed at DOC concentrations of 4 and 9.3 mmol•L^{-1}.

determined in repeated independent experiments to be ± 5.7 %. From this follows that the reported means of %*HDA* are only meaningful with respect to each other, not with respect to their absolute position within the analytical error range. Thus, the null hypothesis that under the experimental conditions the overall magnitude of the DOC-HOC association is zero can not be rejected.

This result is in agreement with the findings of Chiou et al. (1986) who studied the interaction between different HOCs and natural humic and fulvic acids at pH 6.5 (the materials were centrifuged at 3000 *g*). They observed a significant interaction between DDT and PCB's ($K_{OW} \approx 10^6$) with the humic materials, but no effect could be observed for compounds with a lower K_{OW}, such as 1,2,3 - trichlorobenzene. They concluded that little DOC-HOC association should be expected with compounds having low K_{OW}'s.

To date only two studies have been conducted on the influence of DOC on volatile HOCs with log K_{OW}-values between 2 and 3. Their results conflict with each other, as well as with conclusions reached by Chiou et al. (1986). Haas and Kaplan (1985) found a maximum increase (8%) of the aqueous solubility of toluene at a DOC concentration of 3.5 m*M* (commercial HA filtered through 0.45 μm filter). The solubility of toluene was found to decrease again at higher DOC concentrations. The experimental techniques (solubility enhancement) used in both the aforementioned studies are generally limited because they yield only data for saturated HOC solutions. Since DOC-HOC interactions may not be constant over the whole range of HOC concentrations, these results may not be representative for the low HOC concentrations typically encountered in environmental pollution (Brownawell, 1986). Garbarini and Lion (1985) also used the technique which is employed in the present investigation. They noted a significant association between volatile HOCs (toluene and trichloroethylene) and a commercial humic acid. The pH was not controlled in their experiments. It must be noted that the composition and ash content and thus, the chemical behavior, of commercial humic substances can be dramatically different from natural materials (Malcolm and MacCarthy, 1986). Carter and Suffet (1983) for example determined the binding constant of DDT to humic substances to vary between 0 (purified Suwanee River FA) and $10^{5.7}$ (Aldrich HA). Since Garbarini and Lion (1985) used the HA without modification, it is not clear whether the HOCs associated with dissolved or suspended fine particulate organic matter.

Trends indicated for WSE through regression analysis were confirmed by applying a three-way analysis of variance (ANOVA) model. (Because DOC concentrations of 25.6 and 36.5 were only used in the experiments with toluene, these data were excluded from this analysis). All three factors (DOC concentration, pH, and K_{ow} of the HOCs) were significant. The factors were also found to be highly interactive. The resulting three-way means of this analysis are plotted vs. DOC concentration and pH in Fig. 3. No definite statement can be made about the behavior of the different HOCs used in this study, because the data obtained for WSE are inconsistent with respect to data obtained for HA. Despite the fact that no statistically valid linear correlation between DOC concentration and

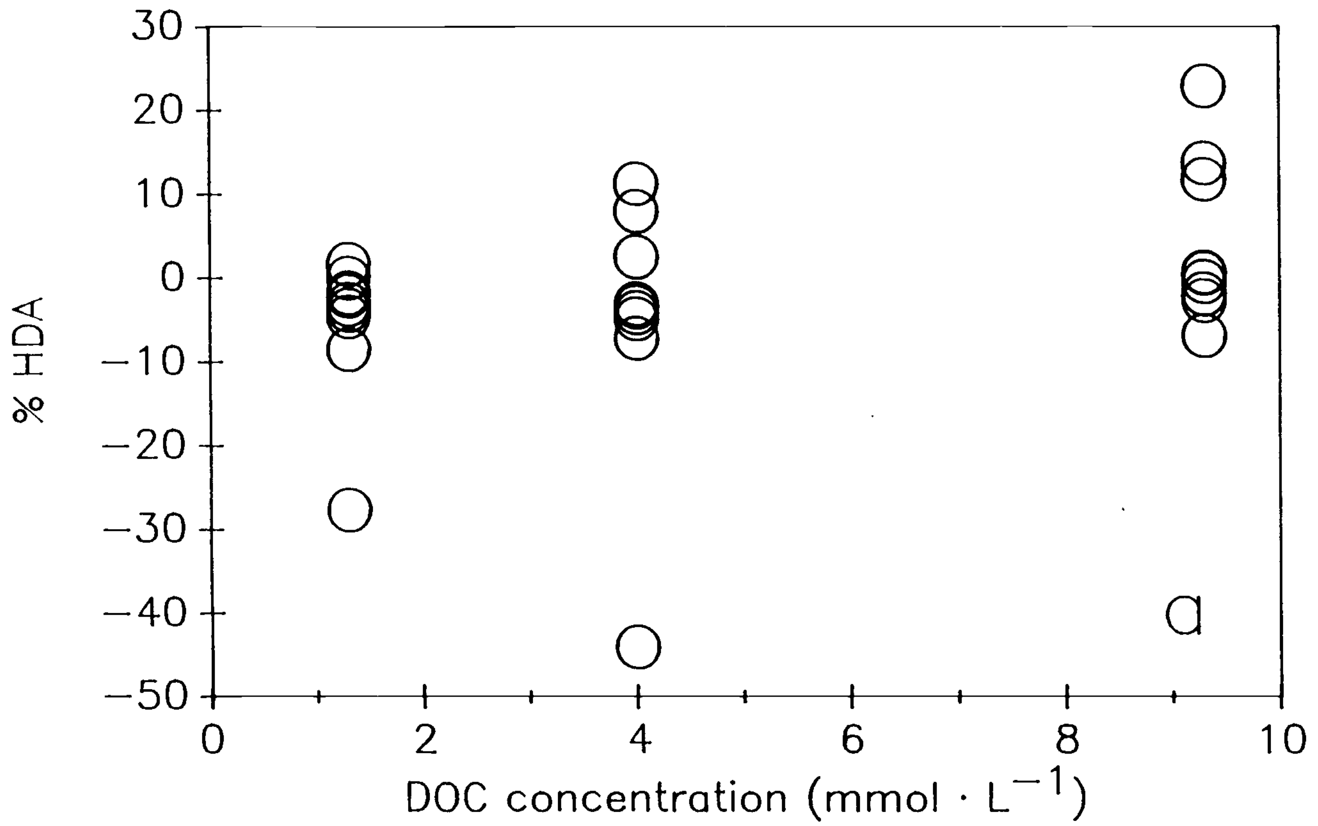

Fig. 3. ANOVA three-way means of the association experiments performed with WSE and benzene, toluene, and chlorobenzene, showing the influence of (a) DOC concentration and (b) pH on WSE-HOC interactions. Each point represents the mean of 6 replicates.

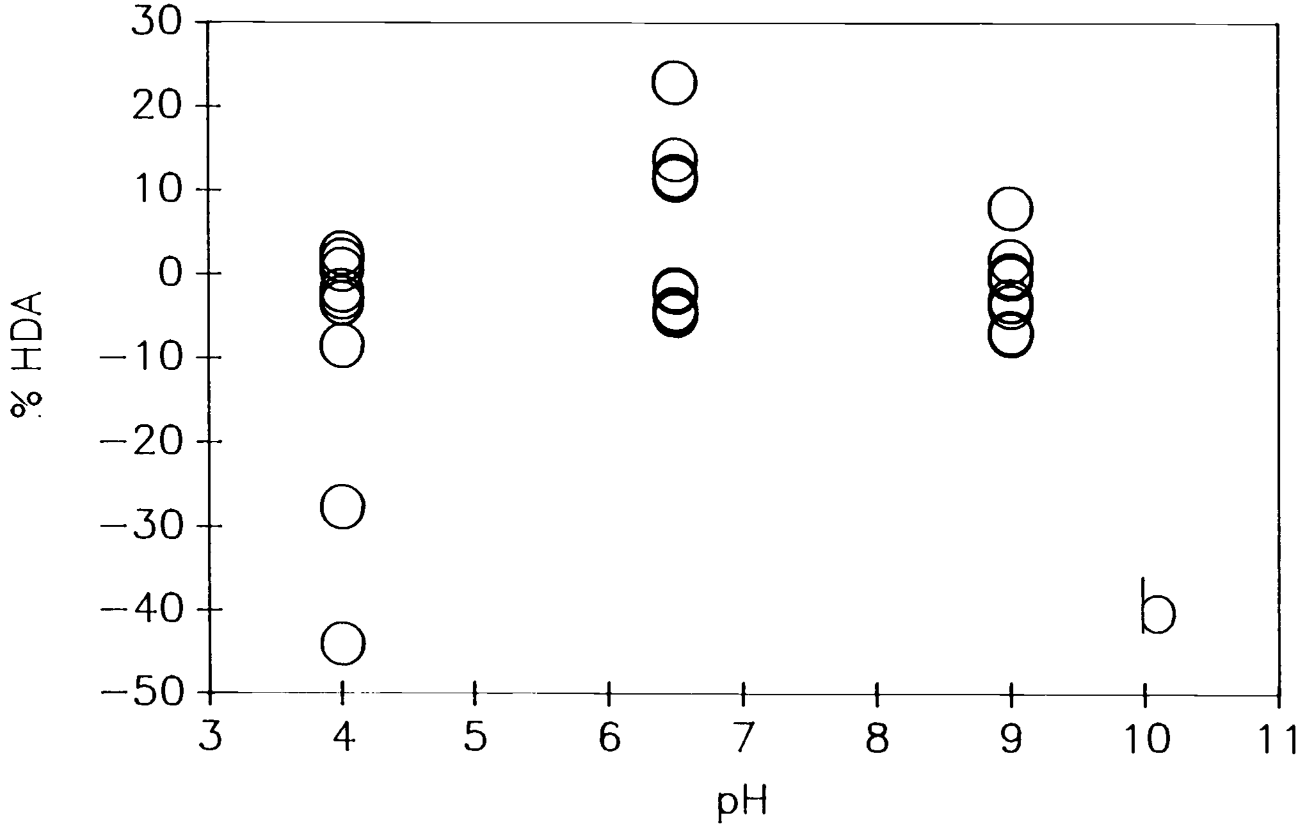

Fig. 3 (continued)

DOC-HOC association could be established, the vials seem to contain less free HOCs at a DOC concentration of 9.3 $\text{mmol}\cdot\text{L}^{-1}$ than at lower DOC concentrations. At pH 6.5, more HOC molecules appear to be associated with WSE than at pH 4.0 or 9.0 (see also Table 3a). This is in agreement with the results of the regression analysis which indicated a positive correlation for all data at pH 6.5. Even if the data set for benzene at pH 4 is not considered in view of its abnormally negative mean %*HDA*-value and regression coefficient, the mean value of %*HDA* at pH 4 is only slightly different from the mean %*HDA* at pH 9 and still much lower than the value for pH 6.5. This is surprising, since in studies concerned with the aggregation of DOC as influenced by the pH, DOC molecules were found to aggregate more as the pH decreases (Wershaw and Pickney, 1973). With other humic materials, a minimum of aggregation in DOC solutions was observed at a pH close to neutrality (Wershaw and Pickney, 1973; Ghosh and Schnitzer, 1980). Therefore, one would expect more HOC molecules to be associated with DOC at pH 4 than at pH 6.5 or pH 9. Carter and Suffet (1982) observed more DDT to be associated with a natural HA at pH 6.5 than at pH 9.2. Unfortunately, they used no pH lower than 6.5, and as yet no other studies were conducted that examined the effect of pH in a controlled way.

Effect of Source and Preparation of DOC

The effect of the source of DOC on the DOC-HOC interaction was evaluated using WSE, HA, and FA as experimental variable. Under identical conditions (pH = 9, [DOC] = 1.3 - 9.3 m*M*, all HOCs) relatively more HOC molecules associate with HA (%*HDA* = -0.52 ± 1.38, n = 51) than with WSE (%*HDA* = -1.68 ± 2.12, n = 53). Since the sole HOC employed in the experiments with FA was toluene, the data in Table 4 have to be used for simultaneous comparisons among WSE, HA, and FA. A large difference in the means of %*HDA* for WSE relative to FA and HA is apparent. An orthogonal contrast constructed with the data pertaining to DOC concentrations of 4 and 9.3 mmol L^{-1} shows that the combined mean of FA and HA is greater than the mean of WSE at the 93 %-level. (Since no significant linear relation between %*HDA* and DOC concentration was apparent, data for HA and WSE at all DOC concentrations could be used for this contrast. In this case, the aforementioned difference would be significant at the 96 %-level. For the sake of statistical correctness, however, only data recorded under identical conditions for WSE, HA, and FA should be used). The fact that WSE behaves differently from both FA and HA with respect to hydrophobic interactions, and the relative similarity of HA and FA reflects the acidic functional group chemistry of the three types of DOC. In a separate study (Ochs and Baham, 1988) we determined through continuous potentiometric titrations that the number of protons complexed at the maximum degree of protonation was about 30 % higher for WSE when compared to FA and HA. This suggests that the relative abundance of acidic organic functional groups along the DOC

Table 4a. Results of association experiments performed with toluene and all three types of DOC.

		pH 6.5		pH 9	
DOC	[DOC] (m*M*)	%*HDA*	n	%*HDA*	n
	mmol•L^{-1}	%		%	
WSE	1.3	-4.64 ± 2.37†	6	0.00 ± 5.36	6
	4	-4.92 ± 6.32	6	-7.21 ± 4.87	6
	9.3	22.92 ± 3.17	6	-0.52 ± 3.37	6
	25.6	4.10 ± 3.16	4	-7.71 ± 6.10	4
	36.5	6.76 ± 2.25	2	-2.00 ± 0.53	2
FA	4	-1.17 ± 15.58	2	-0.03 ± 2.22	2
	9.3	8.19 ± 4.67	2	4.74 ± 2.58	2
HA	1.3	----	--	8.05 ± 4.42	6
	4	----	--	-0.52 ± 2.64	6
	9.3	----	--	4.15 ± 2.64	6
	25.6	----	--	-1.33 ± 3.16	6

†Reported uncertainties are the standard errors of the respective means.

Table 4b. Summarized means of %*HDA* for the data presented in Table 4a.

		pH 6.5		pH 9	
DOC	[DOC]	mean %*HDA*	n	mean %*HDA*	n
	mmol•L^{-1}	%		%	
WSE	4; 9.3	8.99 ± 5.38†	12	-3.86 ± 3.00	12
	1.3 - 25.6	4.38 ± 3.24	22	-3.52 ± 2.39	22
FA	4; 9.3	3.52 ± 7.17	4	2.35 ± 1.96	4
HA	4; 9.3	----	--	1.81 ± 1.56	4
	1.3 - 25.6	----	--	2.59 ± 1.64	12

†Reported uncertainties are the standard errors of the respective means.

molecules has an important influence on the hydrophobicity of DOC. Since organic acidic functional groups contain most of the oxygen bound organically in DOC, it follows that the C/O elemental ratio of DOC should be a better indicator for its interaction with HOCs than the C content alone. The usefulness of this approach was recently demonstrated by Garbarini and Lion (1986), who investigated the interaction of HOCs with solid organic matter and suspended fine particulate humic substances.

With both WSE and HA, no significant difference was found between the standard DOC solutions (filtered through 0.2 μm filters) and materials that were either filtered through 0.6 μm filters or used without any filtration. In the case of WSE this result was obtained irrespectively of the pH used, experiments with HA were only performed at pH 9. Fig. 4 indicates, however, a notable difference between the different types of DOC solutions. Unfortunately, the absence of a significant HOC association with unmodified HA solutions does not allow generalizations, since these materials reportedly show large differences between different batches (Malcolm and MacCarthy, 1986). Table 5 and Fig. 4 show that aged unfiltered WSE and HA have higher tendency to associate with toluene than unfiltered material used immediately after thawing, or any of the filtered DOC solutions. Orthogonal contrasts comparing aged WSE against standard WSE solutions showed that the two types of treatment were significantly different ($\alpha = 0.015$) using the data obtained at pH 9. For the data obtained at pH 6.5 or the pooled data set, no significant difference could be detected. Fig. 5 shows that the value for standard WSE at

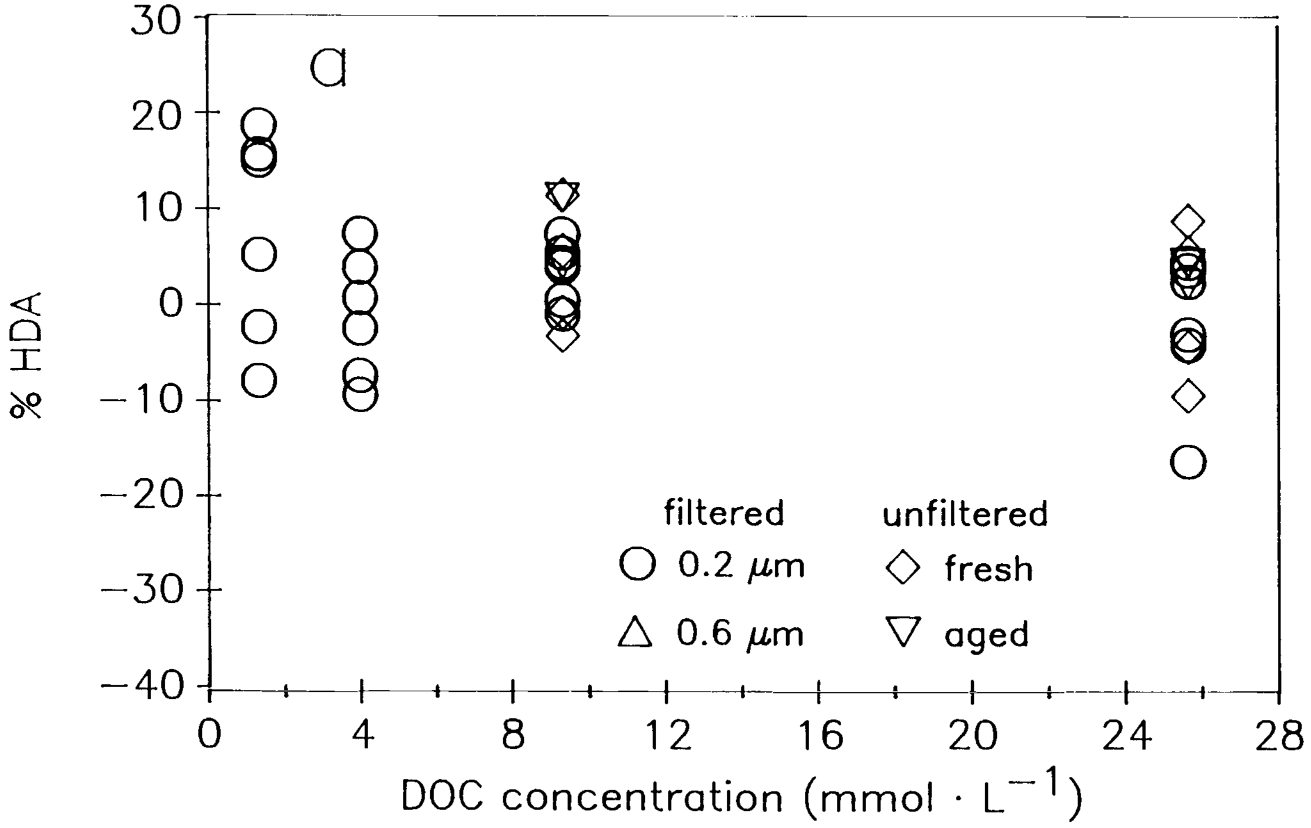

Fig. 4. %*HDA*-values for association experiments with toluene and differently treated solutions of (a) HA and (b) WSE at pH 9.

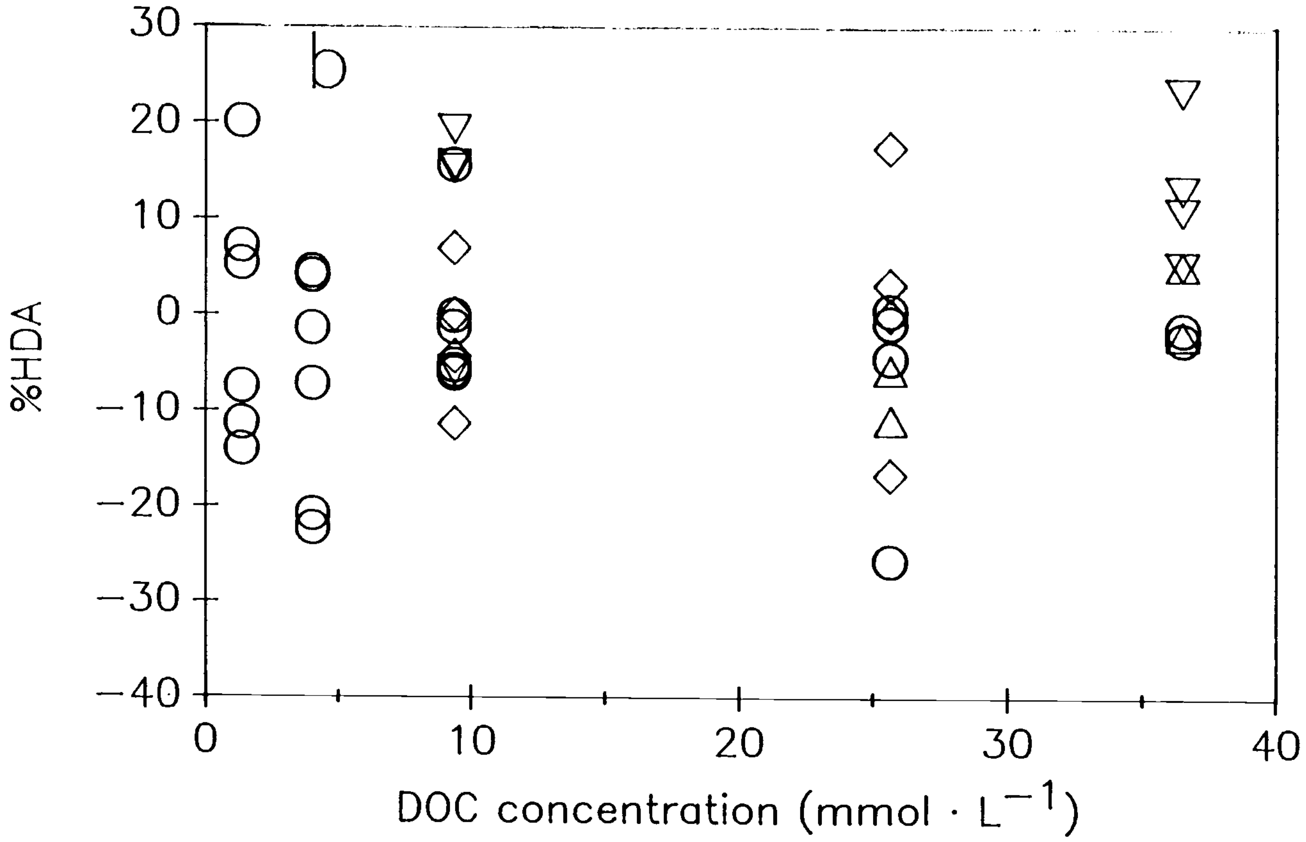

Fig. 4 (continued)

Table 5. Association of toluene with standard and aged DOC solutions.

			standard DOC		aged DOC	
DOC	pH	[DOC]	%*HDA*[†]	n	%*HDA*	n
		mmol•L^{-1}				
WSE	6.5	9.3	22.91 ± 3.17[†]	6	5.61 ± 1.93	4
	6.5	36.5	6.76 ± 2.25	2	14.79 ± 3.52	4
	9	9.3	-0.52 ± 3.37	6	11.04 ± 5.69	4
	9	9.3	4.15 ± 2.64	6	8.39 ± 3.48	2
	9	25.6	-1.33 ± 3.16	6	4.44 ± 0.74	3

[†] Data in this column are compiled from Table 4a.

[‡] Reported uncertainties are the standard errors of the respective means.

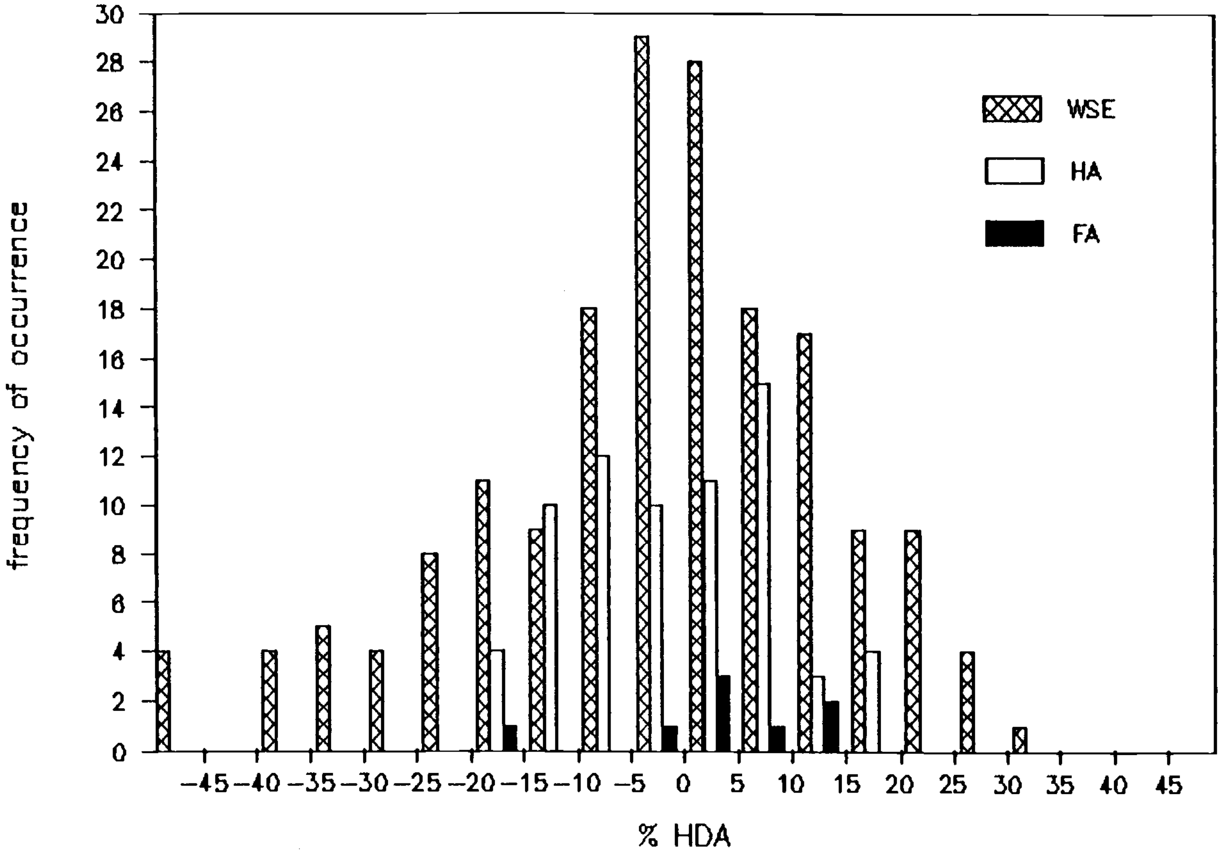

Fig. 5. Frequency distribution for all %*HDA*-values obtained with standard WSE, HA, and FA solutions.

pH 6.5 can be regarded as outlier. Consequently, omitting the data in row 1 of Table 5 in the orthogonal contrast resulted in a highly significant difference ($\alpha = 0.007$) between the two types of treatment. Orthogonal contrasts constructed with %*HDA*-values obtained for HA showed that the aged material behaved different from the standard DOC solutions at the 90 %-level. At this point it should be mentioned that microbial growth was observed in the bottles that contained the aged WSE to be used in the treatments with a DOC concentration of 9.3 m*M*. Before experimentation, this material was filtered through glass wool in order to remove floccules. The increased affinity towards toluene of the aged WSE was probably due to a photochemically (Bauer and Frimmel, 1987) or biologically induced increase in hydrophobicity.

CONCLUSIONS

No statistically significant linear relation between DOC concentration and the association between DOC and HOCs can be observed under the conditions employed in this study. The results suggest that the methods used to extract the different types of DOC determine their chemical behavior with respect to HOCs.

In agreement with the fact that solutions of humic substances represent a complex mixture of polyelectrolytes, it was found that pH exerts a notable influence over the actual hydrophobicity of WSE. Surprisingly, it appears that WSE has a greater affinity towards benzene, toluene, and chlorobenzene at pH 6.5 than at pH 4.0 or 9.0.

WSE, which possesses about 30 % more proton-binding sites than FA or HA, shows the smallest affinity for HOCs. This demonstrates the important influence of acidic functional groups on the hydrophobicity of DOC.

Apparently, extraction and "purification" procedures commonly used to obtain humic and fulvic acids result in a relatively high hydrophobicity when compared to DOC extracted with water. Thus, humic materials frequently used as model substances in laboratory experiments may not necessarily be representative for the whole range of DOC found in natural environments.

Most treatment effects were more pronounced at higher DOC concentrations. This may suggest that extrapolation of results derived from experiments performed at higher DOC concentrations to lower DOC values may not be justified. Likewise, most empirical relations that are used to estimate DOC-HOC interactions from K_{ow} or solubility data were developed with highly hydrophobic compounds, and it may be not realistic to apply these relations to relatively soluble compounds with low K_{ow}'s.

Our results imply that, within the range of realistic DOC concentrations, DOC has no significant overall effect on the speciation of benzene, toluene, and chlorobenzene. On the other hand, DOC in natural environments is likely to get altered through microbial activity or photochemical reactions and become more hydrophobic and more active with respect to HOCs.

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Proton Complexation by Three Sources of Dissolved Organic Carbon (DOC)

MICHAEL OCHS AND JOHN BAHAM*[1]

ABSTRACT

The functional group chemistry of dissolved organic carbon (DOC) exerts an important influence over proton complexation and the fate of pollutants in the environment. The proton complexation characteristics of a simple water-soluble soil extract (WSE) were investigated through continuous potentiometric titration and compared with results obtained using aqueous solutions of fulvic acid (FA) and humic acid (HA). The DOC solutions were titrated with KOH in a 0.1 *M* KCl ionic background at 25°C. The formation functions of WSE, FA, and HA were were calculated from the titration data. Mean conditional protonation constants (^{c}K) of every class of acidic organic functional groups were obtained by fitting these data to a chemical model using a non-linear least-squares minimization routine. The results were compared to mean protonation constants determined with a graphical procedure. Both methods of data analysis described the acidic properties of WSE and FA best by assuming two classes of

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*Corresponding Author.

functional groups. The log ${}^{c}K$ values were determined to be 4.87 and 8.77 for FA, and 5.52 and 9.12 for WSE. The model for HA includes three classes of functional groups with log ${}^{c}K$'s of 4.75, 7.62, and 9.39. The values of the conditional protonation constants remained constant as the degree of protonation increased within a particular class of functional groups. Although the FA and HA functional groups were more acidic, WSE displayed a greater overall capacity to complex protons. The maximum amount of protons complexed by WSE, FA, and HA were 0.196, 0.158, and 0.136 mol H mol^{-1} DOC, respectively.

Additional Index Words: fulvic acid, humic acid, organic functional groups, formation function.

INTRODUCTION

Dissolved organic carbon (DOC) represents an important fraction of the organic matter pool in soil, sediment, and aquatic environments. DOC comprises the water-soluble portion of humic substances which are commonly subdivided into the operational fractions humic acid (HA), fulvic acid (FA), and insoluble humin (Stevenson, 1982). HA and FA possess organic acidic functional groups, the nature and number of which may depend on the source of the DOC (Thurman, 1985).

The significance of DOC with respect to the complexation of protons, and transport and chemical speciation of metals in the environment has been widely recognized (Reuter and Perdue, 1977; Schnitzer, 1978; David and Driscoll, 1984; Cozzarelli et al., 1987). The formation of cation-DOC ligand complexes depends on the concentration and stability constants of the organic acidic functional groups (Bloomfield, 1964; Reuter and Perdue, 1977). DOC also plays an important role in pedochemical weathering and mineral dissolution (Boyle et al., 1974; Furrer and Stumm, 1986; Zinder and Stumm, 1985; Zinder et al., 1986) and may contribute significantly to the acidity of colored natural waters (Oliver et al., 1983).

The functional group chemistry of DOC may also influence it's chemical interactions with nonionic hydrophobic organic compounds (HOCs) and other xenobiotic chemicals. Although the precise structural details of the interaction of HOCs with DOC are not known, it is suggested that the DOC forms micelles or membranes which HOCs can partition into (Wershaw, 1986). Apparently, the formation of charge-transfer complexes is also possible (Ziechmann, 1972; Kress and Ziechmann, 1977). The association of HOC molecules with DOC has been described by a simple linear partitioning model (Chiou et al., 1986; Garbarini and Lion, 1985). The magnitude of this interaction will depend on the overall hydrophobicity of the DOC molecules which is to be correlated mainly with the relative organic carbon content of the DOC (Karickhoff, 1984). However, it appears that the number and dissociation characteristics of DOC functional groups may play a significant role in DOC-HOC interactions (Carter and Suffet, 1982; Wershaw, 1986). In this respect the influence of pH on the degree of dissociation of the organic functional groups is of particular interest. The abundance and distribution of negatively charged unprotonated functional groups on a DOC-molecule will determine it's conformation and chemical behavior and thus the intra- and intermolecular spatial arrangements of DOC (Wershaw, 1986; Ghosh and Schnitzer, 1980; Sposito and Holtzclaw, 1977). If the linear partitioning model as discussed by Wershaw (1986) is appropriate to describe the mechanics of DOC-HOC association, the magnitude of this interaction can be expected to be highly pH-dependent.

The acidic functional group chemistry of DOC can be investigated conveniently through potentiometric titrations. Potentiometric titrations have been employed by Sposito and co-workers (1977, 1982) to investigate the functional group properties of FA extracted from sewage sludge and soil-sewage sludge mixtures. Posner (1966), Borggaard (1974a, 1974b), Stevenson (1978), Perdue et al. (1980), and Oliver et al. (1983) performed titration studies on humic acids extracted from aquatic and terrestrial environments with bases, resins, and EDTA. Continuous and batch titrations were used by Blaser et al. (1984) to investigate the acidic properties of a chestnut leaf litter extract. Baham and Sposito (1986) used potentiometric titrations to study proton complexation by a water-soluble sludge extract.

The goal of this study was to determine and compare the functional group proton dissociation characteristics of FA, HA, and a simple water extract of an agricultural soil (WSE). An attempt is made to evaluate the affinity of these materials towards nonionic volatile HOC as a function of solution pH and source of DOC.

MATERIALS AND METHODS

Dissolved Organic Carbon (DOC)

A water soluble extract (WSE) high in DOC was extracted from the surface layer of a Cumulic Humaquept (Labish Series) (Inskeep, 1982). The air-dried material was extracted with HQW (high quality H_2O, electric resistance >17 MΩ) by shaking for 20 h in 250 mL polyethylene centrifuge bottles using a solid:solution ratio of 1:10. The slurries were centrifuged at 8000 *g* for 20 min after which the supernatants were decanted and filtered through qualitative filter paper (VWR grade 617). The solution was transferred to 50 mL polyethylene centrifuge tubes, centrifuged at 27000 *g* for 20 min, homogenized, and frozen in polyethylene bottles for storage. Prior to experiments, samples were thawed and then centrifuged at 27000 *g* for 20 min.

The water-soluble fraction of a humic acid (Aldrich Chemical Company, lot #018 16 HH), and a standard soil fulvic acid (International Humic Substances Society [IHSS], Arvada, Colorado, USA) were dissolved by mixing the dry materials with HQW (0.990 and 0.20 g L^{-1}, respectively). The extracts were stirred for 5 h and subsequently centrifuged for 20 min at 27000 *g*. A significant amount of insoluble HA remained after centrifugation. The samples were stored and prepared for experimentation in the same manner as the WSE.

DOC concentrations were measured in duplicate for each extract with a TOC-analyzer (Oceanographic Instruments). Elemental composition of the FA was obtained from the IHSS. Elemental analysis of WSE- and HA-solutions was performed on a Jarrell-Ash ICAP-9000 inductively coupled plasma optical emission spectrometer, total N was determined through micro-Kjeldahl analysis.

Orthophosphate in the WSE and HA solutions was determined colorimetrically (ascorbic acid method) as molybdenum blue (American Public Health Association, 1975).

Potentiometric Titrations

Reagents

Carbonate-free base was prepared by dissolving 10 g of KOH in approximately 10 mL HQW. The solution was filtered through Whatman #42 filter paper. Five mL of the filtrate were added to 1 L of freshly boiled HQW and immediately transferred to a polyethylene bottle. The outlet and air inlet of the bottle were equipped with stopcocks, the air inlet was protected from CO_2 with an ascerite trap. The KOH solution was standardized (0.099938 ± 0.00016 *M*; n = 7) against carefully prepared primary standard potassium hydrogen phthalate solutions. The HCl solution used in the titrations was standardized against the standard KOH (= 0.093535 ± 0.00036 *M*; n = 6).

Apparatus

The titrations were carried out in a polyethylene beaker immersed in a 4.5 L waterbath (B. Braun). The bath was equipped for countercooling and the temperature could be held constant at 25.00 ± 0.01°C. A Beckman combination electrode connected to a Beckman Model 3500 digital pH meter, a sparging tube, and a 2 mm polyethylene tube connected to a Kimax 10 mL microburette were immersed into the sample solution through PARAFILM "M" laboratory film covering the reaction vessel. A magnifying ocular attached to the microburette allowed titrant increments of 0.001 mL to be read.

The system was kept CO_2-free by bubbling humidified N_2 through the sparging tube. A N_2-flow rate was established that provided adequate stirring without resulting in a significant loss of the sample solution. (Preliminary tests showed that the loss of solution was less than 0.7% during the course of 6 h.)

Procedure

Potentiometric titrations (Sposito and Holtzclaw, 1977) of basic DOC-solutions with 0.0935 *M* HCl were carried out. Prior to each experiment the combination electrode was filled with AgCl-saturated 4 *M* KCl solution (Beckman). The electrode-pH meter assembly was calibrated using buffers of pH 4.00 ± 0.01 (phthalate, Beckman), pH 6.86 ± 0.03 (phosphate, Beckman), pH 7.42 ± 0.03 (phosphate, Altex), and pH 10.10 ± 0.03 (carbonate, Beckman). Subsequently, the calibration was rechecked against all buffers. In all cases the reading was within 0.01 units of the correct value without readjustments, except in the case of carbonate buffer where the reading was within 0.05 to 0.1 units. Electrode potential drift was less than 0.05 pH units over 48 h.

Prior to the titrations the DOC-solutions were brought to initial concentrations that accounted for all subsequent dilutions. The mean DOC concentration of all solutions during the titrations was 9.356 ± 0.008 m*M*. After the sample pH was adjusted to the approximate starting value, an aliqot of KCl was added to establish a uniform ionic strength (0.099 ± 0.001). During the titrations, DOC concentration and ionic strength changed less than 5% (3.98 ± 0.50%, and 4.1 ± 0.5%, respectively).

The sample solutions were then centrifuged at 27000 *g* for 20 min and subsequently equilibrated together with the electrode under N_2-purging for 2 h before titrations were performed.

A minimum pH-range of 10.70 to 3.00 was covered in every experiment. Titration data were recorded as pH-volume HCl pairs.

For the vast majority of all data points the increments of added HCl were kept at 0.05 mL. Titration experiments took approximately 5 h to complete and comprised 99, 73, and 71 data points for WSE, HA, and FA, respectively.

Data Analysis

The binding of protons by functional groups present in the DOC-solutions was calculated using the expression (see e.g. Rossotti and Rossotti, 1961, p. 155):

$$\delta n_H = (C_H - [H]+[OH])/[DOC] \quad \text{Eq. [1]}$$

where δn_H is the formation function expressed as the number of moles of H bound per mole of dissolved organic carbon, and C_H is the molar concentration of dissociable H in solution, and [DOC] the dissolved organic carbon concentration in molar units. Values for [H] and [OH] were calculated using the relations $\{H\} = [H]\gamma_H$, $\{H\} = 10^{-pH}$, $\{OH\} = [OH]\gamma_{OH}$, and $K_w = \{H\}\{OH\}$, where K_w is the ion-product of water, and γ is the activity coefficient. The value of $1.01 \cdot 10^{-14}$ (Stumm and Morgan, 1981, p. 127) was used for K_w at 25°C. The extended Debye-Hückel equation (see e.g. Stumm and Morgan, 1981, p. 135) was used to obtain values for γ_H and γ_{OH}.

Mean conditional protonation constants ^{c}K for every class of functional groups may be readily obtained through the Henderson-Hasselbalch equation

$$^{c}K = \alpha_H/((1 - \alpha_H)[H]) \qquad \text{Eq. [2]}$$

and the relation (Sposito et al., 1977)

$$\alpha_H = (\delta n_H - \delta n_{HL})/(\delta n_{HU} - \delta n_{HL}), \quad \text{Eq. [3]}$$

where α_H is the degree of protonation. *L* and *U* refer to the values of δn_H at the beginning and end, respectively, of the titration of a given class of functional groups.

Plots of δn_H vs log[H] were analyzed using the expression $\Delta_{i-j}\delta n_H/\Delta_{i-j}p[H]$, where Δ_{i-j} represents the difference between successive data points ($i = 1...n-1$, $j = i+1$, and n is the number of data points), which yields an approximate first derivative of δn_H. Expanded graphs of this derivative were compared to the formation curve to evaluate the endpoints of particular classes of functional acidic groups.

Optimization of Titration Data

The computerized non-linear least-squares minimization procedure FUNMIN, Version 5 (Lindstrom, 1980a, 1980b) was employed to model the formation curves for HA, FA, and WSE. Eq. [4] was used as function and Δn_H and p[H] were used as input parameters. Each formation curve was modeled for one to four conditional protonation constants and both the complete and restricted data sets (see Results and Discussion).

RESULTS AND DISCUSSION

Influence of Inorganic Anions

Titration curves of FA, WSE, and HA represent the combined acidity arising from organic functional groups and protolyzable inorganic anions present in the mixture. Within the p[H] range investigated, orthophosphate species can be considered the most important constituent able to form complexes with protons (Table 6). Furthermore, phosphate species play an important role only in the titration of WSE since phosphate concentrations in the FA and HA solutions are small compared to the total number of protons titrated. The formation curve for the species H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} was calculated using the expression $\delta n_p = \alpha_1 + 2\alpha_2 + 3\alpha_3$, where δn_p is the degree of formation of the protonated species. The distribution coefficients α can be obtained from the titration data as follows: (i) $\alpha_3 = (1 + (K_1/[H]) + (K_1K_2/[H]^2) + (K_1K_2K_3/[H]^3))^{-1}$, (ii) $\alpha_2 = \alpha_3(K_1/[H])$, and (iii) $\alpha_1 = \alpha_3(K_1K_2/[H]^2)$ (e.g. Butler, 1964). K_1 ($10^{-2.1}$), K_2 ($10^{-7.2}$), and K_3 ($10^{-12.3}$) are the acidity constants for the species listed above and were taken from Stumm and Morgan (1981). The formation curve of WSE was then calculated for every respective data point as $\delta n_H = \delta n_{H,p} - \delta n_p$, where $\delta n_{H,p}$ and δn_p refer to the formation function of WSE including phosphate and the formation function of phosphate species, respectively (Fig. 6).

Table 6. Elemental composition of the three sources of dissolved organic carbon (DOC) employed in the titration experiments.

DOC	Elemental Constituents														Ash
	C	H	O	N	P	S	Ca	Mg	Fe	Mn	Cu	Zn	Al	B	%
	$\mathrm{mmol \cdot L^{-1}}$	$\mathrm{mmol \cdot mol^{-1}}$ DOC													
HA	9.356 ± 0.008	---	---	13.4	<0.4	21.1	1.8	1.0	3.5	<0.06	0.05	<0.02	2.0	5.2	---
FA+	9.356 ± 0.008	150	600	50.0	0.4	4.4	---	---	---	---	---	---	---	---	0.78
WSE	9.356 ± 0.008	---	---	56.0	30.4‡	13.2	57.6	13.5	2.8	0.3	0.12	0.12	3.2	<1.1	---

+Concentration values for FA are determined from the solid sample (ash-free basis); the FA dissolved completely in water. WSE and HA values are determined on dissolved samples.

‡Total inorganic phosphate determined as Mo-blue.

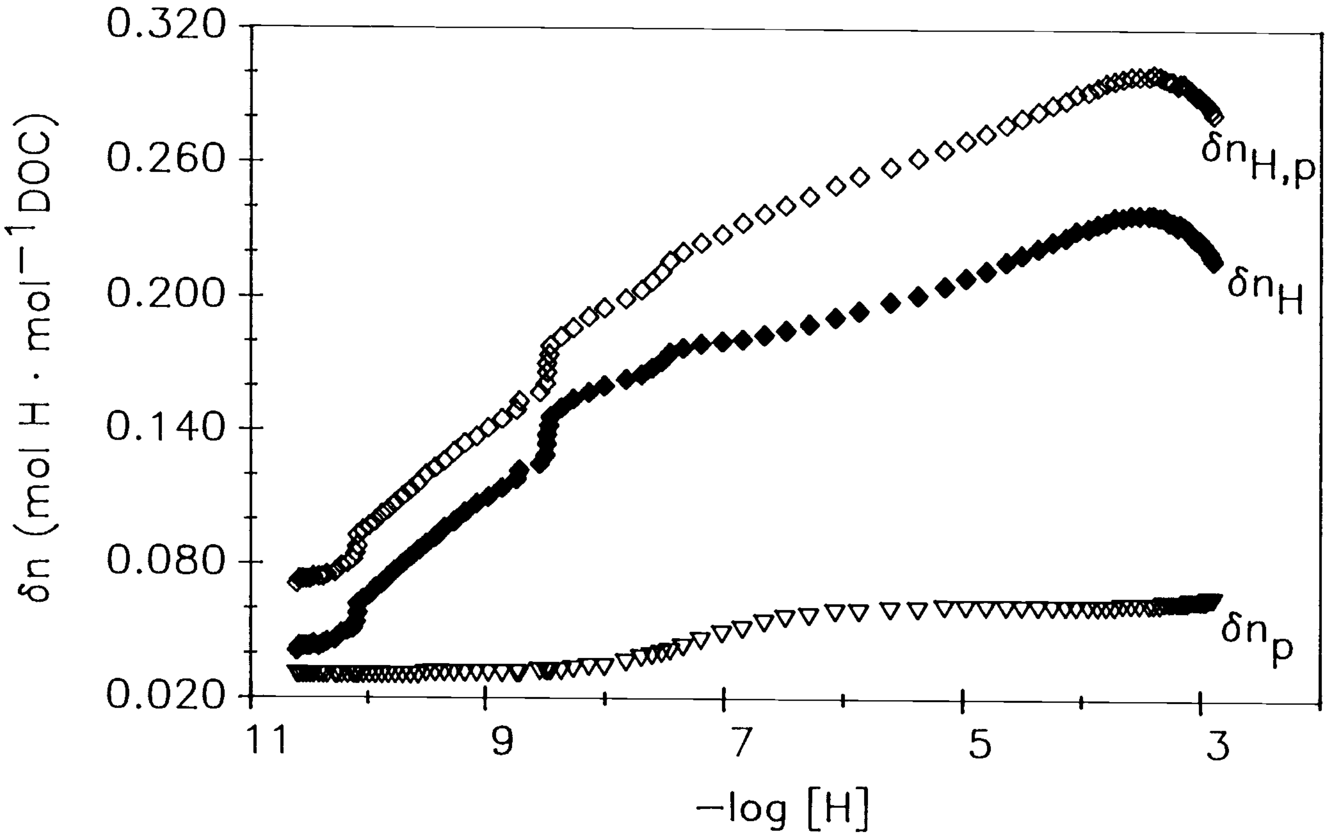

Fig. 6. Formation functions $\delta n_{H,p}$ (WSE including phosphate species), δn_H (WSE corrected for phosphate species), and δn_p (phosphate species).

Continuous Proton Titration Curves

The normalized formation function $\Delta n_H = \delta n_H - \delta n_{H_{min}}$, where the subscript *min* refers to the minimum of the formation function, provides a measure for the absolute amount of protons consumed by organic functional groups (Fig. 7). Values of $\Delta n_{H_{max}}$ and $\Delta n_{H_{iso}}$ are given in Table 7. The subscipts *max* and *iso* refer to the formation function at the maximum and at the isoionic point. At the isoionic point, $C_H = OH^0$, where the superscript ^{0} refers to the initial value at the beginning of a titration experiment.

Qualitatively, the titration curves in Fig. 7 show typical characteristics of a mixture of polyfunctional organic acids: a wide range of acidity constants and considerable overlap of the stability constants of functional groups (Dubach et al., 1964). Evidently not all of the functional groups were titrated within the pH range investigated since no plateau regions can be observed at either end of the titration curves.

The maximum in the value of Δn_H exhibited in all titration curves at low p[H] values suggests a change in the acidity of the DOC. This may be explained through a conformational alteration of the polyanions and an accompanying change of the dissociation properties of the functional groups caused by the reduced electrostatic free energy (Tanford, 1961). It may also be possible that the increased flexibility of the polyelectrolyte molecules at a lower p[H] actually exposes acidic functional groups which for steric reasons had not been in contact with the solution yet. In the p[H]

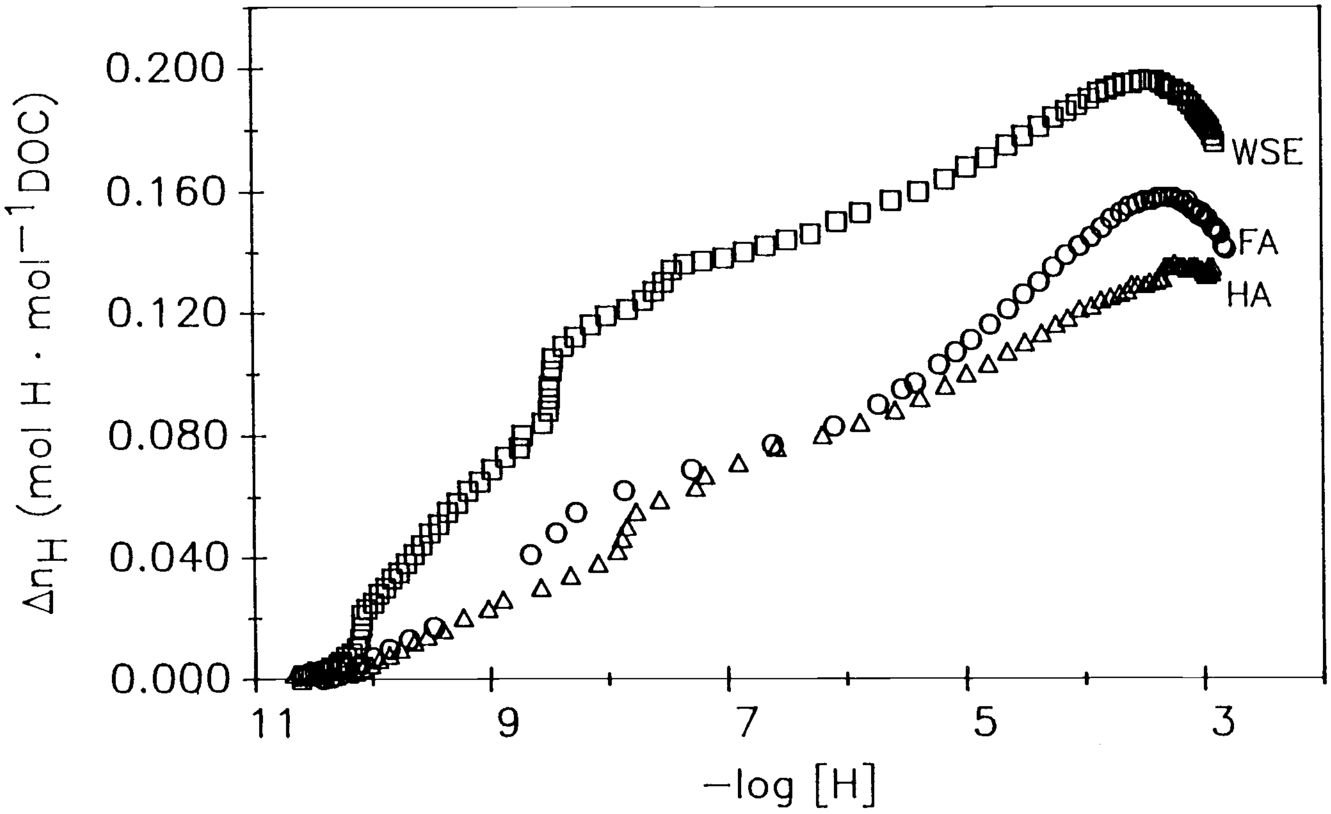

Fig. 7. Normalized formation functions Δn_H of WSE, FA, and HA.

Table 7. Values for the maximum number of protons complexed ($\Delta n_{H_{max}}$) and the number of protons complexed at the isoionic point ($\Delta n_{H_{iso}}$) with their corresponding p[H] values.

DOC	$\Delta n_{H_{max}}$	p[H]	$\Delta n_{H_{iso}}$†	p[H]
	$mmol \cdot mol^{-1}$ DOC		$mmol \cdot mol^{-1}$ DOC	
HA	0.136	3.24	0.013	9.59
FA	0.158	3.33	0.028	9.07
WSE	0.196	3.40	0.022	10.07

† Δn_H at the isoionic point where $C_H = C_{OH^o}$, where C_{OH^o} is the initial OH concentration

region characterized by this proposed conformational change, the accumulation of foam on the surface of the titrated solutions could be observed during experimentation. This phenomenon, whose intensity decreased in the order HA > WSE >> FA, suggests a change in the surfactant characteristics of the DOC. Further, it should be noted that in all titrations the achievement of the new protolytic equilibrium was relatively slow (a stable pH reading could be obtained after about 15-30 min) between approximately p[H] 6.5 and p[H] 8.5. Usually, the pH readings were perfectly stable after about 1 min which agrees with the findings of other researchers (Borggaard, 1974a; Baham and Sposito, 1985). Together with the irregular shape of the formation curves in the respective p[H] region, this delay in the establishment of protolytic equilibria may also indicate a structural change of DOC molecules (Bell, 1973; Borggaard, 1974a). Similar irregularities in titration curves of polyelectrolytes were observed by Tanford et al. (1955), Terbojevich et al. (1972), and Van Der Veen and Prins (1974), and could be ascribed to a change of molecular structure. Although molecular structure was not monitored directly during the titrations, formation curves may be regarded as sensitive indicators of structural changes (Steinhardt and Zaiser, 1955; Tanford, 1961; Crescenzi, 1974; Perdue et al., 1980).

Determination of Conditional Protonation Constants

The determination of protonation constants of the organic acidic functional groups is complicated, in principle, by the polyacidic and polynuclear character of DOC (Sposito and Holtzclaw, 1977).

Neighboring-group effects and hydrogen bridging within and among polyelectrolyte molecules make it unlikely that any two functional groups of a DOC-polyacid have the same acidity constants.

Plateau regions of the formation curve corresponding to relatively distinct classes of acidic functional groups could be delineated by analyzing the approximate first derivative of the formation curve. Consequently, the "quasi-particle" model developed by Sposito et al. (1977) can be applied to the determination of protonation constants. A "quasi-particle" represents a hypothetical organic macromolecule comprising one or more distinct classes of functional groups. Mathematically, the acidity of this hypothetical molecule can be described by a single ${}^{c}K$. The formation curve then is defined as

$$\Delta n_H = \Sigma_i((\Delta n_{Hi}\ {}^{c}K_i\ [H])/(1 + {}^{c}K_i\ [H])) \qquad \text{Eq. [4]}$$

where Δn_{Hi} is the number of mols of protons complexed by the ith hypothetical macromolecule with the conditional protonation constant ${}^{c}K_i$ (Sposito et al., 1977). The formation curves thus calculated are shown in Fig. 8, the respective conditional protonation constants are given in Table 8.

Fig. 9 shows a plot of the conditional protonation constants vs. the normalized formation function. The log of the protonation constants does not change appreciably with Δn_H. Thus, the protonation constants of every class of functional groups are homogeneous, i.e. do not change with the degree of protonation of a particular class of

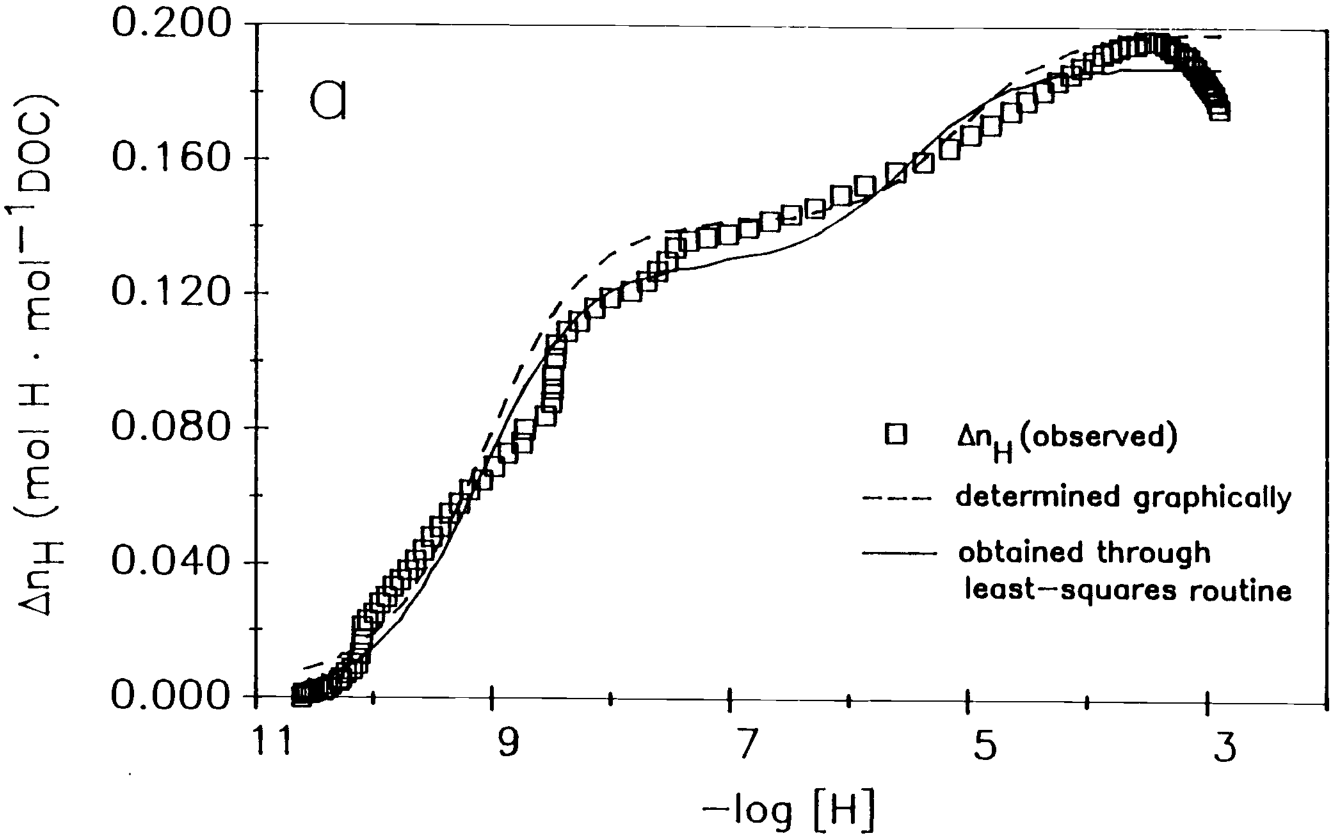

Fig. 8. Modeled and observed normalized formation curves of WSE (a), FA (b), and HA (c). Formation functions were fitted to a chemical model through: (i) graphical determination of functional group class endpoints, and (ii) a non-linear least-squares minimization routine.

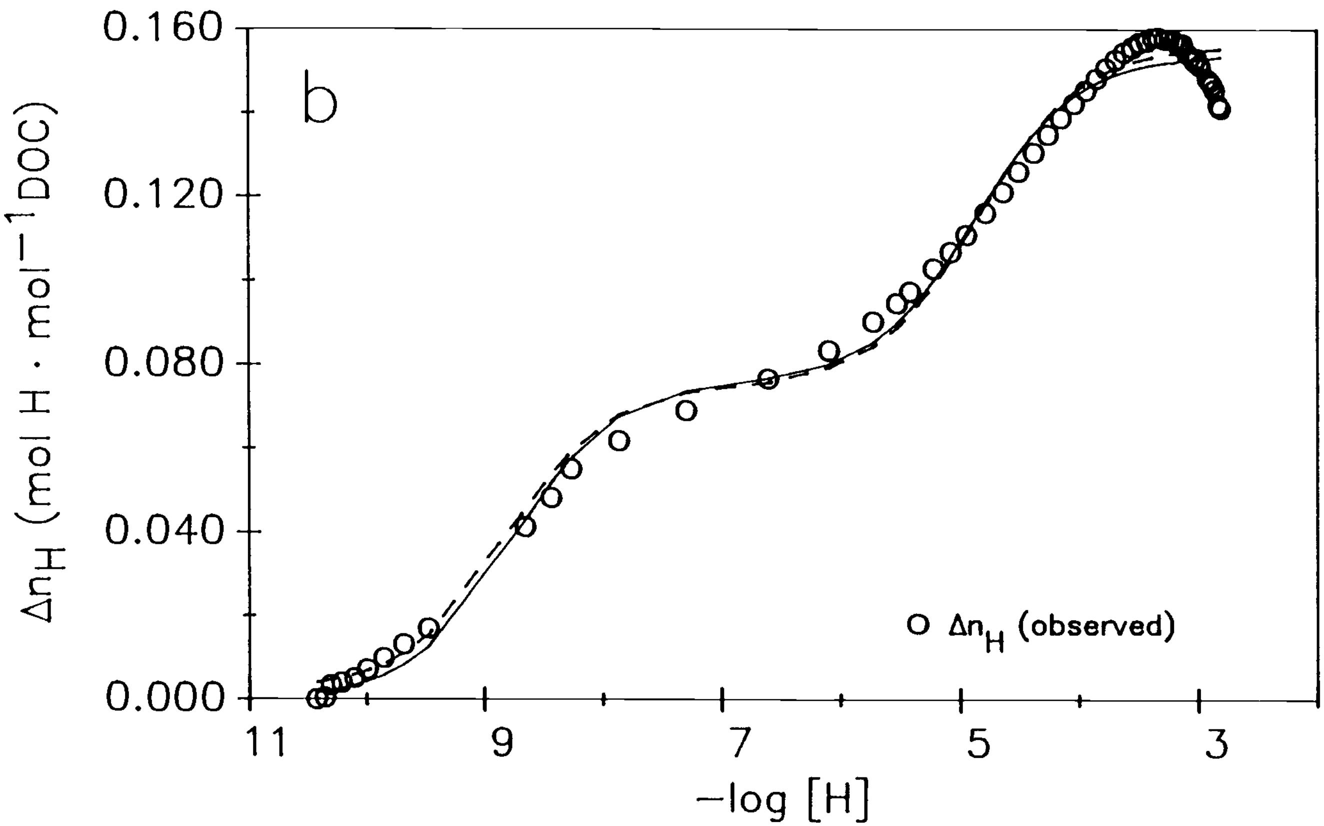

Fig. 8 (continued)

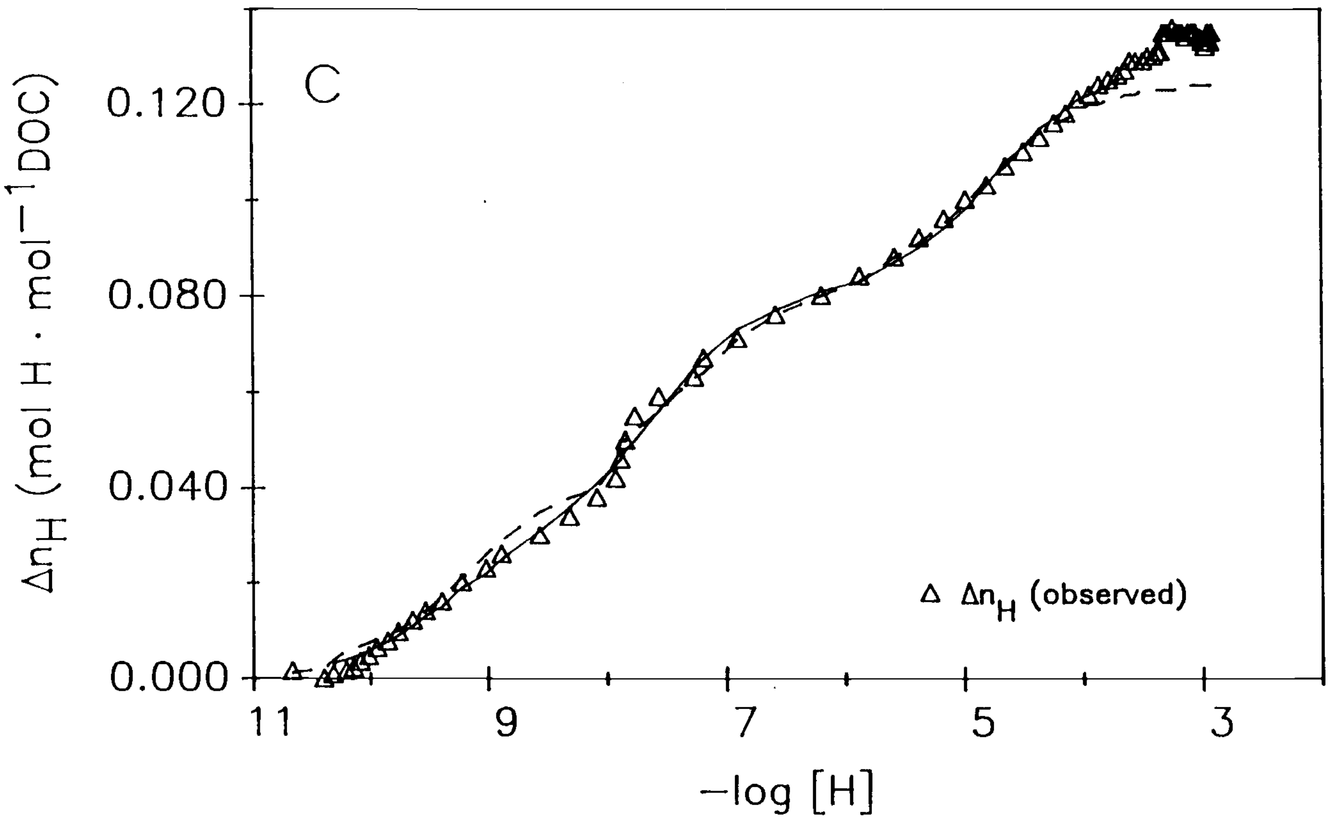

Fig. 8 (continued)

Table 8. Conditional protonation constants and total acidity of classes of FA-, WSE-, and HA- functional groups.[†]

		class *I*		class *II*		class *III*	
DOC	Procedure[‡]	$\log {}^{c}K_{I}$[§]	$\Delta n_{H_{I}}$[¶]	$\log {}^{c}K_{II}$	$\Delta n_{H_{II}}$	$\log {}^{c}K_{III}$	$\Delta n_{H_{III}}$
HA	*ls*	4.752 ± 0.060	0.043	7.624 ± 0.060	0.042	9.396 ± 0.067	0.041
	dg	4.833 ± 0.020		7.282 ± 0.042		9.153 ± 0.026	
FA	*ls*	4.871 ± 0.071	0.081	----	----	8.772 ± 0.101	0.073
	dg	4.836 ± 0.007		----		8.818 ± 0.065	
WSE	*ls*	5.524 ± 0.133	0.057	----	----	9.119 ± 0.037	0.137
	dg	5.086 ± 0.133		----		9.092 ± 0.035	

[†] At an ionic strength of 0.099 ± 0.001 and a temperature of 25.00 ± 0.01°C.

[‡] The designation *dg* stands for "determined graphically," *ls* refers to the least squares optimization.

[§] The uncertainties reported in the case of *ls* and *dg* are the standard error of the regression coefficients and the mean conditional protonation constants, repectively.

[¶] These values represent the total number of mols of protons complexed in the titration of a particular class of functional groups (as measured in the expermiments).

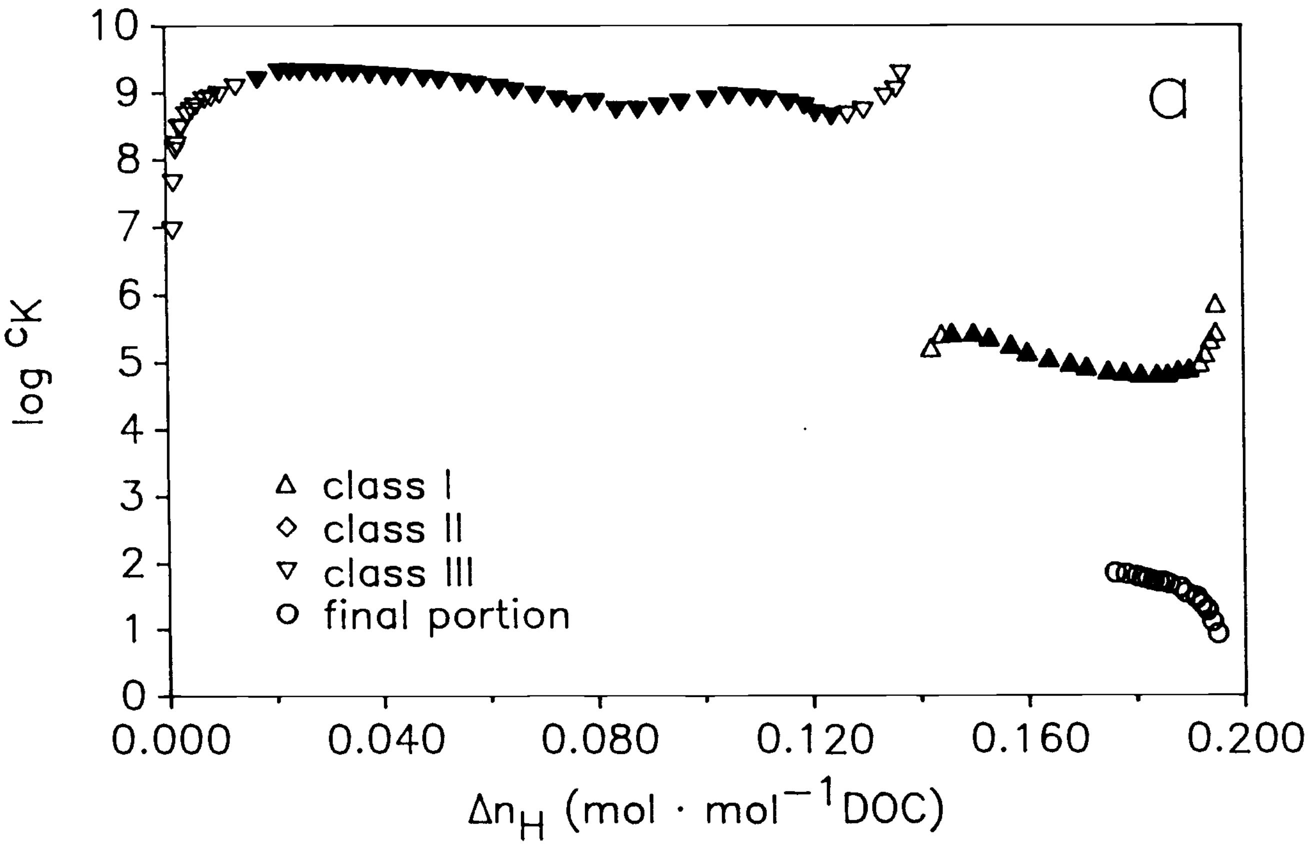

Fig. 9. The log ^cK value for every data point within the classes of functional groups (as determined graphically) of WSE (a), FA (b), and HA (c) plotted vs. the normalized formation function . The points characterized by open symbols were not considered in the calculation of the protonation constants of model *dg* in Table 3.

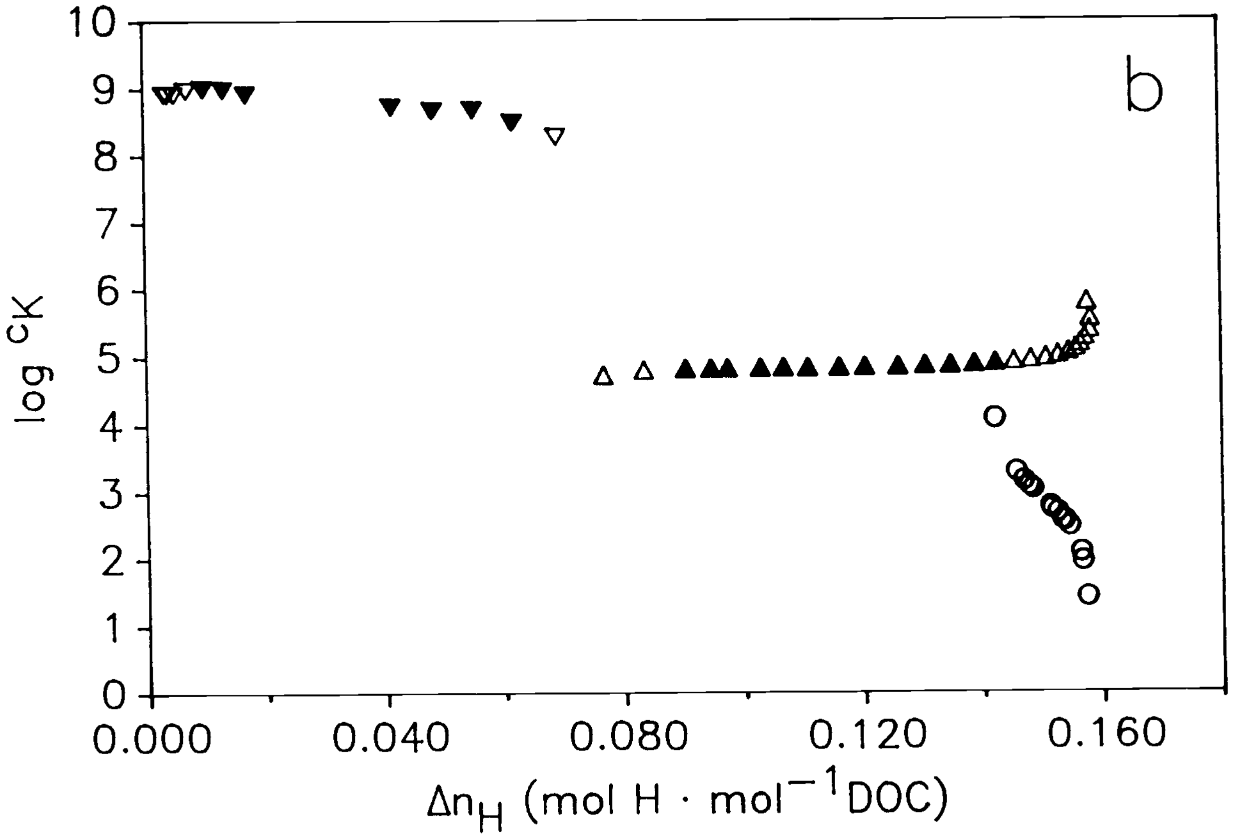

Fig. 9. (continued)

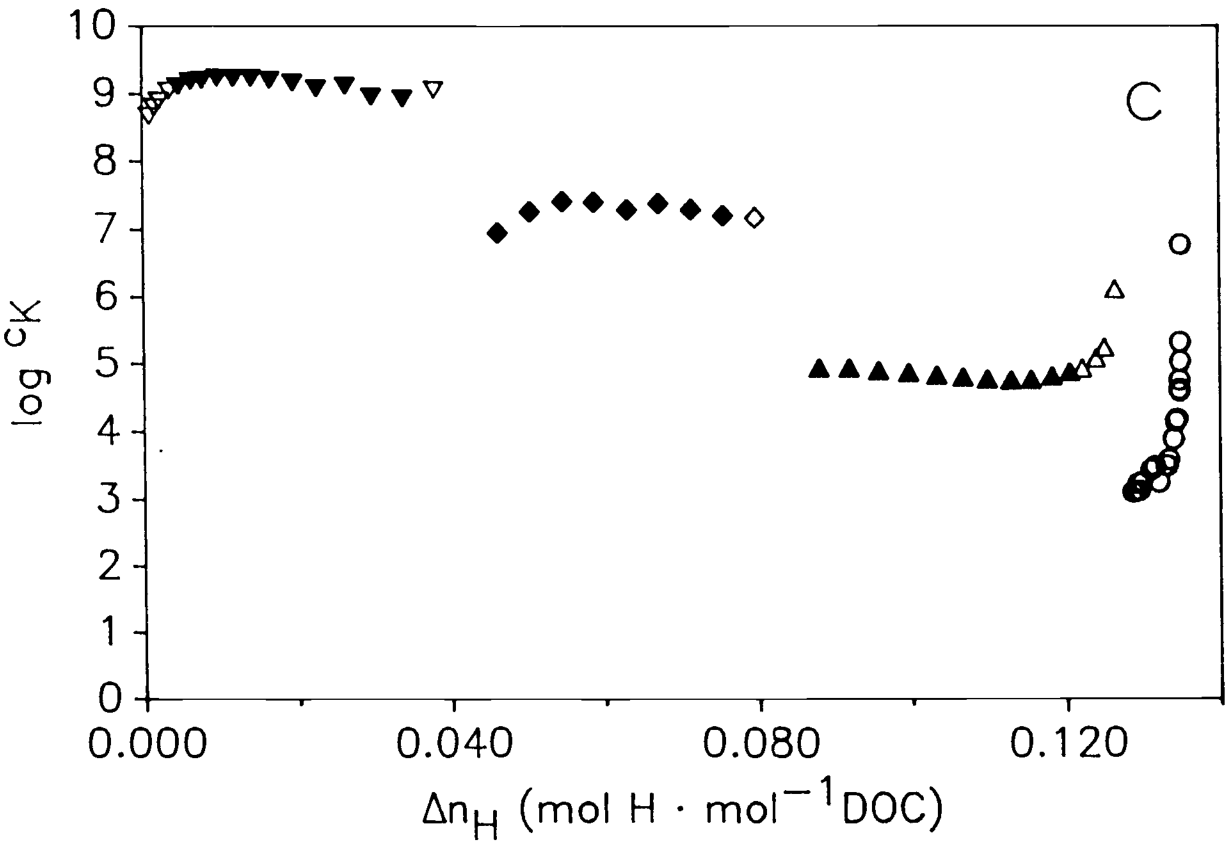

Fig. 9. (continued)

functional groups. Where acidities of functional groups overlap, the variation among the protonation constants starts to increase. Therefore, only data within the range $0.10 < \alpha_H < 0.90$ were used for the calculation of the protonation constants in Table 8 (this results in relatively small standard errors of the mean log ${}^{c}K$ values when compared with the results of the least-squares routine).

The WSE and FA acidic functional groups titrated after the maximum of Δn_H display a large and systematic deviation of their log ${}^{c}K$ values. With HA, a random variation among log ${}^{c}K$ values occurs somewhat earlier in the course of the titration (this becomes also apparent in Fig. 7). For WSE and FA, these findings are in agreement with the conformational changes proposed in the previous section, whereas the final portion of the formation curve of HA must be interpreted as experimental noise.

Non-linear least-squares minimization was performed on the entire range of data as well as on data sets where values from the final portions of the formation curves were not considered ("restricted data sets"). All six data sets were modeled assuming the polyelectrolyte mixture to consist of one to four hypothetical macromolecules. Log ${}^{c}K$ values for the models which gave the best fit are given in Table 8. The discussion in the previous section suggests the use of the complete data sets for the description of WSE and FA, whereas in the case of HA the restricted data set should be more meaningful. In the case of WSE, the use of the complete data set results in a better fit, according to the chemical interpretation. All models for FA including 2 or 3, and HA including 3 or 4 protonation constants, respectively, fit the experimental data very well ($r^2 > 0.99$). Therefore, the least-squared minimizations most consistent with the results obtained graphically were selected.

The agreement between the data obtained with the graphical procedure and FUNMIN5 is excellent for all three extracts.

Comparative Characteristics

The capacity of the different types of DOC to complex protons decreases in the order WSE > FA > HA. This reflects well the operational nature of every source of DOC. As a result of the commonly used extraction scheme, fulvic acids have usually a higher functional group content than humic acids. Since only water was used to extract the WSE, this material presumably contains a higher percentage of hydrophilic molecules or functional groups per mol organic carbon than materials obtained through more selective procedures, such as FA and HA.

FA and WSE exhibit two classes of functional groups. This is in agreement with findings for typical soil-derived fulvic acids (Gamble, 1970; Perdue et al., 1980; Sposito et al., 1982) and the fact that natural DOC usually bears a close resemblance to soil fulvic acids. Both dissociation constants determined for FA and WSE are within the range found by Sposito et al. (1982). The class *I* and class *III* functional groups are believed to be mainly carboxyl and phenolic OH groups, respectively. FA seems to possess a smaller amount of functional groups than WSE, but the acidity of these functional groups is higher in the case of FA.

In agreement with the findings of Borggaard (1974b), three classes of functional groups were outlined for HA. The acidity of the class *I* functional groups of HA and FA is very similar. Some, but not all of the class *II* functional groups are probably also carboxyls, and the class *III* functional groups are believed to comprise mainly hydroxyl groups.

The high acidity of the class *I* functional groups of HA and FA as compared with WSE may be the result of a high percentage of these COOH groups being ortho to phenolic OH on aromatic rings. Carboxyl groups in this position are more acidic than carboxyl groups on aliphatic molecules due to mesomeric stabilization of the anion. A possible explanation could be that the procedures used to obtain FA and HA are rather selective in the sense that these materials contain relatively more hydrophobic aromatic molecules. On the other hand, the relative lipophobicity of WSE results in a larger number of functional groups overall.

Despite the small degree of association between DOC and volatile nonionic HOC (with log K_{OW} values between 2 and 3) under realistic environmental conditions (Ochs and Baham, 1988), it is possible to distinguish between WSE and HA and FA. In agreement with the respective values of Δn_{Hmax}, HA and FA showed a higher affinity for toluene than WSE. This allows the conclusion that the relative number of acidic functional groups exerts an important influence over the hydrophobicity of DOC. Further, in the case of WSE an influence of pH on the DOC-HOC interaction has been observed. The magnitude of the association as expressed by the relative amount of free HOCs in solution reached its maximum at pH 6.5. This is somewhat surprising, since one would expect DOC to become more hydrophobic with increasing protonation of the organic polyanions, and may indicate that not only partitioning plays a role in DOC-HOC interactions.

CONCLUDING REMARKS

Continuous potentiometric titrations are a convenient technique for the investigation of the proton dissociation behavior of DOC. The use of the formation function for data analysis is advantageous because information about number and acidity of functional groups is obtained. In addition, this method presents evidence of conformational changes in a qualitative way. The conformation and aggregation of DOC molecules would be expected to be an important factor for the interaction with HOC and is influenced by the degree of protonation of DOC. The overall hydrophobicity of DOC is influenced by the acidic organic functional group content.

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CONCLUSIONS AND IMPLICATIONS

Under conditions realistic for natural environments, DOC has no significant overall effect on the total water solubility of benzene, toluene, and chlorobenzene. For a range of DOC concentrations between 1.3 and 36.5 $mmol \cdot L^{-1}$, regression analyses showed no statistically significant linear relation between DOC concentration and the extent of DOC-HOC interactions. At DOC concentrations ≥ 9.3 $mmol \cdot L^{-1}$, however, a slight positive effect could be observed.

According to the toluene-distribution coefficient between water and a humic acid reported by Garbarini and Lion (1985), a %*HDA*-value of about 8 % could have been expected at the higher DOC concentrations. In contrast, Haas and Kaplan (1985) observed a maximum DOC-toluene association (≈ 8 %) at DOC concentrations as low as 3.3 $mmol \cdot L^{-1}$. Using a K_{ow} of $10^{2.69}$ (Chiou et al., 1982) as distribution coefficient, %*HDA*-values of approximately 20 % should have been observed in this study. Also, assuming a simple partitioning model, one would have expected chlorobenzene to behave more hydrophobically than benzene or toluene. However, the relative affinity for DOC of the HOCs used varied with the type of DOC. With HA, both benzene and toluene behaved more hydrophobically than chlorobenzene.

This discussion suggests that it might not be appropriate to envision the interaction between DOC and HOCs as partitioning into independent liquid phases, especially since the organic DOC-phase is presumably very heterogeneous. Instead, the formation of complexes between DOC and HOC molecules should be considered in addition to partitioning.

The differences observed in the behavior of WSE, HA, and FA show the importance of distinguishing between different sources of DOC when trying to predict or model the environmental fate of organic pollutants. With respect to the problem of underground storage tank failure, a careful evaluation of the types of DOC found in the respective soils may be necessary. Moreover, it might be important to know into which soil horizons the pollutants were introduced.

The differences between WSE and humic and fulvic acid may be attributed to differences in the extraction methods used to obtain the materials. It appears that the procedures used with HA and FA selectively extract a suite of natural organic compounds which displays a higher hydrophobicity - and probably a higher aromaticity - than DOC actually present in natural environments.

It is also shown that the centrifugation and filtration methods used to prepare the DOC-solutions influence the affinity of DOC for HOCs. In cases where the "DOC" solutions used in laboratory experiments are not subjected to rigorous centrifugation and filtration procedures, effects ascribed to "DOC" may be due to suspended particles. For environmental modeling purposes, it is important to distinguish between these two phenomena, since a much higher mobility can be expected for the DOC-associated pollutants.

In the titration studies, the relatively higher hydrophobicity of HA and FA as compared to WSE was confirmed based on the relative number of functional groups. Formation functions calculated from titration data showed that WSE possesses approximately 30 % more acidic organic functional groups, when expressed on a molar carbon basis, than FA or HA. Since acidic functional groups contain most of the oxygen bound covalently in DOC, it is suggested that the elemental C/O ratio can be used as a good indicator of the relative hydrophobicity of DOC and other natural organic "sorbents".

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