

Characterization of carbonaceous resins for soil organic matter and labile carbon studies
by Mitchell Mitrey Johns

A thesis submitted in partial fulfillment of the requirements for the degree Of Doctor of Philosophy in Crop and Soil Science
Montana State University
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Abstract:
Carbonaceous resin capsules were characterized and evaluated for soil testing of various organic parameters. Six carbonaceous adsorbents developed specifically for organic contaminant adsorption were employed. Resin capsule types were characterized by adsorption of dissolved soil Mvic (FA) and humic (HA) acids in a non-mixing resin sink system where only diffusion controls adsorption. Testing evaluation was made by placing resin capsules in saturated soil pastes of thirty-one Montana and Pennsylvania soils. Soil labile C (LC) adsorbed by the capsule types was calibrated to organic C, N, P, and S. Labile C was further identified through nuclear magnetic resonance and infrared spectroscopy, and atomic absorption spectrophotometry of trace metals. Kinetic studies with both solutions and soils indicated an initial high adsorption rate followed by slower adsorption (days), similar to the behavior of other porous adsorbents. Intraparticle diffusion was adsorption rate-limiting. The constant partitioning isotherm model described adsorption, indicating linear adsorption ($r^2>.96$, $P<.01$) over all temperatures (13 °C to 50 °C), at pH 7.0, and within the concentration ranges of FA and HA. This indicated potential use of the resins in pHs and temperatures normally found in natural environments. Thermodynamic calculations for FA adsorption indicated an entropy driven adsorption process. Soil LC was composed of molecular weights less than 1000 daltons (64-94 % of LC) and all less than 10,000 daltons. Labile C was successfully calibrated to organic C, N, P, and S. Ambersorb XEN-564 resin resulted in the highest calibration with MT soils and a Carboxen-Carbotrap resin mixture was the highest in PA soils. These calibrations can be used to determine C, N, P, and S simultaneously. It is proposed that capsule adsorption of LC actually modeled the natural partition behavior of soil organic C. Labile C contained aliphatic and aromatic structures, as well as containing carbohydrates and amino groups. Labile C strongly resemble the FA fraction of soils. The resins were able to concentrate the metals Cu, Fe, Mn, and Zn (100 to 1000 fold) over that normally found in soil solutions, and at sufficient levels for analytical evaluation. This resin methodology showed excellent potential and versatility for soil testing.

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Bozeman, Montana

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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VITA

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ABSTRACT

Carbonaceous resin capsules were characterized and evaluated for soil testing of various organic parameters. Six carbonaceous adsorbents developed specifically for organic contaminant adsorption were employed. Resin capsule types were characterized by adsorption of dissolved soil fulvic (FA) and humic (HA) acids in a non-mixing resin sink system where only diffusion controls adsorption. Testing evaluation was made by placing resin capsules in saturated soil pastes of thirty-one Montana and Pennsylvania soils. Soil labile C (LC) adsorbed by the capsule types was calibrated to organic C, N, P, and S. Labile C was further identified through nuclear magnetic resonance and infrared spectroscopy, and atomic absorption spectrophotometry of trace metals. Kinetic studies with both solutions and soils indicated an initial high adsorption rate followed by slower adsorption (days), similar to the behavior of other porous adsorbents. Intraparticle diffusion was adsorption rate-limiting. The constant partitioning isotherm model described adsorption, indicating linear adsorption ($r^2 > .96$, $P < .01$) over all temperatures (13 °C to 50 °C), at pH 7.0, and within the concentration ranges of FA and HA. This indicated potential use of the resins in pHs and temperatures normally found in natural environments. Thermodynamic calculations for FA adsorption indicated an entropy driven adsorption process. Soil LC was composed of molecular weights less than 1000 daltons (64-94 % of LC) and all less than 10,000 daltons. Labile C was successfully calibrated to organic C, N, P, and S. Ambersorb XEN-564 resin resulted in the highest calibration with MT soils and a Carboxen-Carbotrap resin mixture was the highest in PA soils. These calibrations can be used to determine C, N, P, and S simultaneously. It is proposed that capsule adsorption of LC actually modeled the natural partition behavior of soil organic C. Labile C contained aliphatic and aromatic structures, as well as containing carbohydrates and amino groups. Labile C strongly resemble the FA fraction of soils. The resins were able to concentrate the metals Cu, Fe, Mn, and Zn (100 to 1000 fold) over that normally found in soil solutions, and at sufficient levels for analytical evaluation. This resin methodology showed excellent potential and versatility for soil testing.

CHAPTER 1

INTRODUCTION

Testing water and soil for agricultural and environmental purposes is becoming increasingly important. Conventional methods for soil analysis involve sampling, drying, grinding, sieving, and other physical or chemical procedures unique to the elements or compounds being tested. In many instances, these procedures are costly and time-consuming which can place limits on sample numbers. Interpretations and reliability of the testing results may be inaccurate due to physicochemical changes in samples brought from the field, or because of poor correlation between the testing method and what is actually occurring in the natural environment.

An alternative approach to soil testing is based on use of a sphere of mixed-bed ion exchange resin to accumulate dissolved constituents in response to diffusive movement through the soil, simulating nutrient movement to plant roots (Skogley et al., 1990; Yang et al., 1991). This approach was expanded in the current studies to determine the potential for using carbonaceous resins for adsorption, measurement, and characterization of soil organic matter constituents which may be important in soil fertility, chemistry, and pollution research. It was also of interest to investigate the agronomic soil testing potential for soil organic matter using carbonaceous resins.

Carbonaceous resins are polymer C adsorbents which were developed as an alternative to granular activated C (Neely and Isacoff, 1982). The resins have a polynuclear aromatic structure similar to graphite with very few ions or functional groups, contain a large number of C-C bonds, and are porous with high internal surface area. These adsorbents are classified as type I adsorbents (Ościk and Cooper, 1982), which interact non-specifically with organic compounds possessing both polar and non-polar surfaces. They have been recently used for contaminant sampling of BXTs, straight-chain alkanes, chloroalkanes, and naphthalenes in air, water, and soil (Betz et al., 1989; Hazard et al., 1991).

Carbonaceous resins, packaged as porous spherical capsules, offer numerous advantages for soil testing. The capsules can be placed directly in the soil where they can adsorb surrounding humics under indigenous soil conditions. The process can be likened to present adsorption chromatography fractionation techniques (Leenheer, 1985) for humic substances. More importantly, results from this approach more obviously reflect the dynamic soil chemical processes occurring *in situ*. Since the capsules act as a non-specific organic sink, they retain a potential for detection, measurement, and identification of numerous elements or compounds simultaneously. The capsules provide a solid site for partitioning due to the non-polar structural character of the resins, and may be useful in predicting the partitioning behavior of soil organic matter (Rutherford et al., 1992) in relation to soil pollutants and availability of plant nutrients. In addition, the methodology may apply to measurement of available C (Sikora and McCoy, 1990).

The research objectives were 1) characterization of six selected developmental and commercial carbonaceous resins through their reaction with soil fulvic (FA) and humic (HA) acids; and 2) application of resin capsule methodology for soil testing and prediction. Fulvic acid and HA are appropriate materials for characterizing resin behavior in natural systems. Soil testing and prediction potentials were evaluated through measuring and correlating soil labile C (LC), adsorbed by these resins, to soil organic C, N, P, and S. Labile C is defined in Chapter 2, Page 8. A group of MT and PA soils were used. The studies included identification and characterization of the LC fraction through nuclear magnetic resonance spectroscopy, infrared spectroscopy, and atomic absorption spectrophotometry.

CHAPTER 2

LITERATURE REVIEW

Carbonaceous resins have adsorption properties similar to activated C (Chrostowski et al., 1983) and are found to be cleaner than the polymeric Amberlite XAD series resins (Hunt and Pangaro, 1982). The manufacturing process for carbonaceous resins involves pyrolysis of synthetic polymers or petroleum pitches under pressure and non-oxidizing atmosphere (Neely and Isacoff, 1982). This results in a resin possessing the C skeletal framework of the precursor. The physical characteristics of a resin (surface area, micropore percentage, etc.) are a function of the precursor and the employed manufacturing parameters. The carbonaceous Ambersorb XEN series resins are described as having excellent physical integrity and extremely reproducible properties[1]. Recent applications of these resins were for the adsorption of hydrophobic pollutants (Betz et al., 1989; Hazard et al., 1991).

For characterizing the adsorption behavior of the resins, FA and HA were used since they are the major C source of dissolved, natural occurring substances in aquatic and soil environments (Aiken et al., 1985). Both FA and HA can be considered as a heterogenous mixture of compounds for which no structural formula will suffice. These acids must be regarded, therefore, as being made up of a series of different size

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[1] Rohm and Haas Comp., Technical Notes, 1990.

molecules, few having precisely the same structural configuration or array of reaction groups (Stevenson, 1982). They possess nonpolar and polar groups. From nuclear magnetic resonance spectroscopy (Hayes, 1985), both acids were shown to be composed of aromatic and aliphatic carbon structures containing carbonyl, carboxyl, and phenolic groups. Also, included are C-O linkages that represent alcohol, ether, or ester groups. Carbohydrates and peptides could be associated with the acids. Fulvic acids are lower in molecular weight than HA and contain more acidic functional groups, particularly COOH (Stevenson, 1985). Current information indicates that the acids possess more aliphatic structures than aromatic (Malcolm, 1990), with FA having greater aliphatic structures than HA.

Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy are widely used in the identification of humic structures. An extensive review of IR research is given by Stevenson (1982). Piccolo and Stevenson (1982) used IR to study complexation of Cu, Pb, and Ca in soil humic substances. Lobartini and Tan (1988) applied ^{13}C-NMR to identify aliphatic, polysaccharide, aromatic, and carboxyl groups in HA from soils from several countries. Schnitzer et al. (1988) used ^{13}C-NMR to identify naturally occurring long-chain aliphatics associated with soil clay. Application of ^{1}H-NMR has been extensively employed in the structural identification of FA and HA (Wilson, 1981; Wilson et al., 1983).

The conditions of the medium will strongly affect the adsorption of FA and HA. In soils, the macromolecular structure of humic substances is controlled by the solute concentration, pH of the system, and the ionic strength of the medium (Ghosh and

Schnitzer, 1980). The macromolecular structure governs nearly all the properties and reactions of these materials, including the affinity of FA and HA for adsorption onto a resin surface. Humic substances are spherocolloids and behave like uncharged polymers when solute concentrations are high or the pH of the medium is low, or when appreciable amounts of neutral electrolytes are present. These conditions allow for the maximum hydrophobic, non-polar character of these substances to be expressed, and are most favorable for the greatest adsorption to a hydrophobic resin. Fulvic and HA are flexible linear colloids at low solute concentrations, provided H ion and neutral salt concentrations are not too high. These conditions, found normally in most soils, allow for the expression of the polar character of these substances, resulting in a relatively high degree of solubility. In describing the effect of pH on hydrophobic adsorption to Amberlite XAD-8 resin, Thurman (1985) states that for organic acids to adsorb completely, the pH of the solution should be 2 pH units below the pKa. For efficient desorption, the pH of the solution should be 2 pH units greater than the pKa.

Adsorption onto a hydrophobic resin from solution occurs when the Gibbs free energy of adsorption (ΔG) is negative. The free energy of an adsorption reaction can be negative because of the enthalpy change (ΔH) or because of the entropy change (ΔS) or due to a combination of both. Hydrophobic adsorption tends to be an entropy driven process with enthalpy being of less influence (Voice and Weber Jr, 1983; Hassett and Banwart, 1989). The large favorable entropy change found in hydrophobic adsorption appears to be due to an entropy gain for water upon removal of a nonpolar solute from aqueous solution (Eisenberg and Crothers, 1979). Small exothermic and even

endothermic enthalpies have been described for the adsorption of nonpolar solutes by soil organic matter (Chiou et al., 1989). Jardine et al. (1989) concluded that the predominant mechanism of dissolved organic C (DOC) retention by a soil is physical adsorption driven by favorable entropy changes.

If soil organic matter behavior includes a specific partition coefficient, resin adsorption could probably be developed as a soil test for organic constituents. A general adsorption partition coefficient (K) for a nonpolar organic compound can be defined as $K = C_s/C_w$ where C_s is the concentration in the soil and C_w is the concentration in water. Nodvin et al. (1986) reported a partition coefficient between the soil solid and solution phases for DOC. Using a modified adsorption isotherm model, a linear relationship was developed, the slope of which described a simple partition for DOC between soil and solution. Soil organic matter has a high affinity for adsorption of nonpolar organic pollutants in soils from soil solution, with a partition coefficient between the solid and solution phases that remains essentially constant up to high relative concentrations (Chiou, 1989). The relationship is defined by: K_{OM} = K / soil organic matter fraction, where K_{OM} is the adsorption partition coefficient for a specific nonpolar organic substance adjusted to organic matter content. Soil organic matter partitioning has been described as analogous to separation of nonionic species with synthetic resins (Chiou et al., 1983). Others (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981) indicated that the partition coefficient should be normalized to organic C content, K_{OC} = K / soil organic C fraction. Partition coefficients are reported for soil pollutants, and are considered to be nearly constant among soils (Karickhoff, 1981; Chiou et al., 1983).

Use of a K_{oc} value and knowledge of the soil organic C content allows the calculation of a K that predicts the capacity of that soil for adsorption of a particular organic compound (Karickhoff, 1985). Conversely, it is hypothesized that a simple partition coefficient might exist for soil C where soil organic C content can be predicted from solution phase DOC.

Labile C (LC) is defined as DOC, which in soil interstitial waters has been reported to range from 2 to 50 mg kg^{-1} (Thurman, 1985). Labile C is associated with available C, or soil organic C that heterotrophic microorganisms can readily utilize as an energy and C source (Davidson et al., 1987; Rolston and Liss, 1989). Labile C was assumed by Smith (1979) to be composed of free carbohydrates derived from decaying plant material. It may include dissolved FA (Linehan, 1977), making LC closely related to the FA fraction (Malcolm, 1990). It is likely that LC contains metal-organic complexes (Stevenson, 1982; Stevenson and Fitch, 1986). Schoenau and Bettany (1987) reported that the FA fraction contained levels of organic N, P, and S important in soil fertility. Leaching of FA provided a valid explanation for the observed narrowing of soil organic matter C/N, C/P, and C/S ratios with increasing soil depth. Staley et al. (1988) observed statistically significant correlations between soluble organic C and organic N, P, and S for a soil surface layer. Schnitzer et al. (1988) indicated that dissolved FA could mobilize and transport naturally occurring water-insoluble aliphatics throughout the soil profile. Similarly, dissolved FA can act as a partition medium for the movement of organic soil pollutants (Chiou et al., 1986).

CHAPTER 3

MATERIALS AND METHODS

Procedures Employed for Chapter 4: Resin Characterization Experiments

The resins employed are all specific for adsorbing hydrophobic organic compounds (Table 1). Carboxen-569 is reported to be specific for 2-5 C molecules, Carbotrap-B for 6-12 C molecules, and Carbotrap-C for 12-20 C compounds (Supelco, Inc., Bellefonte, PA). Because no information was available on their performance in soils, a mixture of equal proportions (by volume) of all three resin types was used. The carbonaceous adsorbents Ambersorb XEN-563, XEN-564, and XEN-572 (Rohm and Haas Co., Independence Mall West, Philadelphia, PA) and Amberlite XAD-8 (Rohm and Haas Co.) were used individually. Polymeric Amberlite XAD-8 resin was included as a standard for comparison because this resin has been extensively studied and recommended for isolation and extraction of aquatic humic substances (Thurman and Malcolm, 1981). The hydrophobicity of the XEN resins decreases in the order XEN-563 > XEN-564 > XEN-572 (Rohm and Haas Co.).

Carbonaceous Resin Capsules.

Spherical resin capsules of 5cm^3 volumes were constructed using polyester sieves as described by Yang et al. (1991). Bulk resins were degassed in water under vacuum,

Table 1. Physical and Chemical Properities of Hydrophobic Carbonaceous and XAD-8 Resins.

RESIN	MANUFACTURING PRECURSOR	SURFACE AREA (m^2/g)	POROSITY (cm^3/g)	MESH SIZE
CARBOXEN 569†	coconut hulls	485	N/A¶	20-45
CARBOTRAP B†	coconut hulls	100	N/A¶	20-40
CARBOTRAP C†	coconut hulls	10	N/A¶	20-40
XEN 563‡	S/DVB§	550	0.60	20-45
XEN 564‡	S/DVB§	550	0.51	20-45
XEN 572‡	S/DVB§	1100	0.84	20-45
XAD 8‡	acrylic ester	160	0.48	20-60

†Supelco, Inc., Bellefonte, Pa.

‡Rohm and Haas Co., Philadelphia, Pa.

§Styrene/divinylbenze macroeticular resin.

¶Information not available.

prior to construction of resin capsules. Equal proportions (by volume) of the carbonaceous resins, Carboxen-569, Carbotrap-B, and Carbotrap-C for a total wet volume of 5 cm^3 were packed into polyester (150 mesh; 30 μm thread, 140 μm openings) cloth and tied with polyester thread to form a tight sphere. The dry weight of the resin mixture was 2.11 grams per 5cm^3 volume. All resin capsules were stored under double distilled water until used. Bleeding (decomposition) of the resins was monitored by organic C analysis of water aliquots. The organic C content never exceeded 0.3 mg L^{-1} C during the study period. Similarly, resin capsules were made using each of the XEN adsorbents and XAD-8. Carbonaceous resin beds of 5 cm^3 volume (Table 1) would possess approximate surface areas of 424 m^2 for Carboxen-Carbotrap mixture (MX), 1177 m^2 for XEN-563 or XEN-564, and 2354 m^2 for XEN-572.

Soil Fulvic and Humic Acid Extraction

FA and HA were extracted with 0.5 N Na_2CO_3 from a sample of A_p horizon from Enbar loam (Cumulic Haploborolls). The soil has a pH 6.3 and an organic C content of 29 g kg^{-1}. Decanted liquid from a Na_2CO_3 - soil mixture after 24 hours was acidified to a pH below 2.0 with HCl. After an additional 24 hours, the FA was decanted from the precipitated HA. Excess salt was removed from FA with repeated dialysis. Excess salt was removed from the HA through repeated distilled water (adjusted at pH 2.0 with HCl) rinsing and centrifugation. Both FA and HA were then freeze-dried. The C contents, determined by wet combustion (Synder and Trofymow, 1984), were 420 g kg^{-1} for FA and 520 g kg^{-1} for HA. Total acidity was determined by $Ba(OH)_2$ adsorption (Stevenson, 1982) and estimated at 3.8 cmol kg^{-1} for FA and 5.7 cmol kg^{-1} for HA. The

hydrophobic (48 %) and hydrophilic (52 %) acid contents of FA were determined using a XAD-8 resin column separation (Leenheer and Huffmann, 1979). The molecular weight distribution of the FA and HA fractions was determined by ultrafiltration (Wershaw and Aiken, 1985), using Amicon (Beverly, MA.) disc membrane filters. Approximately 59 % of C in the FA fraction was within 3,000 - 100,000 daltons and 67 % of C in HA was within 10,000 - 300,000 daltons (Table 2).

Adsorption Studies

Adsorption-time studies were carried out using capsules of Carboxen-Carbotrap mixture (MX) at a pH of 7.2, 24 °C, and an ionic strength (I) of 0.01M ($NaNO_3$) using two concentrations of FA (43 and 85 mg L^{-1} C) and HA (46 and 90 mg L^{-1} C) each, replicated twice. Capsules were completely immersed in 50 mL of FA or HA solutions in capped 125 ml glass containers at time zero. No shaking was employed. At specific times, 1 ml aliquots of the solutions were removed and analyzed for organic C using the Dohrmann DC-80 Total Organic C Analyzer (Santa Clara, Ca). About ten 1 ml aliquots were taken over the study time, ranging from 0 to 264 or 336 hours. Total mass of C adsorbed per unit time was calculated by mass balance, taking into account decreasing equilibrating volumes. Similarly, adsorption-time studies were carried out using the XEN adsorbents at a pH of 7.0, 22 °C, and I = 0.01M. Two concentrations of FA (60 and 120 mg L^{-1} C) and one concentration of HA (55 mg L^{-1} C) were studied, without replication.

Film diffusion was evaluated using a shell progressive film diffusion equation (Hodges and Johnson, 1987). A plot of the relative fraction adsorbed (C_s/C_o) versus time

Table 2. Molecular Weight Determinations by Ultrafiltration† of Soil Fulvic and Humic Acids.

DISC MEMBRANE‡	MOLECULAR WEIGHT CUT-OFF (DALTONS)	% C RETAINED OF INITIAL CONCENTRATION	
		FULVIC	HUMIC
XM 300	300,000	----	26
YM 100	100,000	32	55
PM 30	30,000	85	93
PM 10	10,000	88	93
YM 3	3,000	91	----

†Initial concentrations were 109ppm C for fulvic (pH 7.0) and 107ppm C for humic acid (pH 7.2). Ionic strength 0.01M. Filtration pressure of 55-173 kPa, with XM 300 and YM 100 membranes used at 55 kPa.

‡Amicon Company, Beverly, Ma.

should be linear if adsorption is controlled by film diffusion, where C_s is total C (μg) adsorbed on the resin with time and C_o is total C (μg) in solution at time 0.

Intraparticle diffusion was evaluated using the parabolic diffusion equation described by Sparks (1989), where a plot of C_s/C_o versus time$^{1/2}$ should provide a linear relationship (Jardine and Sparks, 1984; Aiken et al., 1979).

Adsorption isotherms were determined for the MX capsules at four temperatures, 13, 23, 36, and 50 °C. At each temperature except 23 °C, capsule-FA equilibrations were conducted for 96 hours at four concentrations ranging from 14-102 mg L^{-1} C, each at pH 7.0 and I = 0.01M. At 23 °C, five concentrations of FA and HA were used ranging from 9-126 mg L^{-1} C and 11-138 mg L^{-1} C , respectively. Adsorption isotherms

were obtained for the XAD-8 resin at 23 °C and at a pH of 6.3. Two replicates were used for all treatments. Kinetic studies indicated that at 96 hours the adsorption rate, $d(C_s/C_o)/d(time)$, decreased to about 10 percent of the initial rate (<96 hrs). Numerous adsorption studies in soils, sediments, organic matter, and activated-carbon (Karickhoff, 1984; Miller and Weber, 1984; Leenheer and Ahlrichs, 1971; and Kaastrip and Halmo, 1989) are characterized by an initial adsorption rate followed by slower adsorption which may proceed indefinitely. This has required an assigned equilibrium time (Karickhoff, 1985).

Adsorbed C was removed by vacuum extraction (Centurion model 24) using 50 ml 2N NaOH with an extraction time of 1 hour. Greater detail of this extraction process is described on Page 20. Adsorbed C was determined on a Dohrmann DC-80 Total Organic C Analyzer. Resin capsules were regenerated by two successive vacuum extractions using 50 ml 2N NaOH each extraction, and then a final 10 ml 1N HCl extraction. Capsules were then rinsed with double-distilled water until free of Cl.

Procedures Employed for Chapter 5: Resin Experiments for Soil Testing

The carbonaceous resins employed were described on Page 9. Filtersorb-400 (Calgon Carbon Corp., Pittsburg, PA), an activated C of 12-40 mesh, was also included (Montana soils only) in these experiments.

Construction of spherical resin capsules of 5 cm^3 volumes was described on Page 9. Filtersorb-400 resin (F-400) capsules possessed an approximate surface area of 2160 m^2.

Adsorption Studies

The surface 30 cm of 19 Montana agricultural soils (Table 3) and 12 Pennsylvania soils (Table 4) were used. These soils provided a range of soil organic C contents from 0.6 to 15.7 g kg^{-1} and represented a broad range of other soil characteristics as well. Soils were air-dried, sieved (2 mm), and stored at room temperature prior to use.

For soil labile C (LC) adsorption, 50 g samples of soils were made into saturated pastes in 60 mL sample cups. Resin capsules were inserted into the center of the saturated pastes (Figure 1), replicated three times. Total contact between soil pastes and resin capsules was ensured through manipulating the paste. Sample cups were sealed with a screw-on lid and maintained at a temperature of 22°C for 96 hours for all resin types, except for the MX resin which was for 72 hours. In a separate experiment, several soils with MX capsules were maintained at 45 °C. After 72 or 96 hours, resin capsules were removed and washed with double-distilled, deionized water, taking precautions to remove all soil particles. Each resin capsule was then placed into a 60 mL syringe (middle syringe) of a vacuum extractor (Model no. 24-01 Centurion International Inc., Lincoln, NE). A glass microfiber filter (Whatman GF/A) was placed in the outlet of the middle syringe prior to resin capsule insertion to trap resin or cloth particles. Adsorbed soil humics were removed by extraction with 50.0 mL of 2 N NaOH placed in the upper syringe and drop-wise extraction done at the rate of 0.6 mL min^{-1}. The filtrate solution was collected in the lower syringe. Total organic C (TOC) was determined using the Dohrmann DC-80 Total Organic C Analyzer (Santa Clara, CA).

Table 3. Montana Soils

Soil Series	Subgroup	Texture	pH	% OC[1]
Edgar	Ustollic Camborthids	l	6.8	0.7
Sappington-Amesha	Aridic Argiborolls	l	7.9	1.0
Amsterdam	Typic Haploborolls	sicl	8.2	1.1
Kevin	Aridic Argiborolls	cl	7.0	1.5
Beaverton	Typic Argiborolls	cl	5.7	2.8
Round Butte	Borollic Natargids	sil	6.2	1.7
Creston	Udic Haploborolls	l	5.7	2.4
Fort Collins	Ustollic Haplargids	l	6.2	0.6
Manhattan	Typic Calciborolls	sil	8.2	1.2
Cherry	Typic Ustochrepts	cl	7.4	1.5
Bear Paw	Typic Argiborolls	c	8.0	1.7
Flathead	Pachic Udic Haploborolls	sl	7.2	2.1
Rothiemay	Aridic Calciborolls	cl	7.6	1.8
Tanna	Aridic Argiborolls	l	8.3	0.9
Stryker	Typic Eutroboralfs	sicl	7.9	1.7
Chinook	Aridic Haploborolls	sl	8.3	1.0
Enbar	Cumulic Haploborolls	l	6.3	2.9
Farland variant[2]	Typic Argiborolls	sil	6.8	2.8
Amsterdam variant[2]	Typic Haploborolls	sil	6.8	2.7

[1]Percent organic C (OC) determined by wet combustion.

[2]Variant due to high OC; intergrade to Udic moisture regime.

Table 4. Pennsylvania Soils (Blair and Centre Counties).

Soil Series	Subgroup	Texture	pH	% OC[1]
Linden	Fluventic Cystrochrepts	l	6.1	1.7
Morrison	Ultic Hapludalfs	sl	6.0	0.7
Brinkerton	Typic Fragiaqualfs	sil	6.3	1.9
Meckesville	Typic Fragiudults	sil	5.4	2.4
Hublersburg	Typic Hapludults	sil	5.5	2.0
Albrights	Aquic Fragiudalfs	sil	6.0	2.8
Berks-Weikert	Typic Dystrochrepts	sil	5.5	3.7
Berks	Typic Dystrochrepts	sil	5.5	15.7
Hazleton	Typic Dystrochrepts	sl	6.0	2.0
Andover	Typic Fragiaqualfs	l	6.9	3.0
Buchanan	Aquic Fragiudults	sil	5.6	6.2
Murril	Typic Hapludults	cl	6.9	1.4

[1]Percent organic C (OC) determined by wet combustion.

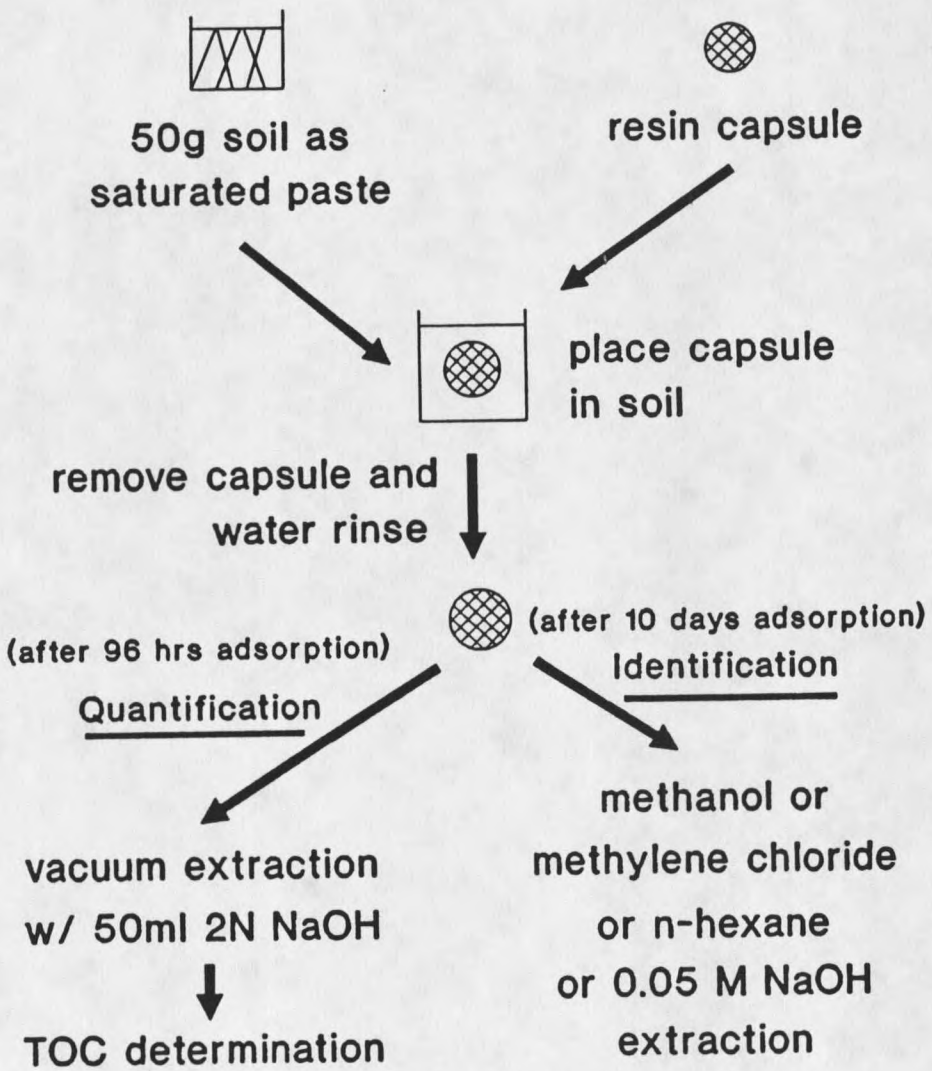


Figure 1. Resin Adsorption and Extraction in Soils.

Extracted soil humic concentration (μg C) was corrected for background resin C. All resin types exhibited low blank C capsule concentrations (< 6 μg C/ mL) with coefficients of variation at < 10 % for MX, XEN-572, or F-400, and < 5 % for XEN-563 or XEN-564 among resin blank replicates.

Due to limited supply, MX capsules were regenerated as described on Page 14. After regeneration, blank C capsule concentration was evaluated and adjusted when necessary. All other resin types were used only once. For identification of LC, resin capsules were placed in soil saturated pastes (Figure 1) as described above for humic TOC, except resin-soil contact was for 10 days. Only the XEN-564 resin capsules were used with this procedure since this resin type showed the best potential for prediction of soil organic C, N, P, and S (see Chapter 5). After capsule removal from soil paste and water rinsing, capsule polyester covers were removed and the loose resin allowed to air-dry. Resins were then placed in 15 mL of either reagent-grade methanol, methylene chloride, n-hexane, or 0.05 M NaOH for 5 days including 24 hours shaking. The MT soils Farland and an Amsterdam variant (Table 3) were used, with 3 replicates per soil for each organic solvent and 5 replications per soil for 0.05 M NaOH. To insure identifiable quantities, extracts of each solvent from both soils were combined to give one composite sample per solvent. All extracts were filtered (Whatman GF/A glass filter). All organic extracts were vacuum dried to solid residue at room temperature, except for methanol at an elevated temperature ($\approx$ 50°C). The 0.05 M NaOH extracts were freeze-dried.

Alternatively, left-over aliquots of 2 N NaOH (initial concentration) solutions

from the humic TOC study were passed over a large quantity of Dowex 50W-X8 H-resin (Dow Chemical Comp.) and repeated until eluent pH was approximately 8. Prior to use, the H-resin was soxhlet extracted in acetone to minimize contamination, H^+ re-saturated (HCl), and rinsed with de-ionized water until no Cl was detected. Treated aliquots were then freeze-dried. To ensure sufficient humic quantities, composite samples were made of each of the MT (Table 3) and PA (Table 4) soils. However, aliquots from the use of the MX, XEN-563, XEN-564, and XEN-572 resin capsules were kept separate for identification studies. All the freeze-dried samples were measured for Cu, Fe, Mn, and Zn by atomic adsorption spectrophotometry (Perkin-Elmer model 560) by redissolving in 6 mL of a 1:1 mixture of 0.05 M NaOH and 0.05 M $Na_4P_2O_7$.

An adsorption-time study using XEN-564 resin and Enbar soil (Table 3) was undertaken for a period of 220 hours and at 12°C. Duplicate capsules were removed from soil at specific times, vacuum extracted using 2 N NaOH, and extract TOC measured. Intraparticle diffusion was evaluated using the parabolic diffusion equation described by Sparks (1989). A plot of C_t/C_{220} versus time$^{1/2}$, where C_t is total C (μg) adsorbed on the resin with time and C_{220} is the total C (μg) adsorbed at 220 hours, should provide a linear relationship (Jardine and Sparks, 1984; Aiken et al., 1979), if the rate of TOC accumulation by the resin capsule is limited by intraparticle diffusion.

The molecular weight distribution of LC extracted by XEN-564 capsules was determined by ultrafiltration (Wershaw and Aiken, 1985) using Amicon (Beverly, MA) disc membrane filters. An identical 0.05 M NaOH extraction was employed as described above for identification purposes, except the extracts were filtered through a 0.45 μm

Gelman Supor-450 membrane filter. Sufficient LC for each of the MT soils Farland and Enbar (Table 3) and PA soil Andover (Table 4) were collected by 3 replications per soil.

Linear regression and correlation matrices were calculated using MSUSTAT[1] statistical software, version 4.12, for soil labile C (dependent variable) with soil parameters. The soil parameters were Walkley-Black C (WB) (Sims and Haby, 1971), wet combustion C (WC) (Snyder and Trofymow, 1984), loss-on-ignition organic matter (LOM) (Davies, 1974), total Kjeldahl N (TKN) (Bremner and Mulvaney, 1982) using an Alpkem (Wilsonville, OR) colorimetric autoanalyzer, organic P (OP) (ignition method) (Olson and Summers, 1982), and organic S (OS) (Bardsley and Lancaster, 1965) except S was determined by inductively coupled plasma emission spectrometry (Perkin-Elmer Model 5500).

Fourier-transformed Infrared Spectroscopy

Fourier-transformed infrared spectra (FTIR) were obtained at a wavenumber range of 4000 - 450 cm^{-1} on a Perkin-Elmer model 1800 FT-IR spectrometer interfaced to the model 1800 computer. A single beam spectrum was calculated from 100 averaged scans, with each scan having an interval of 2 cm^{-1} and a nominal resolution of 4 cm^{-1}. LC extracts, obtained by vacuum- or freeze-drying, were finely ground. The samples were prepared for the analysis by mixing 100 mg of KBr with about 1.5mg of the material and then compressing the mixture to pellets.

[1] MSUSTAT was developed by Dr. Richard E. Lund, Professor of Statistics, Montana State University.

Fourier-transformed Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR were recorded at 300.13 MHz on a Bruker AC300 spectrometer. Integratable ^{1}H spectra were typically run at 6000 Hz spectral width, 64 scans, 16K data points, and with 20-30 sec between 5 μs pulses (60-70° tilt). ^{13}C-NMR spectra were run on a Bruker AC300 spectrometer operating at 74.46 MHz. The ^{13}C spectra were at 20,000 Hz spectral width, 8000 scans, 32K data points, and with 3 sec between 4 μs pulses (45° tilt). Solid residues after extraction from XEN-564 in MT soils were redissolved as follows. A 0.05 M NaOH extraction was dissolved in D_2O and referenced externally to dioxane at ^{1}H = 3.7 ppm. A methylene chloride extraction was dissolved in $CDCl_3$ and referenced to $CDCl_3$ at ^{1}H = 7.24 ppm. A methanol extraction was dissolved in CD_3OD and referenced to CD_3OD at ^{1}H = 3.5 ppm and ^{13}C = 49.3 ppm.

CHAPTER 4

CHARACTERIZATION OF CARBONCACEOUS ADSORBENTS BY SOIL FULVIC AND HUMIC ACID ADSORPTION

Theoretical Considerations

Continuous flow or completely mixed batch reactor systems are customarily used to study adsorption of organics. In this study, a non-mixing resin sink (NMRS) system was used, similar to that described by Yang et al.(1991) for adsorption of plant nutrients from soils to mixed-bed ion exchange resin. No distinction is made between adsorption and sorption (the physical incorporation of the adsorbate into the porous resin). In solutions, as well as in soils, diffusion is the rate limiting process for adsorption in the NMRS system (Neely and Isacoff, 1982). Adsorption is assumed to be a process of 1) molecular diffusion of the adsorbate from the bulk solution to the stationary boundary layer surrounding each resin particle, 2) external mass transfer (film diffusion) across the boundary layer, 3) intraparticle mass transfer (pore diffusion) from the surface to the interior, and 4) micropore adsorption which is considered very rapid (Rosene, 1983; Voice and Weber, 1983). Diffusion from bulk solution to within the tightly packed resin bed (1.06 cm radius sphere) is assumed to be rapid since interparticle pores are relatively large. Advantages of the NMRS system include measurement of ion diffusion from soil to resin sink (Yang and Skogley, 1991).

Kinetics

The adsorption rate with NMRS will likely be controlled by either film or intraparticle diffusion during adsorption (Sparks, 1989). If film diffusion is rate limiting, the adsorption rate is directly proportional to the external adsorbent surface area and is independent of the adsorbent type (Neely and Isacoff, 1982). Therefore, for particles of equal size and shape, adsorbent composition and pore structure would not affect the adsorption rate.

Greater than 98 % of the surface area for carbonaceous resins is within pores <500 Å diameter. Adsorption occurs predominantly within these pores (Neely and Isacoff, 1982). The resin bed external surface directly exposed to bulk solution is 1.4 x 10^{-3} m^2, or less than .001 percent of the total surface area. Stirring will have a smaller effect on film diffusion for this resin bed than for a loosely-packed or unpacked resin system. Further, it would be impossible to stir the solution within the intraparticle pore space.

Adsorption

The linear or constant partitioning adsorption isotherm is described by,

$$Q_{ads} = K_{oc}C_{eq}, \qquad (1)$$

where Q_{ads} is the ug C adsorbed per gram of resin C and C_{eq} is the equilibrium solution C concentration in ug/mL. K_{oc} is the partition coefficient normalized to organic C. The resin C content was 90 %. K_{oc} has been used to model soils where the controlling influence for similar adsorption was soil organic C (Karickhoff, 1981).

Thermodynamics

Adsorption isotherms with FA at various temperatures were used for calculating thermodynamic properties. The change of Gibbs free energy ($\Delta G_{tr}°$) due to the transfer of 1 mole of solute from bulk aqueous phase to the solid resin phase under constant pressure can be calculated according to the equation,

$$\Delta G_{tr}° = - RT \ln (K), \quad (2)$$

where R is the gas constant, T the absolute temperature, and K the equilibrium constant. For adsorption of a solute on a hydrophobic resin surface (S_{res}), the reaction can be described by,

$$Ab + S_{res} \rightleftharpoons AbS_{res}$$

where Ab represents the adsorbate. It is assumed that the adsorbate is not irreversibly bound to the surface, though the desorption rate may be slow. The system's partition constant is defined as,

$$K = a_{ads}/a_{sol} \quad (3)$$

where a_{ads} is the solute's activity in the adsorbed phase, and a_{sol} solute's activity in the solution phase. K_{oc} can approximate K by

$$K \approx K_{oc} = Q_{ads}/C_{eq} \text{ (Means and Wijayaratne, 1989).} \quad (4)$$

The phase transfer of a solute involves changes of the partial molar enthalpy ($\Delta H_{tr}°$) and entropy ($\Delta S_{tr}°$) which are related to $\Delta G_{tr}°$ according to

$$\Delta G_{tr}° = \Delta H_{tr}° - T\Delta S_{tr}°. \quad (5)$$

Substituting equation (2) into equation (5) leads to

$$\ln (K) = - \Delta H_{tr}°/RT + \Delta S_{tr}°/R. \quad (6)$$

A plot of ln (K) versus 1/T allows the calculation of $\Delta H_{tr}°$ and $\Delta S_{tr}°$.

Results and Discussion

Kinetics

Both FA and HA were adsorbed by the resin capsules with an initial high relative adsorption rate (slope) that decreased with time (Figures 2-5). This trend was more prominent with the Carboxen-Carbotrap mix (Figure 2) than with the XEN resins (Figures 3-5). Adsorption was greater for Carboxen-Carbotrap than for the XEN resins with all treatments at all times. Curvature in Figure 2 indicates that film diffusion alone does not control the adsorption rate (Hodges and Johnson, 1987). The kinetic behavior during adsorption of FA and HA on these resins is similar to many organic adsorbates and porous adsorbents, such as activated C (Weber and Smith, 1989), soil organic matter (Leenheer and Ahlrichs, 1971), and polymeric resins (Aiken et al., 1979). Observed linearity of C_s/C_o vs time$^{1/2}$ for the initial 97-100 hours of adsorption (Figures 6-9) suggests that intraparticle diffusion was rate limiting (Sparks, 1989; Leenheer and Ahlrichs, 1971). Linear regressions were highly significant ($P < .01$)(Table 5). Regression y-intercepts were essentially 0, such that slope ($d(C_s/C_o)/dt^{1/2}$) comparisons for regression lines (Snedecor and Cochran, 1989) were indicative of differences in relative fraction (C_s/C_o) adsorption rates. Slope comparisons among FA concentrations within each resin type (Table 5) were non-significant ($P < .05$). There was essentially no change in the relative fraction adsorption rate due to a doubling of initial FA concentration, which is evidence that film diffusion was not rate-limiting. If film diffusion were rate-limiting, then an approximate doubling of initial FA concentration should result in a proportional reduction in C_s/C_o, which did not occur (Figures 2-5).

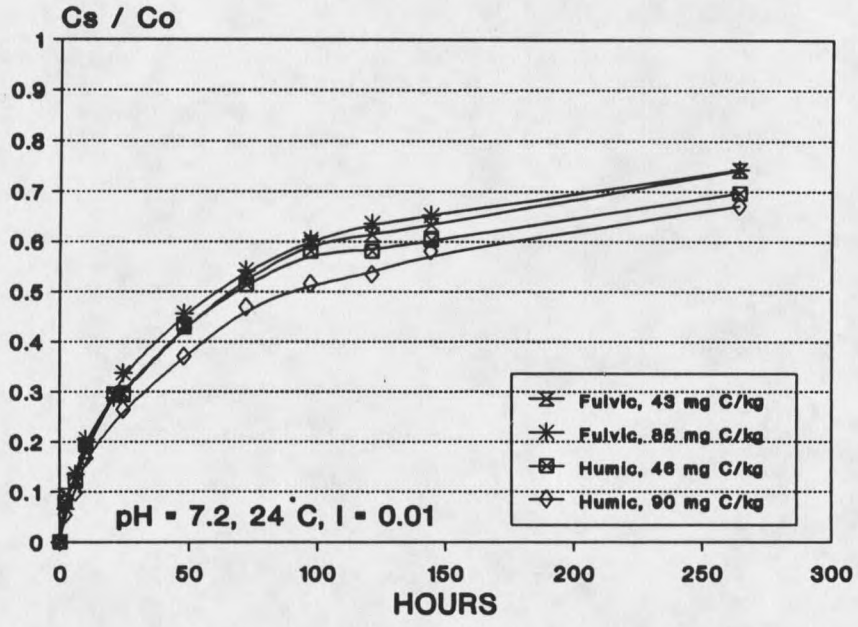


Figure 2. Relative Adsorption (C_s/C_o) of FA and HA with Time on Carboxen-Carbotrap Capsule.

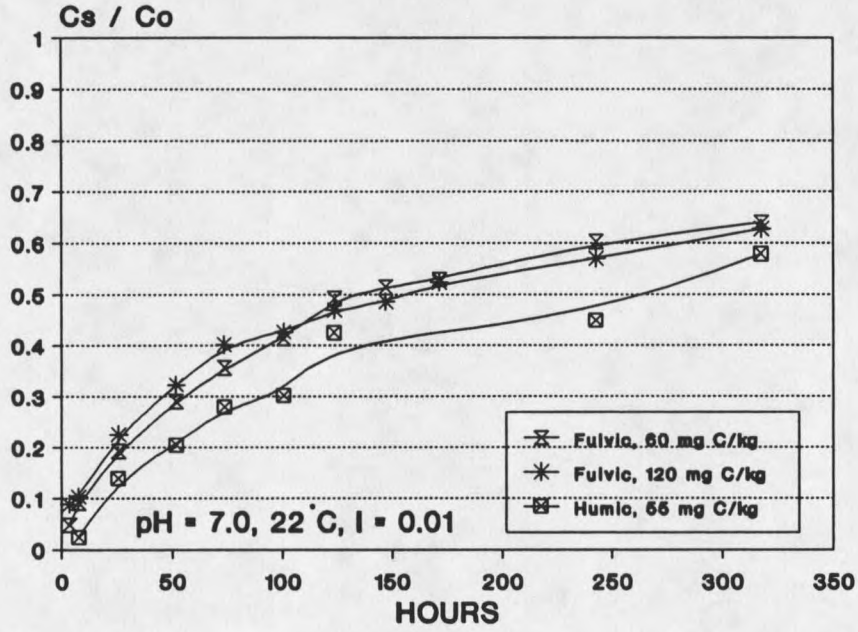


Figure 3. Relative Adsorption (C_s/C_o) of FA and HA with Time on XEN-563 Capsule.

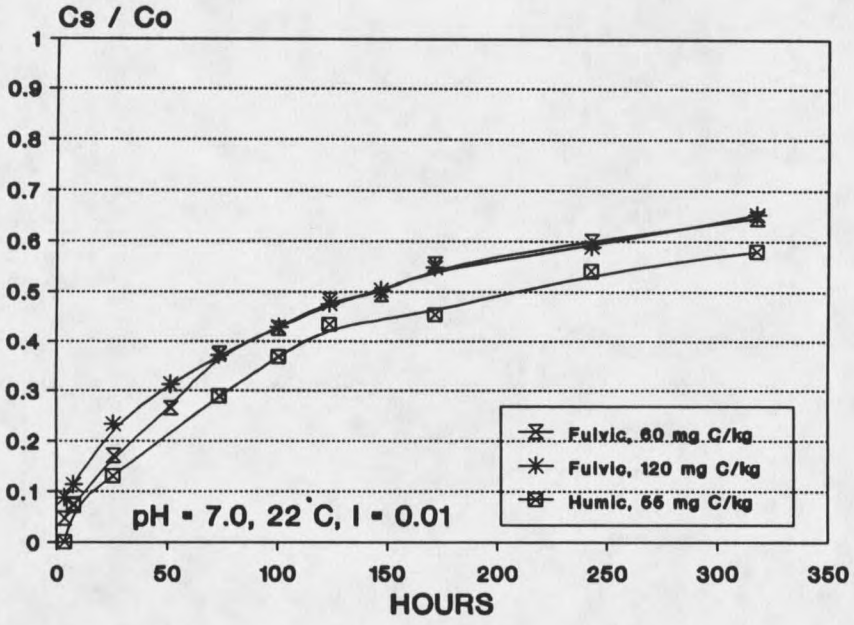


Figure 4. Relative Adsorption (C_s/C_o) of FA and HA with Time on XEN-564 Capsule.

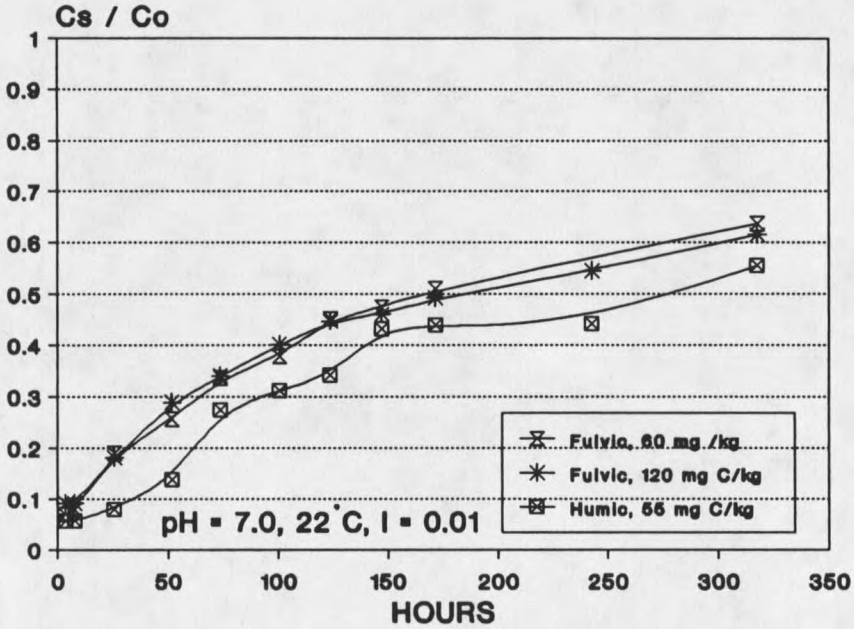


Figure 5. Relative Adsorption (C_s/C_o) of FA and HA with Time on XEN-572 Capsule.

Rather, for the initial 97-100 hours of adsorption, a doubling of initial concentration (C_o)resulted in nearly exactly twice the ug C (C_s) adsorbed, hence no change in C_s/C_o. No change in $d(C_s/C_o)/dt^{1/2}$ between concentrations suggests that more than sufficient adsorption sites were available. The mass of FA (based on C) never exceeded .2 % of the adsorbent mass in any treatment.

Using slope comparisons for FA among resin types (Table 5), adsorption rate decreased in the order Carboxen-Carbotrap > XEN-563 = XEN-564 > XEN 572. Differences in adsorption rate among resin types may be the result of pore size differences and resulting size exclusion effects. Pore diameter characteristics were not available for the Carboxen-Carbotrap resins. Among the XEN adsorbents, the pore diameter distribution ranges from <20Å to >500Å with XEN-572 possessing the greatest porosity volume of <20Å pores (Rohm and Haas Co.). Aiken et al. (1979) deduced that extreme steric restrictions to penetration of FA should occur in pores of <100Å. Resin XEN-572 exhibited the lowest adsorption rate which might be the result of the resin's greater volume of smaller pores.

There was less relative adsorption (C_s/C_o) of HA than FA for all resin types (Figures 2-9). This adsorption difference was more prominent with the XEN resins than with the Carboxen-Carbotrap resins. The Carboxen-Carbotrap mixture showed only a slight decrease in C_s/C_o for HA compared to FA, suggesting a comparable capacity for the larger molecular weight HA (Table 5). As with FA, observed linearity (Figures 6-9) for the initial 97-100 hours of adsorption suggests that intraparticle diffusion was rate limiting for adsorption of HA. Slope comparisons for HA at the lower concentration

Table 5. Regression Parameters for Relative Fraction Adsorbed (C_e/C_o) Versus Hour$^{1/2}$ for Initial 97-100 Hrs of Adsorption.

RESIN TYPE	ACID	CONCENTRATION (mg C/L)	SLOPE ($hr^{-1/2}$)	Y-INTERCEPT	r^2
Carboxen-Carbotrap	Fulvic	43	.062	-.007	.99**
	Fulvic	85	.064	-.006	.99**
	Humic	46	.061	-.003	.99**
	Humic	90	.055	-.020	.99**
XEN 563	Fulvic	60	.043	-.020	.99**
	Fulvic	120	.045	-.002	.99**
	Humic	55	.033	-.030	.97**
XEN 564	Fulvic	60	.044	-.030	.98**
	Fulvic	120	.043	-.004	.99**
	Humic	55	.037	-.037	.96**
XEN 572	Fulvic	60	.039	-.009	.99**
	Fulvic	120	.040	-.003	.99**
	Humic	55	.030	-.020	.89**

**Linear regression significant at $P < .01$.

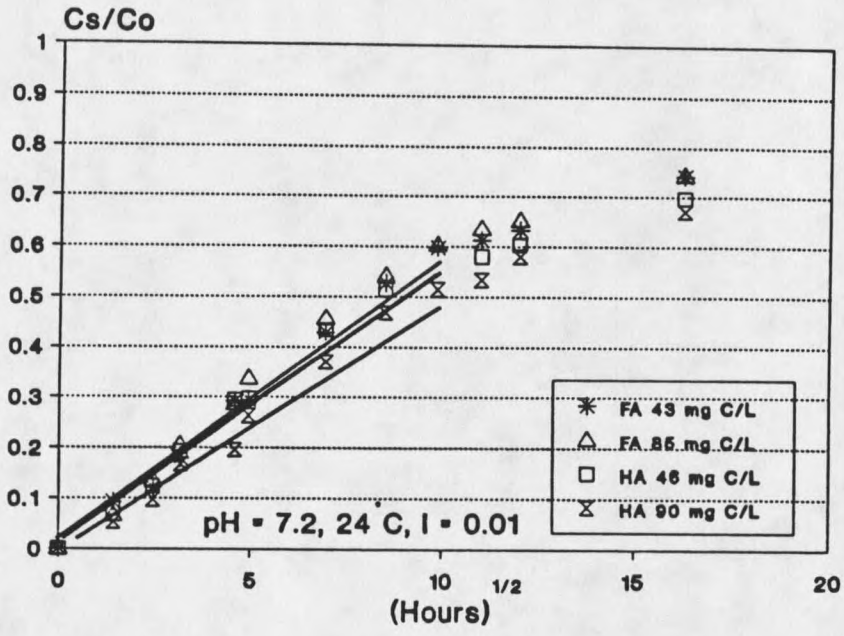


Figure 6. C_s/C_o vs Time$^{1/2}$ for Adsorption of FA and HA on Carboxen-Carbotrap. Linearity (97-100 Hrs) Describes Intraparticle Diffusion.

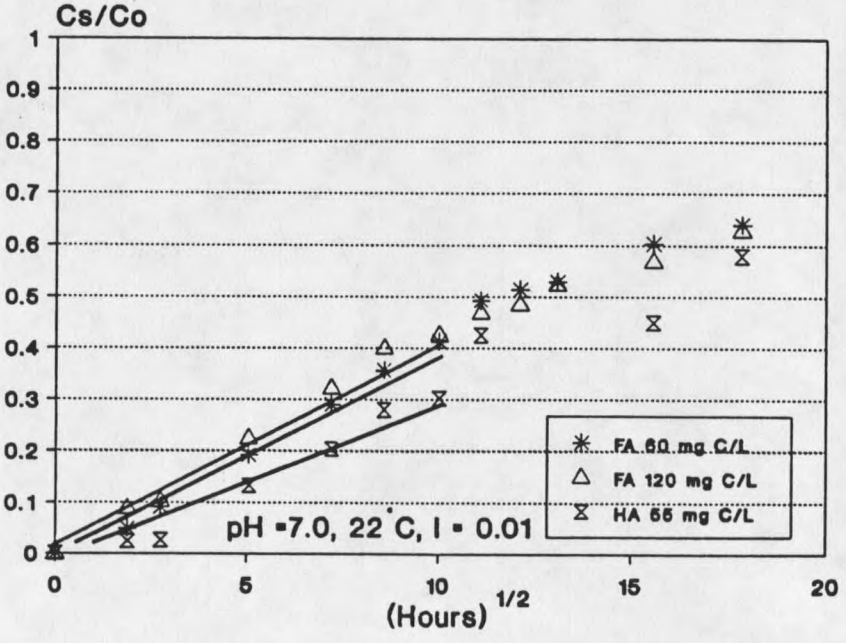


Figure 7. $C_s\backslash C_o$ vs Time$^{1/2}$ for Adsorption of FA and HA on XEN-563. Linearity (97-100 Hrs) Describes Intraparticle Diffusion.

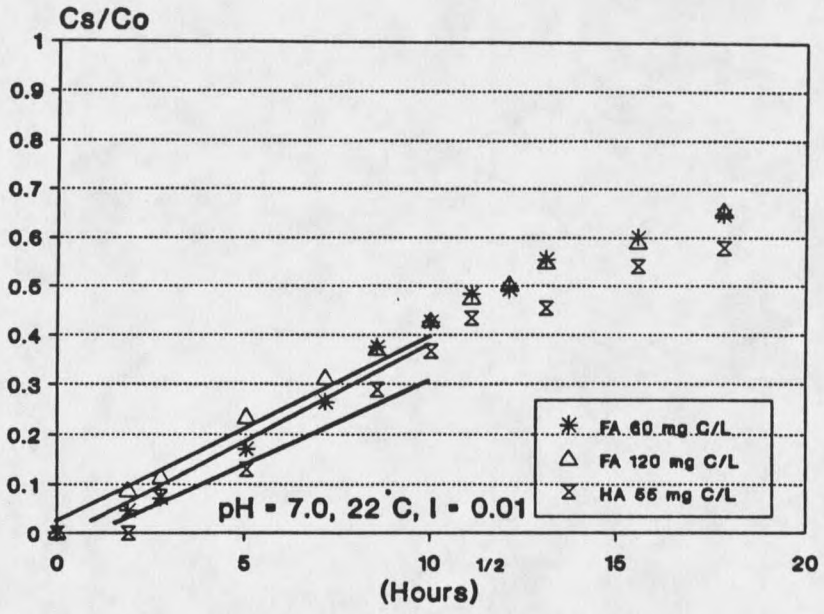


Figure 8. C_s/C_o vs Time$^{1/2}$ for Adsorption of FA and HA on XEN-564. Linearity (97-100 Hrs) Describes Intraparticle Diffusion.

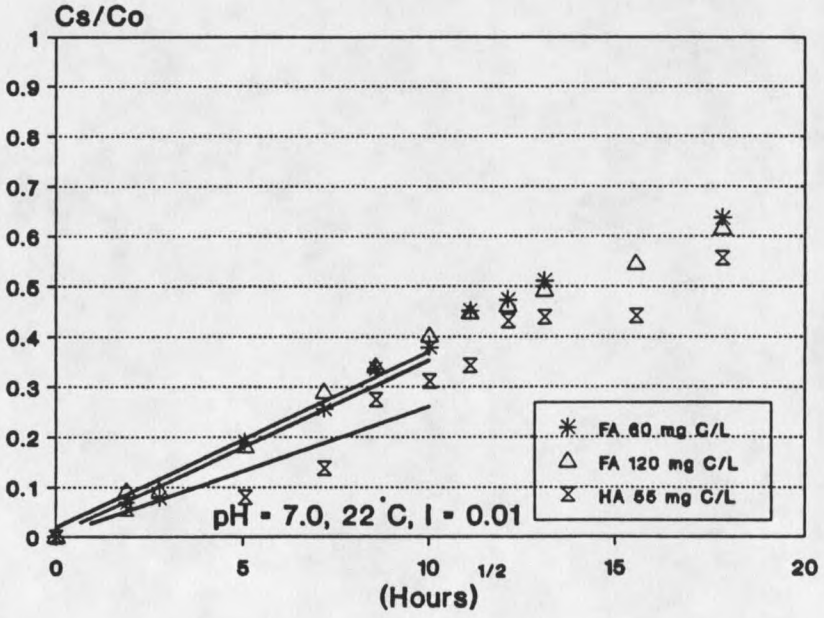


Figure 9. C_s/C_o vs Time$^{1/2}$ for Adsorption of FA and HA on XEN-572. Linearity (97-100 Hrs) Describes Intraparticle Diffusion.

(Table 5) indicated that adsorption (C_s/C_o) decreased Carboxen-Carbotrap > XEN-563 = XEN 564 = XEN-572. The larger HA molecules would be subject to size exclusion at a greater pore diameter than for FA (100Å).

Adsorption

The constant partition adsorption isotherm was applied to the adsorption of FA and HA on Carboxen-Carbotrap capsules at different temperatures (Figure 10). Regression lines were highly significant ($r^2 > .96$, $P < .01$). All isotherms can be described as indicating linear adsorption (constant slopes) within the concentration ranges used. This condition results from the presence of an excess of relatively homogeneous adsorption sites (Dragun, 1988). This differs from activated C which is described as having a heterogenous surface and, in many cases, a curvilinear adsorption isotherm (Suffet and McGuire, 1980). Since over 70 % of FA was adsorbed over a 264 hr period (Figure 2), both the hydrophobic (48 %) and hydrophilic (52 %) fractions were being adsorbed to some extent.

Adsorption of FA increased with increasing temperature (Figure 4). This trend would suggest that adsorption is entropy (i.e. hydrophobic adsorption) rather than energy (of FA-resin interaction) favored (Adamson, 1990). Since FA must surely lose entropy on adsorption, the effect must come from a gain in H_2O (solution) entropy. Little difference, however, is seen for FA at 13 and 23°C. Less adsorption of HA at 23°C occurred than for FA (23°C) over the isotherm range.

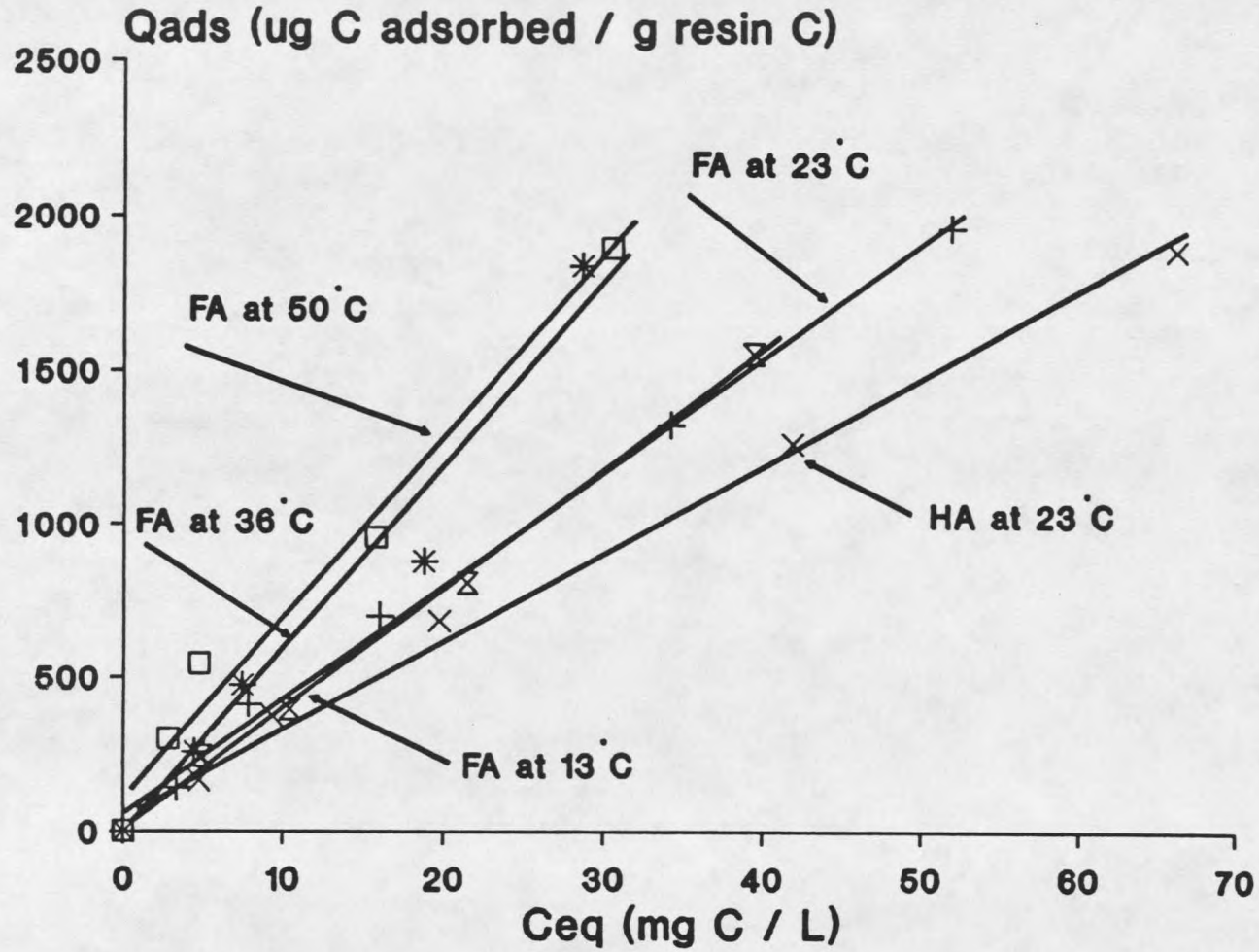


Figure 10. Isotherms for FA at 4 Temperatures and HA at 23 °C.

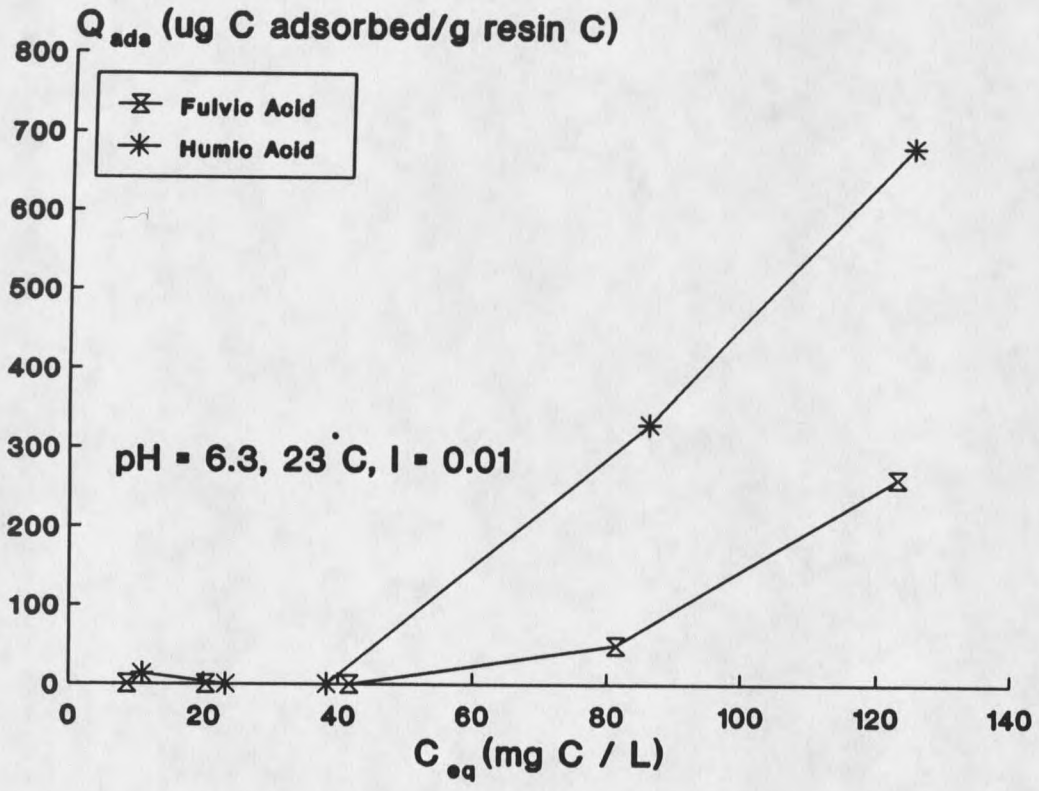


Figure 11. Adsorption of FA and HA on XAD-8 Resin.

In contrast, the XAD-8 resin at pH 6.3 showed no adsorption for either FA or HA at lower concentrations (Figure 11). A pH of 6.3 is above the operational pH range (pH 2.0) reported for XAD-8 resins (Aiken et al., 1979). These results suggest that carbonaceous resins can function at normal pHs of soils and waters, while XAD-8 cannot.

Partition coefficients normalized to resin C (K_{oc}) were calculated two ways. First, K_{oc} values were calculated from mean Q_{ads} and C_{eq} values of each individual initial FA and HA concentration used in the adsorption studies. Second, slopes of each isotherm were used to obtain K_{oc}. Variation in concentration means for FA at 50°C led to a difference in the isotherm K_{oc} of 82 in Table 6 and the K_{oc} (slope) discernable in Figure

Table 6. Linear Adsorption Isotherm Parameters and Calculated K_{oc}s' (Carboxen-Carbotrap Capsules).

TEMP. (°C)	ACID	INITIAL SOLUTION CONCENTRATIONS (mg C/L)	Q_{ads} (MEAN) (ug C adsorbed/ g resin C)	C_{eq} (MEAN) (mg C/L)	K_{oc} (MEAN)	ISOTHERM K_{OC}
13	Fulvic	14	242	5	48	
		25	395	10	39	41
		52	809	21	38	(CV=11%)
		102	1554	39	40	
23	Fulvic	9	141	3	47	
		23	410	8	51	
		43	701	16	44	44
		85	1324	34	39	(CV=12%)
		126	1961	52	38	
36	Fulvic	14	254	4	63	
		25	473	7	68	60
		52	879	19	46	(CV=16%)
		102	1837	29	63	
50	Fulvic	14	298	3	99	
		25	544	5	109	82
		52	958	16	60	(CV=32%)
		102	1788	31	58	
23	Humic	11	165	5	33	
		24	372	9	41	
		46	684	20	34	33
		90	1262	42	30	(CV=15%)
		138	1878	66	28	

4 through statistical best fit. This discrepancy is not unusual in isotherm studies at this relatively high temperature for macromolecules such as FA. The temperature of 50°C is likely where FA undergoes some macromolecular structural changes in solution (i.e. denaturation or macromolecule coiling) that can result in abnormalities in adsorption behavior (Eisenberg and Crothers, 1979; Ghosh and Schnitzer, 1980). This can explain the variable adsorption (C.V. = 32%) seen by concentration mean K_{oc}s at 50°C (Table 6). An increase in temperature for FA led to an increase in isotherm K_{oc}s (Table 6) which agreed with the adsorption seen in Figure 10.

Thermodynamics

Thermodynamic parameters for FA adsorption on Carboxen-Carbotrap resins (Table 6) were calculated by plotting (Figure 12) ln K_{oc} versus 1/T (°K) (r^2 =.96, P<.05). The calculated enthalpy value ($\Delta H°_{tr}$) was 15.1 kJ/mole and entropy ($\Delta S°_{tr}$), 84 J/mole °K. Free energy change of phase transfer ($\Delta G°_{tr}$) ranged from -8.8 to -11.7 kJ/mole as temperature increased from 13 to 50°C. The positive $\Delta S°_{tr}$ indicates that the adsorption of FA was entropy driven. This is supported by a positive (endothermic) $\Delta H°_{tr}$. A positive $\Delta S°_{tr}$ must come from a gain in solvent (H_2O) entropy, since the adsorbate presumably loses entropy on adsorption (Adamson, 1990). A low $\Delta G°_{tr}$ and a positive $\Delta H°_{tr}$ suggests that a weak physical adsorption process, such as hydrophobic bonding (Voice and Weber, 1983), is responsible for the adsorption of FA by carbonaceous resins. Adsorption may include the London-van-der-Waals attractive force as the adsorbate nears the resin surface.

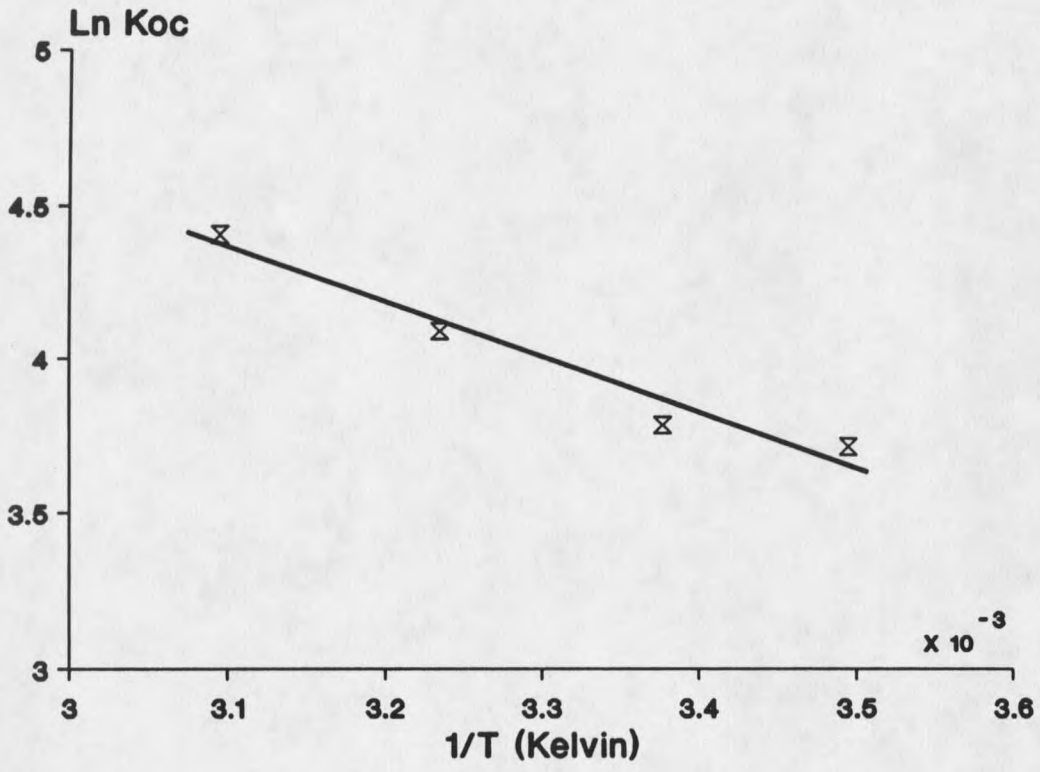


Figure 12. Plot of ln K_{oc} for Partitioning of FA on Carboxen-Carbotrap Resin over 1/T.

Desorption

Insight into desorption of adsorbed species from the Carboxen-Carbotrap adsorbent can be gained from the stripping process employed. Use of 0.1 N NaOH as the stripping solvent resulted in an average recovery of 25.5 % for adsorbed FA (C.V. = 45.2 %) and 37.9 percent for HA (C.V. = 27.9 %). The use of 2 N NaOH resulted in an average recovery of 24.2 % for adsorbed FA (C.V. = 17.9 %) and 21.7 % for HA (C.V. = 22.0 %). The extraction times for 0.1 N NaOH were double (2 hr) those used for 2 N NaOH. Recovery was similar with both 0.1 N NaOH and 2 N NaOH, but C.V.s were lower with the latter. Thus, the more concentrated solution appears to be a better

choice for this purpose, but more studies are needed to determine the most effective concentration. For volatiles and semi-volatiles, thermal desorption is recommended[1].

Desorption from porous C adsorbents often results in incomplete recovery of the adsorbate (Adamson, 1990). Much of this study was done using regenerated resin extractors, and we assume that the regeneration procedure did not remove all the adsorbate. In many cases, extreme tortuosity and/or steric restriction can prevent movement of adsorbate out of small pores even though the adsorbate is not irreversibly bound to the surface. This hysteresis effect may be significant considering that FA and HA molecules are large. For example, a pilot study using Carboxen-Carbotrap resins adsorbed with citric or ascorbic acids, resulted in a recovery (2 N NaOH) of 54.5 % (C.V. = 5.8 percent) and 37.9 % (C.V. = 5.8 %) ,respectively, for these smaller acids. Further, for large organic molecules adsorbed in small pores, multiple van-der-Waals attraction forces arising from many points of contact between the surface and the adsorbate can make desorption difficult or slow (Dragun, 1988). The few surface functional groups reported for the Carboxen-Carbotrap resins[2] and the small positive ΔH_{tr} found for adsorption makes it unlikely that chemisorption or chemical bonding occurred.

The fact that initial solution concentrations of FA and HA can be predicted from resin extractable C (Figure 13) indicates the usefulness of carbonaceous resin capsules for environmental analysis and *in situ* monitoring. The correlation of initial solution C

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[1] Supelco, Inc., 1989.

[2] Supelco, Inc., 1989.

with resin extractable C (2 N NaOH) was highly significant (r^2 =.99, P<.001) for both acids (Figure 13).

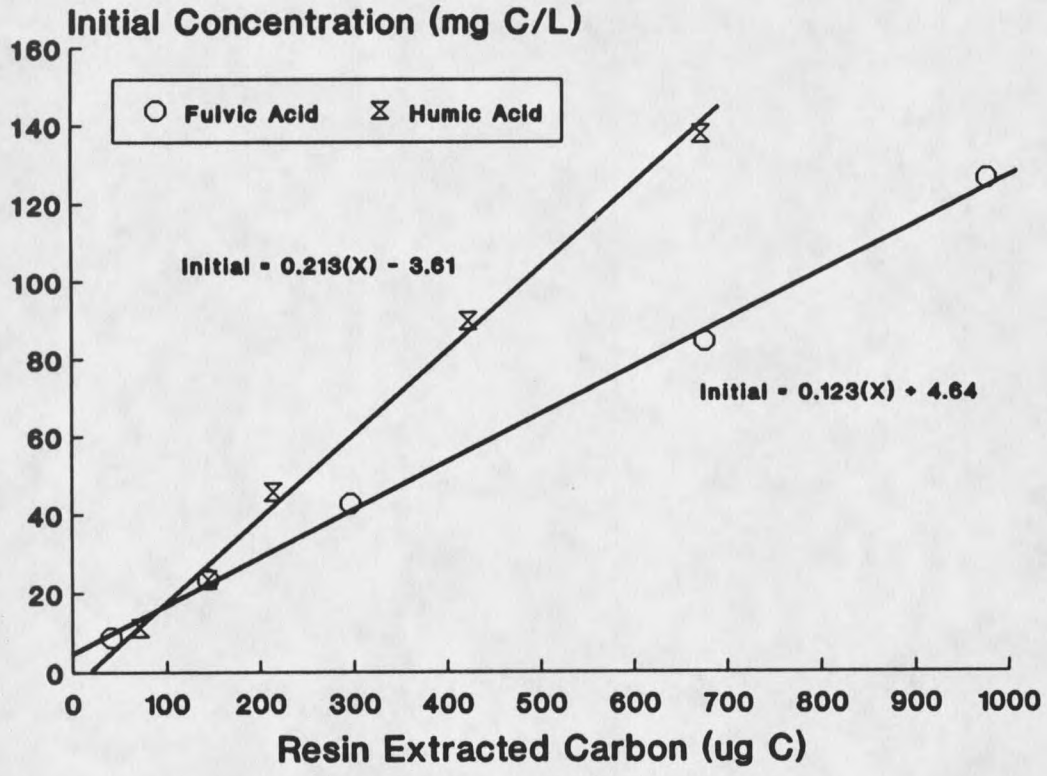


Figure 13. Predicting Initial Concentrations of FA and HA from Carboxen-Carbotrap Capsules (Mean Values of Extracted C).

CHAPTER 5

DETERMINATION OF SOIL C, ORGANIC N, P, and S, AND IDENTIFICATION OF, ADSORBED LABILE C

Adsorption Studies

All resin types adsorbed LC from saturated soil samples at all soil pHs (5.4-8.3; Tables 3 and 4). Labile C desorption by 2 N NaOH will remove, by definition, the acid and neutral fractions of this water soluble C. Cumulative resin extracted LC (TOC) of all soils was 2-3 times greater in PA soils among resin types used than in MT soils. For PA soils, means (n = 12 soils) for extracted LC among resin types ranged from 449 to 1401 μg C per soil sample. For MT soils, means (n = 19 soils) among resin types ranged from 199 to 277 μg C per soil sample. In PA soils, the XEN-572 resin (1401 μg C/soil X 3 replicates X 12 soils) extracted the highest cumulative TOC, while in MT soils the XEN-564 resin (277 μg C/soil X 3 replicates X 19 soils) did.

Adsorption observed at 12°C (Figure 14), 22°C, and 45°C indicated that the amount of LC adsorbed increased with increasing temperature. Some of these results are discussed on Page 41. This adsorption behavior in soil suggests an entropy driven adsorption process over that of an energy (of LC-resin interaction) favored process (Adamson, 1990). Jardine et al. (1989) observed a similar increase in dissolved organic C (DOC) adsorption in soil with an increase in temperature. An entropy driven

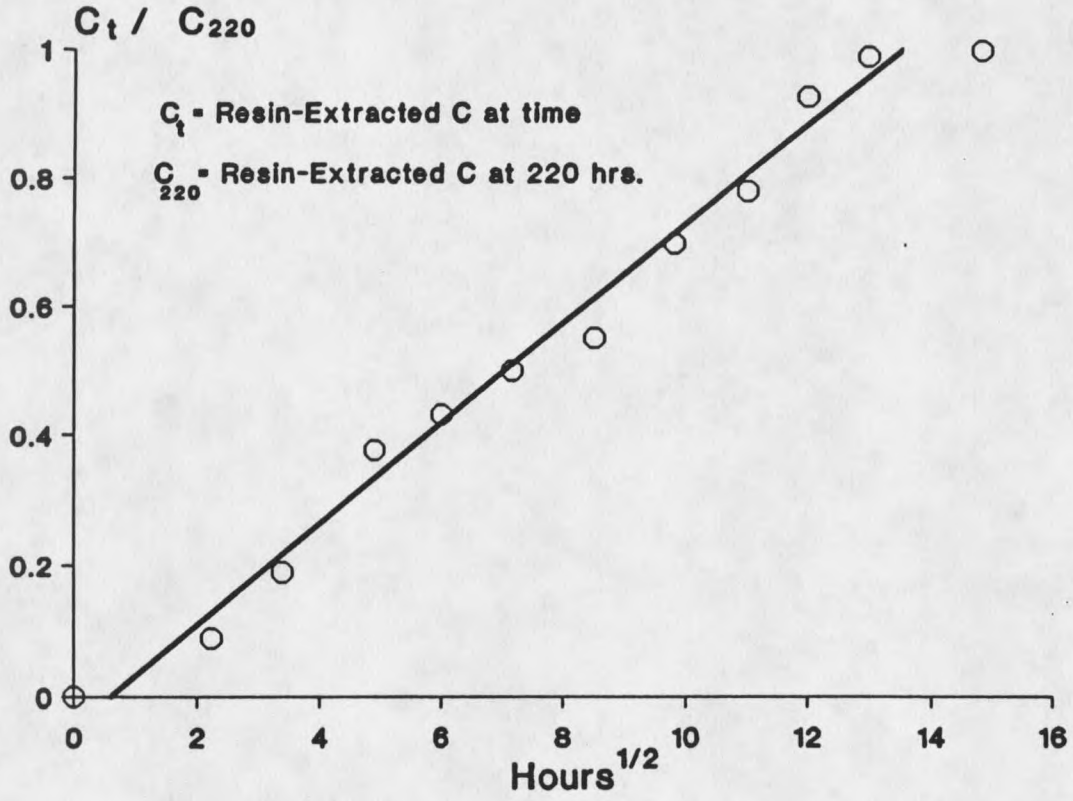


Figure 14. Parabolic Diffusion Model of Enbar Loam with XEN-564 Capsule at 12° C.

adsorption process was indicated for carbonaceous resin adsorption of soil fulvic acid in solution (Chapter 4).

Linearity of $C_t/C_{220\ hrs}$ with $hours^{1/2}$ seen in Figure 14 ($r^2 = 0.99$, $P < .001$) suggests that intraparticle diffusion is rate-limiting with resin capsule adsorption in soils (Jardine and Sparks, 1984; Aiken et al., 1979). This is in distinction to adsorption controlled by film diffusion (boundary layer) which might be expected during static (soil environment) adsorption (Sparks, 1989). Intraparticle diffusion was found to be rate-limiting in capsule adsorption from solution (non-stirring system) of soil fulvic acid (Chapter 4). In soil (Figure 14), the intraparticle diffusion rate for adsorption can be interpreted as slow (days).

Ultrafiltration used with XEN-564 resin extracts (Table 7) indicated that most (64-94%) of LC is less than 1000 daltons. All (95-100%) of the LC was less than 10,000 daltons. Low molecular weights (less than 2000) determined by other than ultrafiltration, are reported for soluble soil humics collected by lysimeter (Berdén and Berggren, 1990) and by water extraction (Linehan, 1977).

Initial resin research was exclusively with MX resin employing a soil incubation time of 72 hours at 22 °C. Later information indicated that performance might be improved using longer incubation times. Hence, all other resin types were at 96 hours at 22 °C. For Enbar loam with XEN-564 resin for 96 hours, 570 μg C was adsorbed at 22 °C. This was near the maximum adsorption obtained for XEN-564 for 220 hours (530 μg C) at 12 °C (Figure 14). Limited availability of MX resin prevented repeating soil-resin adsorption for 96 hours.

Table 7. Ultrafiltration of Labile C Extracted with 0.05 M NaOH from XEN-564 Capsules after 10 Days Adsorption.

Soil Series	Disc Membrane[1]	Molecular Wt. Cut-Off (Daltons)	% C Retained of Initial C
Farland (MT)	PM-10	10,000	0
Enbar (MT)	PM-10	10,000	5
Andover (PA)	PM-10	10,000	0
Farland	YM-1	1,000	36
Enbar	YM-1	1,000	15
Andover	YM-1	1,000	6

[1]Amicon Company, Beverly, Ma.

The relationship of resin-extracted LC to several soil parameters are reported by (regression lines) correlation (r) matrices (Tables 8-9). Wet combustion soil C (WC) was considered to be the most accurate measure of soil C in this study. Very significant ($P < .001$) correlations between LC and related soil parameters (Tables 8-9) among all resin types suggests that this methodology may be useful for studying these soil parameters. Statistical comparison of regression lines (not shown) (Snedecor and Cochran, 1989) of LC with WC for each resin type with MT soils indicated that the lines (slopes, intercepts, and residual variances) were statistically different ($P < .01$). Likewise, an identical comparison with the PA soils indicated statistical differences

Table 8. Simple Correlation Coefficient (r) Matrix for Labile C Extracted by Resins[†] and Soil Parameters[‡] for Montana Soils.

	XEN-563	XEN-564	XEN-572	MX	F-400	WC	WB	LOM
WB	.74**	.88**	.79**	.83**	.80**	.97**	--	.96**
WC	.82**	.94**	.83**	.86**	.83**	--	.97**	.97**
LOM	.77**	.92**	.82**	.85**	.84**	.97**	.96**	--
TKN	.85**	.95**	.86**	.84**	.82**	.94**	.93**	.96**
OP	.85**	.95**	.90**	.88**	.87**	.93**	.90**	.91**
OS	.70**	.76**	.63*	.62*	.64*	.84**	.83**	.86**

[†] MX = Carboxen-Carbotrap resin mixture; F-400 = Filtersorb 400 activated C

[‡] WB = Walkley-Black soil C; WC = Wet combustion soil C; LOM = Loss-on-ignition organic matter; TKN = Total Kjeldahl nitrogen; OP = soil organic phosphorus; OS = soil organic sulfur.

* Regression line of correlation significant at $P < 0.01$.

** Regression line of correlation significant at $P < 0.001$.

Table 9. Simple Correlation Coefficient (r) Matrix for Labile C Extracted by Resins† and Soil Parameters‡ for Pennsylvania soils.

	XEN-563	XEN-564	XEN-572	MX	WC	WB	LOM
WB	.75*	.80*	.77*	.73*	.83*	--	.76*
WC	.84**	.82*	.79*	.95**	--	.83*	.97**
LOM	.89**	.90**	.84**	.98**	.97**	.76*	--
TKN	.84**	.89**	.81**	.86**	.77*	.92**	.89**
OP	.29	.30	.26	.29	.25	.64	.38
OS	.84**	.84**	.81*	.93**	.97**	.78*	.97**

† MX = Carboxen-Carbotrap resin mixture; F-400 = Filtersorb 400 activated C

‡ WB = Walkley-Black soil C; WC = Wet combustion soil C; LOM = Loss-on-ignition organic matter; TKN = Total Kjeldahl nitrogen; OP = Soil organic phosphorus; OS = Soil organic sulfur

* Regression line of correlation significant at $P < 0.01$.

** Regression line of correlation significant at $P < 0.001$.

($P < .01$). Therefore, this indicates adsorption differences among resin types. The correlation of LC with WC indicates that the potential for predicting soil C decreased XEN-564 > MX > XEN-572 = F400 = XEN-563 in the MT soils (Table 8), and MX > XEN-563 > XEN-564 > XEN-572 in the PA soils (Table 9).

All the resin types showed very good correlations with the MT soil parameters TKN, OP, and OS (Table 8). The XEN-564 extracted LC had the highest and significant ($P < .001$) correlations with these soil parameters. These results suggest that this method of determining LC can potentially be used to determine organic N, P, and S, as well as soil C. Since each element was an independent test, it also supports the authenticity of resin extracted LC as a linear calibrated measure of soil C (Figure 15). Linear calibration appropriately describes the approach employed in this study where regression X values (i.e. soil parameters WC, TKN, OP, and OS) are regarded as essentially fixed, because soil samples were deliberately picked (Table 3 and 4). Therefore, only the regression of Y on X has statistical meaning and stability (Snedecor and Cochran, 1989) and prediction must be made from measurement of Y (LC) on X (soil parameters). An approximate C/N/P/S soil ratio exists for these MT soils, which can be observed by WC over TKN, OP, and OS (Table 8). Figures 16-18 indicate that XEN-564 extracted LC has an excellent calibration with TKN and OP, and a fair calibration to OS. One statistical and very significant outlier (Rothiemay soil, Table 3 in Chapter 3) was removed by statistical analysis (Snedecor and Cochran, 1989) from Figure 10. If this outlier was included, the r^2 would be 0.77 ($P < .001$). Significant correlations were also found by Staley et al. (1988) between soluble soil organic C (water

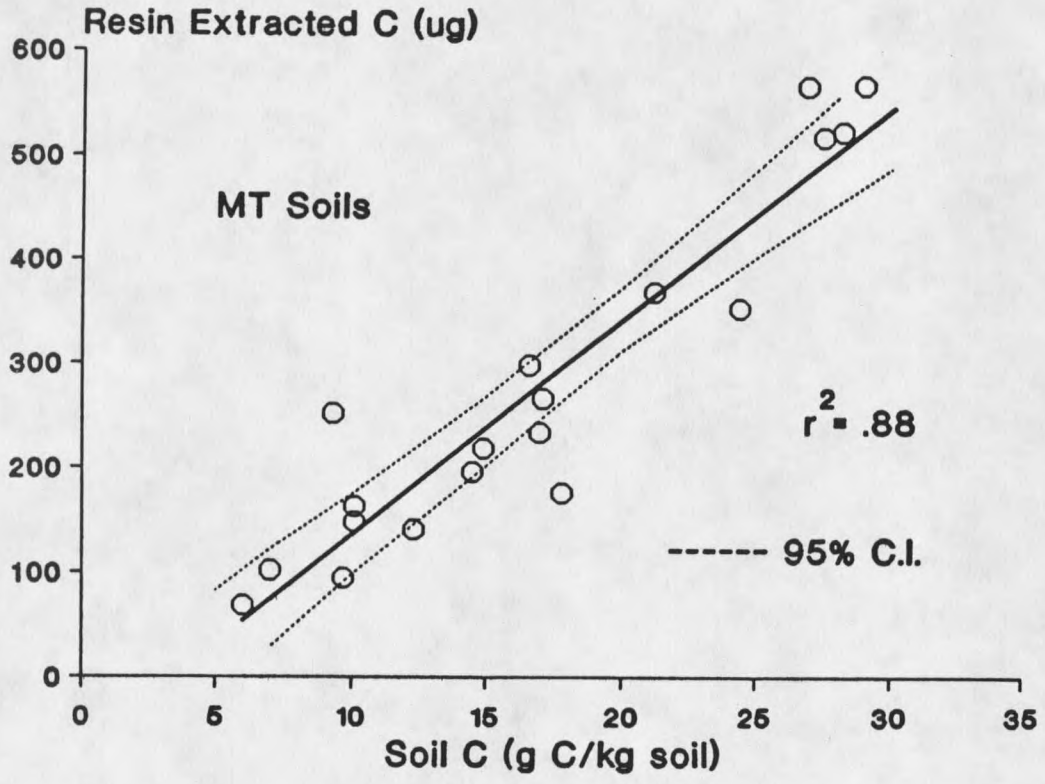


Figure 15. Regression of Wet Combustion Soil C and Labile C by XEN-564 Capsule.

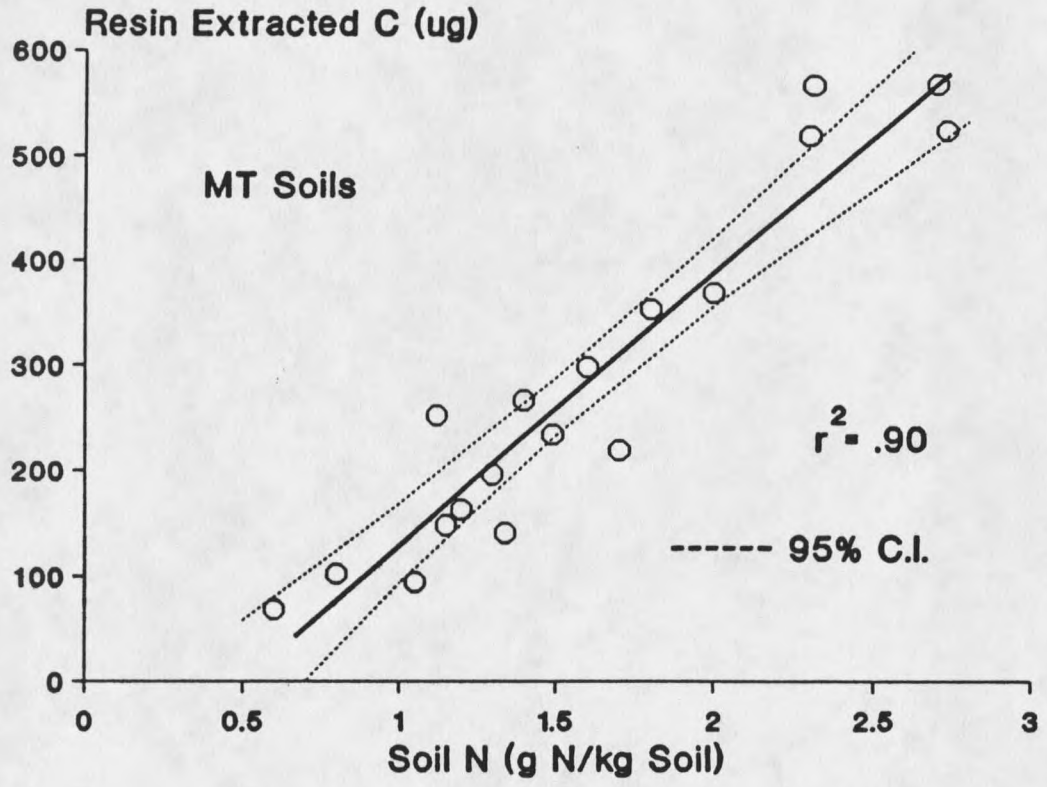


Figure 16. Regression of Total Kjeldahl N and Labile C by XEN-564 Capsule.

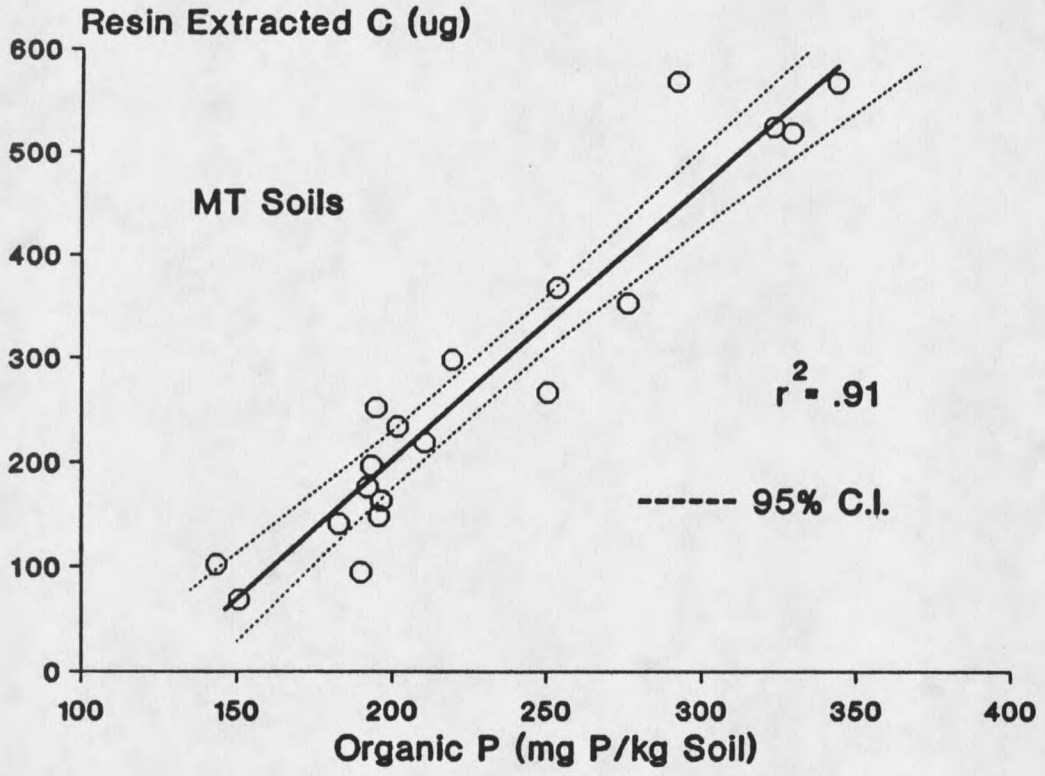


Figure 17. Regression of Organic P and Labile C by XEN-564 Capsule.

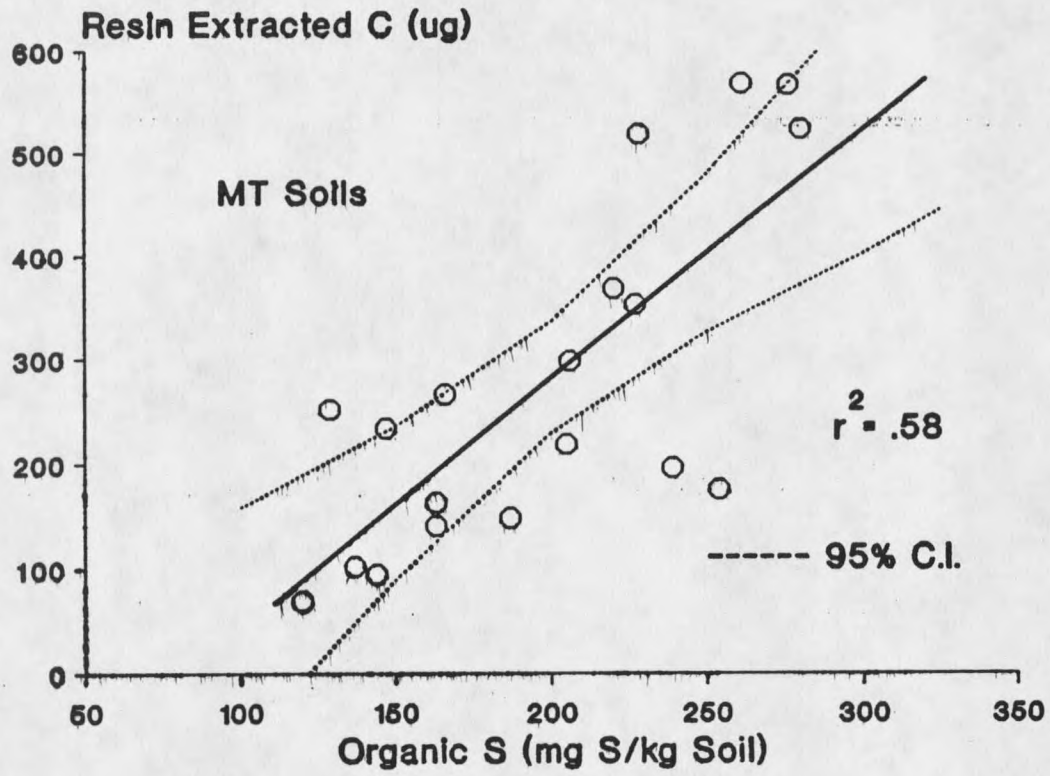


Figure 18. Regression of Organic S and Labile C by XEN-564 Capsule.

extracted) and TKN, OP, and OS. Direct measurements of N, P, and S were not attempted at this time, though these elements are likely constituents of this LC fraction (Thurman, 1985). The results suggest that direct measurement could provide useful insight into bio- or geochemical processes or cycles affecting nutrient availability, soil chemistry, or microbial activity. For example, organic N, P, and S are abundant in the low-molecular weight, mobile fraction of organic matter (Schoenau and Bettany, 1987) and measurement of this fraction would help explain soil profile distributions of these elements (Roberts et al., 1989; Honeycutt, et al., 1990).

WB and LOM were very significantly ($P < .001$) correlated with resin extracted LC, TKN, and OP (Tables 8-9). Slightly better results were found with WB than for LC for predicting WC and LOM in MT soils, but not in PA soils using MX resin. None of the resin types nor WC, WB, LOM, were significantly correlated with OP in PA soils (Table 9). All PA soils had high levels of OP (350 - 500 μg P/g soil) relative to the MT soils. No correlations are likely due to error in measurement of OP. The ignition (550 °C) procedure for OP determination likely overestimated the OP content by an increase in the solubility of Al- and Fe- bound P in 1 N H_2SO_4 (Olsen and Summers, 1982).

The very significant correlations ($P < .001$) expressed between resin extracted LC and WC shown in Tables 8-9 would suggest a partition-like relationship may exist between solid soil C and DOC. If this is true, this implies that C would be solubilized in direct proportion to its concentration in the solid soil phase. It is important to recognize the heterogenous nature of soil organic matter (i.e. fulvic and humic acids, humin) and such partitioning may only be a property of the more soluble organic

fractions, such as fulvic and humic acids. Using a modified adsorption isotherm model, Nodvin et al. (1986) noted the existence of a constant partition coefficient between soil solid C and solution DOC. A further implication is that the resin capsule adsorbed DOC in proportion to its concentration in the solution phase. This is supported by data shown in Figure 15. Results from the characterization study (Chapter 4) indicated a good fit between the linear adsorption isotherm model and resin adsorption of soil fulvic and humic acids from solution (Figure 10). The existence of such a partition coefficient would be analogous to that of partition coefficients normalized to soil organic C (K_{oc}) used in predicting the sorption of non-ionic organic compounds in soils. These K_{oc}s remain nearly constant over all soils (Karickhoff, 1981; Chiou et al., 1983), indicating a high soil C dependency and the non-polar character of soil organic matter (Rutherford et al., 1992) for the sorption of non-ionic organics. Carbonaceous resins have a high C content ($\approx$90%), as well as hydrophobic character. It is proposed that resin C responds similarly to soil C in this partitioning behavior.

Identification Studies

Figure 19, A-D illustrates FTIR spectra of MT LC extracts from XEN-564 and MX resins removed with either hexane (Figure 19A), 2 M NaOH (Figure 19, B-C), or methanol (Figure 19D). Interpretations of the IR spectra are based on Stevenson (1982), Schnitzer and Schuppli (1989), Thurman (1985), and Boyd et al. (1979).

All spectra (Figure 19, A-D) exhibited a main absorbance band at about wavenumber 3400 (H bonded O-H stretching). The presence of aliphatic compounds in the XEN-564 extracts is suggested by aliphatic C-H stretching (CH_3 or CH_2) in Figure

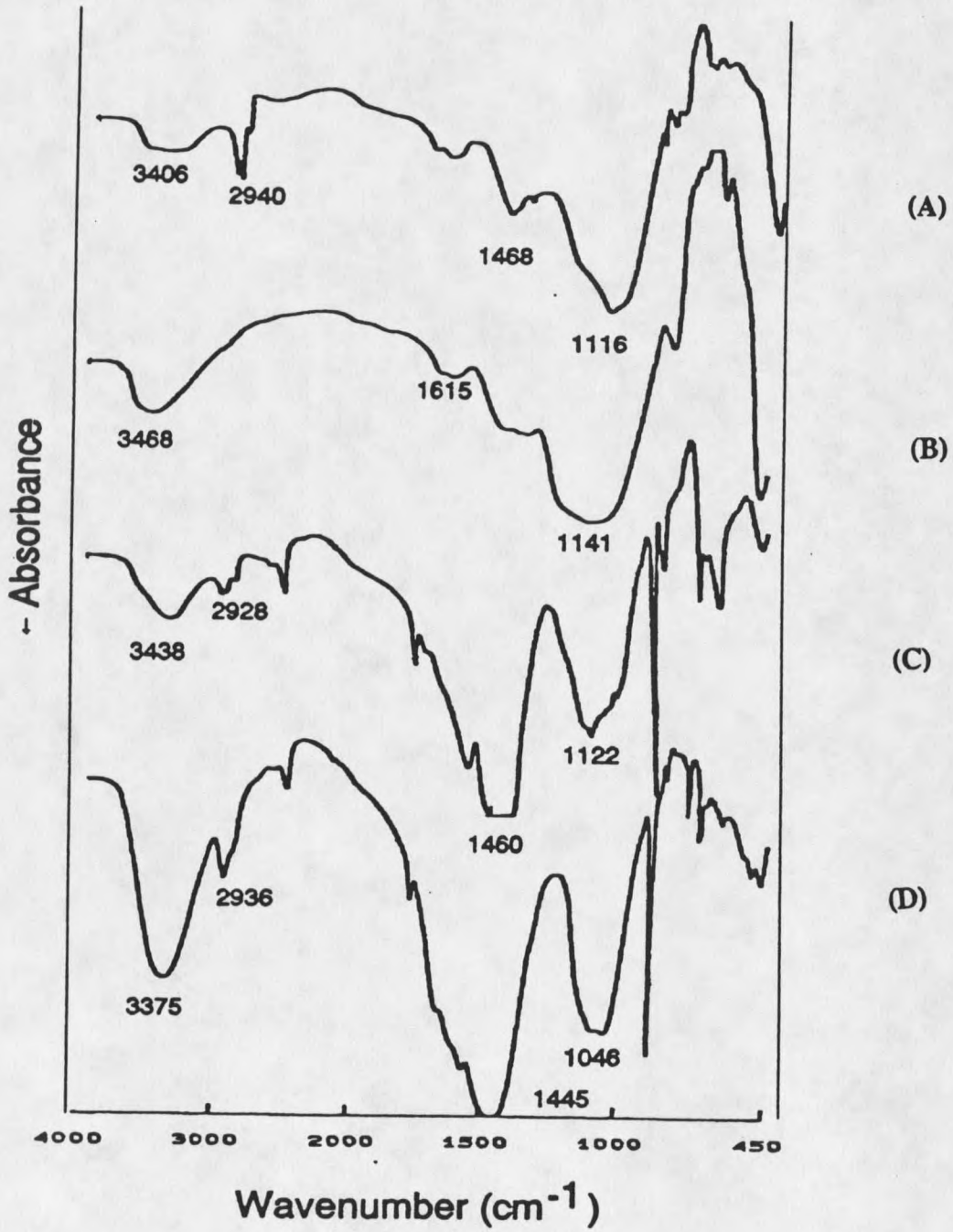


Figure 19. FTIR Spectra of Resin Extracts from Montana Soils with (a) n-hexane Extract Using XEN-564; (b) 2 M NaOH Extract Using MX Passed Through H-Resin; (c) 2 M NaOH Extract Using XEN-564 Passed Through H-Resin; and (d) Methanol Extract Using XEN-564.

19A (major bands 2940, 1468), Figure 19C (2928, 2875, and major band 1460), and Figure 19D (major bands 2936, 1445). The MX extract (Figure 19B) showed no direct aliphatic bands, but did show an aromatic C=C stretch or possibly a C=O stretch at 1615. Carboxylic C=O stretch is assigned at minor bands 1750 (Figure 19C), and 1776 (Figure 19, C-D). No heating of KBr samples suggests that the band at 1776 was not due to cyclic anhydrides (Stevenson, 1982). Minor bands at 1580 (Figure 19C) and 1564 (Figure 19D) are assigned as COO^- symmetric stretching and/or N-H deformation plus C=N stretching (amide II band). Other major bands are observed at 1116 (alcohols) in Figure 19A and 1141 (Figure 19B), 1122 (Figure 19C), and 1046 (Figure 19D) which are assigned to C-O stretching of polysaccharide or polysaccharide-like substances and/or Si-O of silicate impurities. Analysis of several LC extracts gave intense color reaction with phenol-disulfonic acid, a positive color test for simple sugars, oligosaccharides, or polysaccharides. Wavenumbers less than 1000 cm^{-1} in all spectra are assigned Si-O. A spectra (not shown) of PA soils (composite sample) showed OH, aliphatic, carboxylic, and probable polysaccharide groups similar to spectra in Figure 19, A-D. These spectra have functional groups in common to the soil fulvic acid fraction (Malcolm, 1990) with greater aliphatic character over aromatic.

Figure 20 presents a ^{13}C-NMR spectrum of a methanol extraction from XEN-564 in MT soils. Several other attempts made to obtain other ^{13}C spectra were unsuccessful. Sufficient LC (about 700 mg) was obtained by 0.05 M NaOH extraction. However, the carbonyl band, due probably to carbonate, overwhelmed and masked any possible identification of other structures. Hence, several ^1H-NMR spectra (Figures 21-24) must

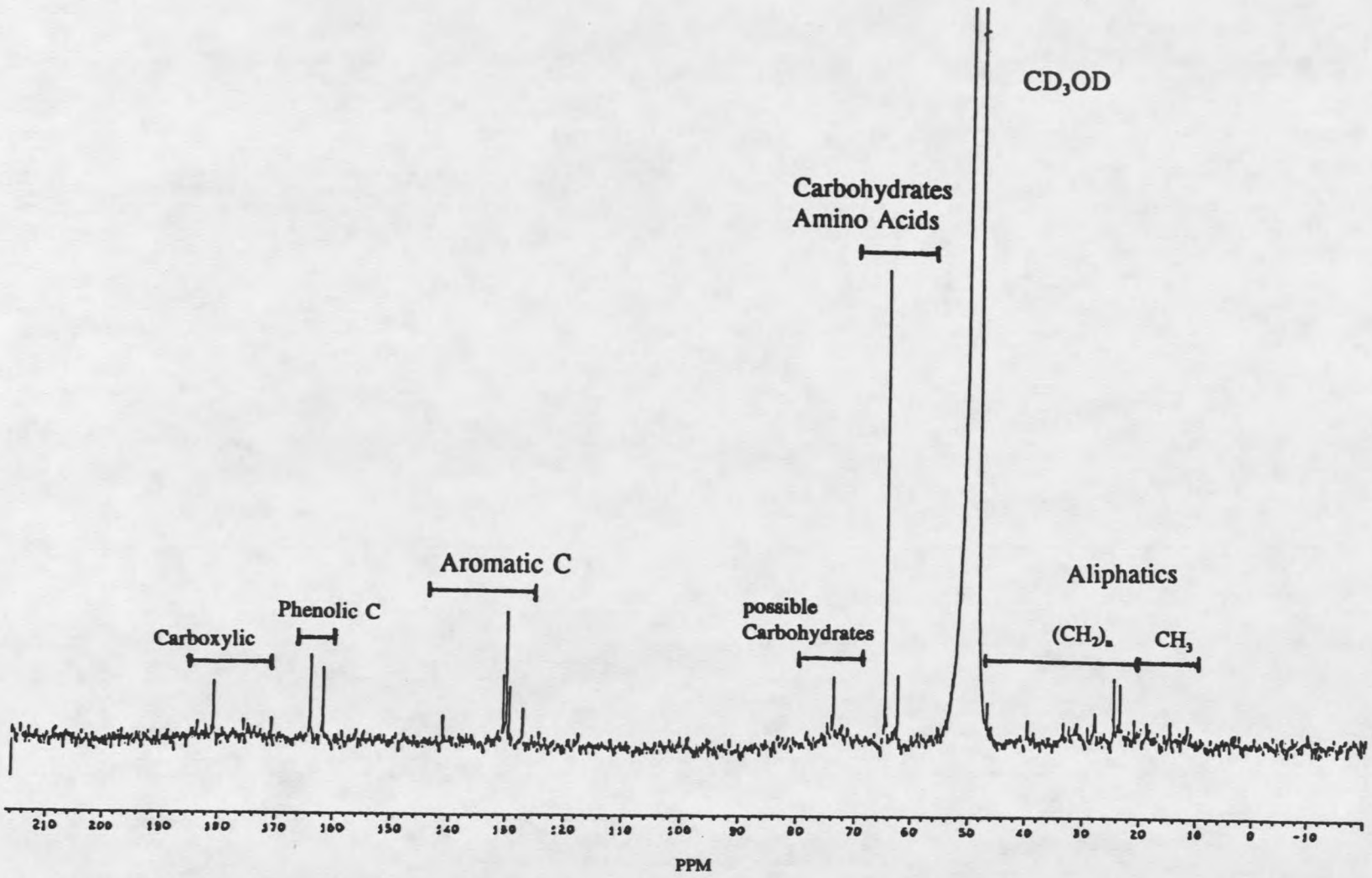


Figure 20. ^{13}C-NMR Spectra of LC of XEN-564 in MT Soils Extracted by Methanol, Dissolved in CD_3OD.

suffice presently for additional structural identification. Assignment of C in liquid ^{13}C-NMR spectra was assigned based by Wilson (1981) and Schnitzer and Preston (1986; 1987). Assignment of H in ^{1}H-NMR are based on Wilson (1981) and Wilson et al. (1983).

The region in Figure 20 from 0 - 50 ppm is attributable to alkyl C chains with 10-20 as CH_3 and 23.9, 25, and 34 -47 region due to CH_2. The peaks at about 29.6, 31.5, and 33.8 are likely polymethylene C as $(CH_2)_n$. All CH_2s occur in normal, branched, and cyclic aliphatics. The region 48-56 is masked by the methanol (CD_3OD). The peaks at 62.6 and 64.8 (highest spectral peak) are chemical shifts that can be due to C in amino acids and carbohydrates. The shifts at 73.9 and 72-77 above baseline resonance can be carbohydrates or non-carbohydrate C's such as those reported by Schnitzer and Preston (1987). The peaks from 127-142 are shifts due to aromatic C. The sharp peaks at 161.9 and 164 are likely phenolic C. The peaks in the 171-184 region are possibly different types of COOH groups.

Figure 21 presents data for the ^{1}H-NMR spectrum from the same sample as that illustrated for Figure 20. Assignment of protons was as follows. The peaks at 0.85 and 1.0 are H of terminal methyl groups of methylene groups; 1.21 for H of methylene of methylene chains; 1.5 for H in methylene of alicyclic compounds; 1.8 and 1.95 for H of methyl and methylene groups α to aromatic rings or β H of indanes and tetralins; 2.08, 3.15, and 3.23 for H of methyl groups and methylene groups α to aromatic rings, H α to carboxylic acid groups, or α H of indanes and tetralins; 3.39, 3.6-3.8 for H α to C attached to O groups or sugars of carbohydrates; and 7.9 for H of aromatics

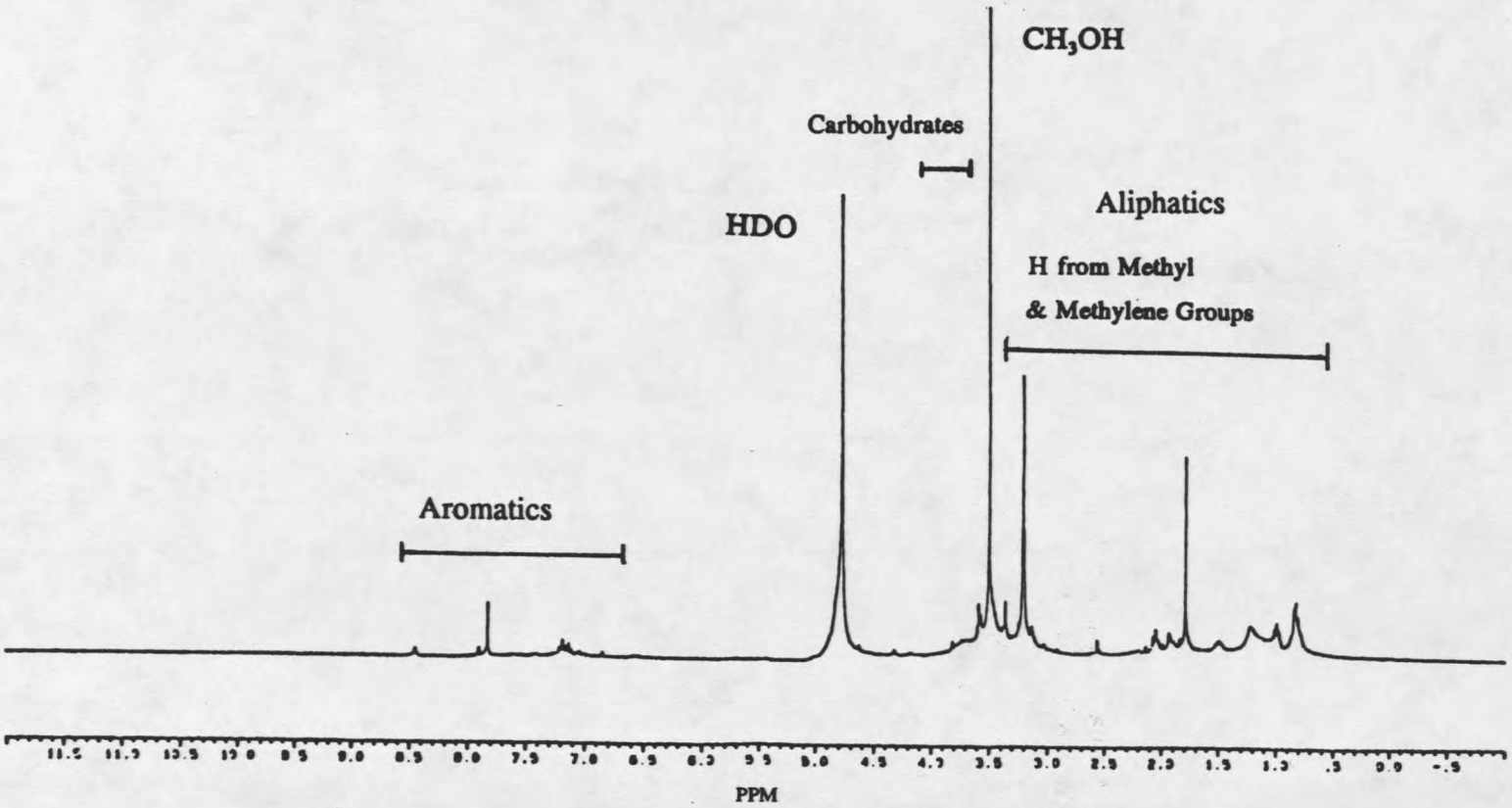


Figure 21. ^{1}H-NMR Spectrum of LC of XEN-564 in MT Soils Extracted by Methanol, Dissolved in CD_3OD.

including quinones, phenols, and O containing heteroaromatics. Integration after irradiation of the water peak of Figure 21, assuming non-exchangeable protons, indicated H attached to aromatic C at 8 percent, and to aliphatic C at 92 percent of which non-exchangeable carbohydrate H was at 26 percent. Similar groups were identifiable in Figure 22 (methylene chloride extract dissolved in $CDCl_3$). Figure 23 (NaOH extraction) showed peaks from 0.45 to 2.0 (aliphatic H) and peaks at 7.48 and 8.05 (aromatic H). Figure 24 resulted from a NaOH extraction acidified to pH = 5.8 (HCl), and exhibited peaks from 0-2 (aliphatic H) and the above baseline resonance region from 3.6-4.8 for H α to C attached to O groups which probably included carbohydrates, as well as HDO. Treatment of HCl will minimize, due to shifting, the influence of exchangeable H found in the 3-5 ppm area shift (Ruggiero et al., 1978). HCl treatment of NaOH extract should favor the expression of carbohydrates. Peaks for phenol (OH) and carboxyl were not present, suggesting no exchangeable H from these groups.

Elemental analysis (atomic absorption spectrophotometry) of resin extracted LC indicated the presence of measurable quantities of Cu, Fe, Mn, and possibly Zn. Many of these extracts were passed through a H^+ resin prior to measurement, which should have removed the majority of free or uncomplexed metals. The results should, therefore, represent metal-organic complexes (Sanders, 1983). Furthermore, carbonaceous adsorbents generally favor adsorption of organically complexed metals over free metals. Resin capsule controls (blanks) were made with identical 2 N NaOH extraction as the samples, but without H^+ treatment. No measurable amounts of free or complexed Cu, Fe, Mn, and Zn were attributable to the resin blanks. However, Zn contamination was

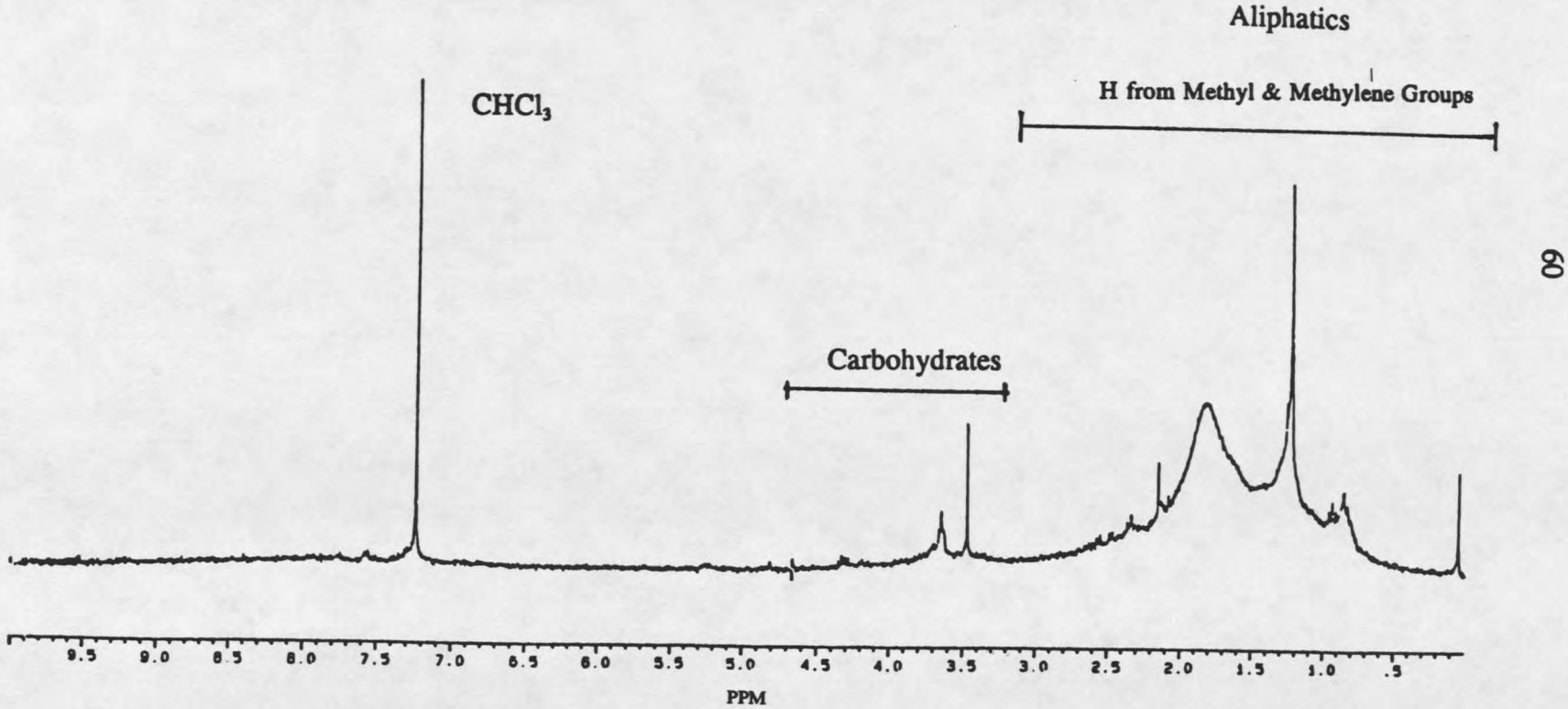


Figure 22. ^{1}H-NMR Spectrum of LC of XEN-564 in MT Soils Extracted by Methylene Chloride, Dissolved in $CDCl_3$.

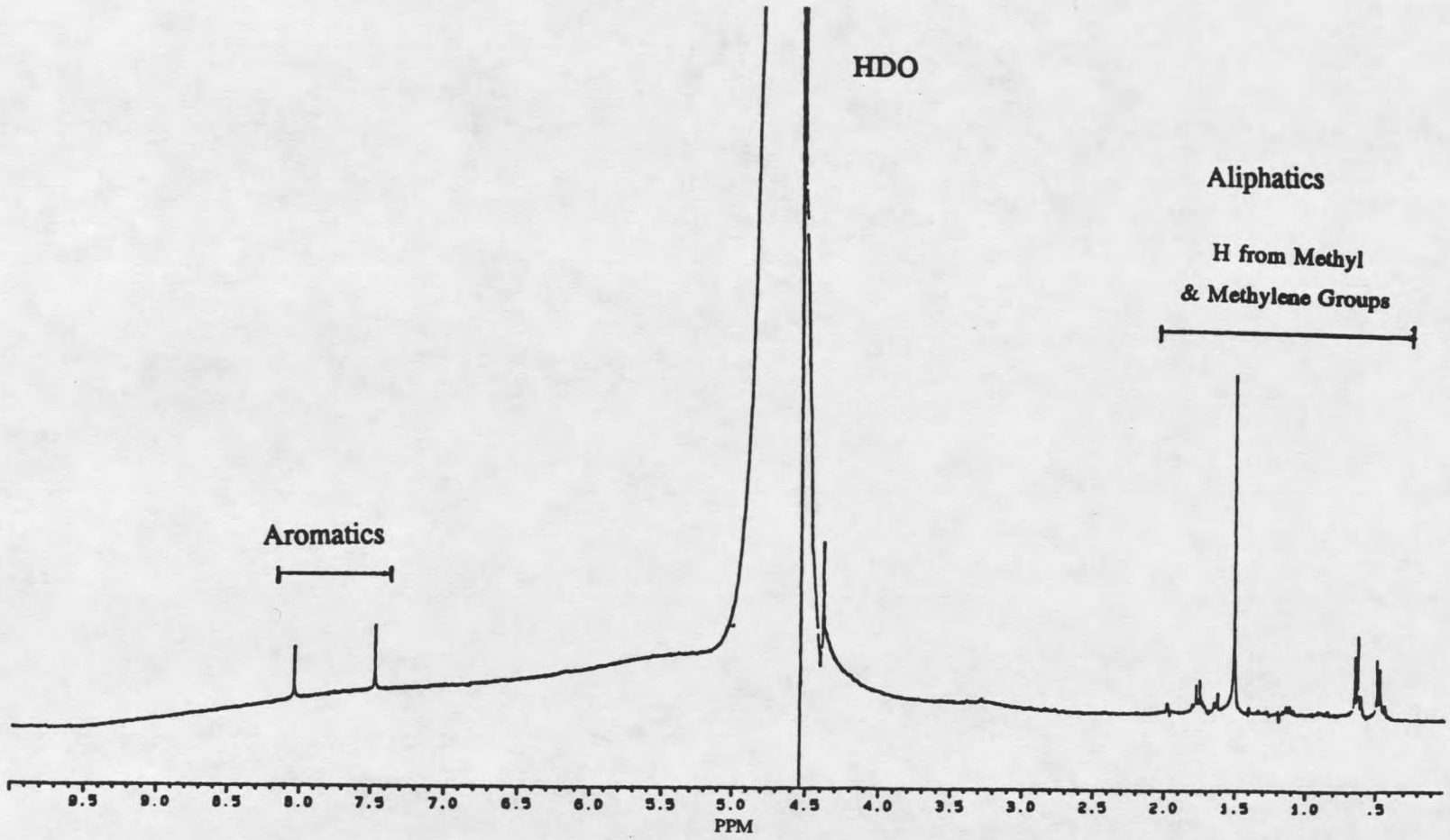


Figure 23. ^{1}H-NMR Spectrum of LC of XEN-564 in MT Soils Extracted by 0.05 M NaOH, Dissolved in D_2O.

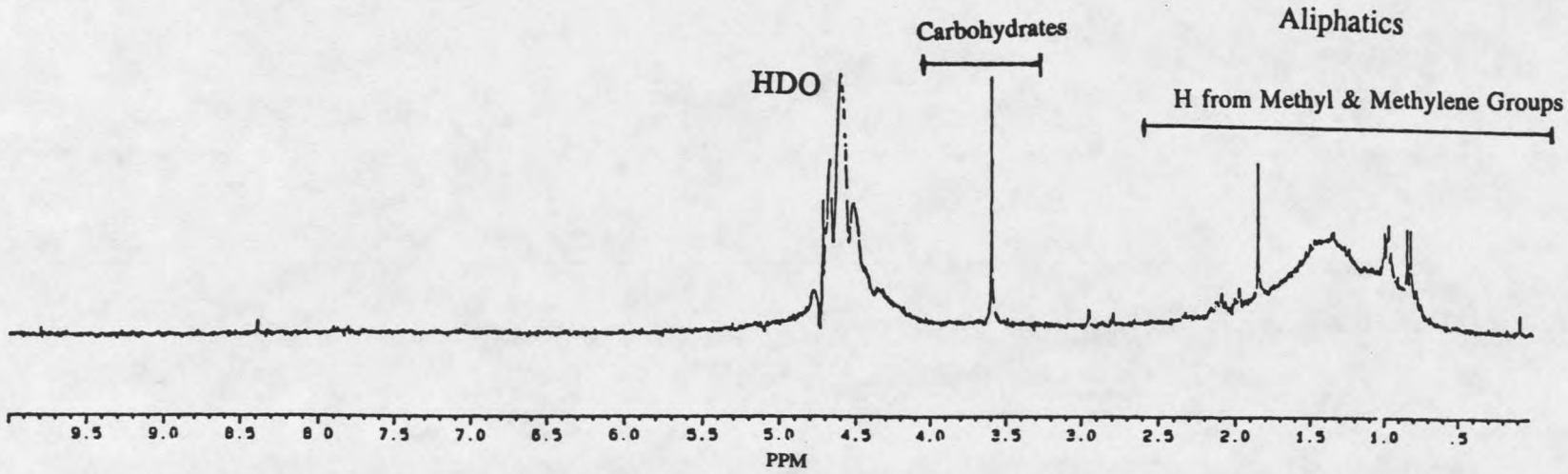


Figure 24. ^{1}H-NMR Spectrum of LC of XEN-564 in MT Soils Extracted by 0.05 M NaOH, Acidified to pH 5.8, Dissolved in D_2O.

sourced to the glass fiber filter (Whatman GF/A) employed in the extraction procedure.

The MX LC extracts of MT and PA soils showed levels (M x 10^{-6}) of 2.4-3.2 Cu, 7.2-15.6 Fe, and 0-7.8 Mn as probable organic complexes. These concentrations are 100 to 1000 times greater than those normally reported for these metals in soil solutions (Stevenson and Fitch, 1986). High levels of Zn were also found, but it remained impossible to quantify the levels originating from the LC sample and that coming from the glass fiber filter paper. It is most probable that some of this Zn was organically complexed since H^+ resin treatment should have removed a majority of the free Zn likely originating from this glass filter.

Measurable levels (M x 10^{-6}) of Cu, Fe, Mn, and Zn were also found in the extracts from the XEN-563, XEN-564, and XEN-572 resins for MT soils. Similar metal concentrations to those mentioned above were also found in an methanol extract from XEN-564 in MT soils. Methanol extraction is likely less destructive than NaOH (2 N) and could be more useful for specific organic identification studies. All sample weights were based on available quantities remaining after other analyses were completed, and no attempt was made to compare levels among resin types. Sample weights were all less than 150 mg. These results would suggest that the methodology has a potential for use in concentrating soil solution metal-organic complexes to allow analytical determination and evaluation.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Carbonaceous resin capsules were characterized and evaluated for testing of various soil organic characteristics (or properties) in two separate studies (Chapters 4 and 5). Six resin types were employed in this study. The carbonaceous resins were Carboxen-569, Carbotrap B and C, and the Ambersorb series XEN-563, XEN-564, and XEN-572. Also, Amberlite XAD-8 and Filtersorb-400 activated C were included for comparison because these are currently "standard" adsorbents. Resin capsule types were characterized by adsorption of dissolved soil fulvic (FA) and humic (HA) acids in a non-mixing resin sink (NMRS) system. These acids are appropriate materials for characterizing resin behavior in natural systems. This system allows for evaluation of rate-limiting processes which may not be determined from either a continuous flow or completely mixed batch reactor system. Such a system would be useful, for example, for *in situ* adsorption studies in soil. Soil testing evaluation was made by placing resin capsules in saturated soil pastes. The fraction of soil organic matter that can be adsorbed by the carbonaceous resin is described as labile soil C (LC). Thirty-one Montana and Pennsylvania soils were used in this study. Quantities of LC adsorbed by the resin capsule types were calibrated to soil organic C, N, P, and S. Components of LC were identified and characterized through the use of nuclear magnetic resonance spectroscopy,

infrared spectroscopy, and atomic absorption spectrophotometry.

The carbonaceous resins (type I adsorbents) used for the adsorption in solutions of dissolved soil FA and HA were characterized as having an initially high adsorption rate, followed by slower curvilinear adsorption over a period of several days. This behavior is common for many synthetic and natural porous adsorbents. Intraparticle diffusion appears to be adsorption rate-limiting in this NMRS system, as suggested from results of adsorption versus time relationships and effects of different FA concentrations. Differences in the amount of adsorption by specific resin types may be due to pore size differences, resulting in molecular size exclusion effects. The constant partitioning isotherm model described adsorption, resulting in linear adsorption ($r^2 > .96$, $P < .01$) over all temperatures (13 °C to 50 °C), at pH 7.0, and within the concentration ranges of FA (9-126 mg C/L) and HA (11-138 mg C/L) studied. Linear adsorption of FA over the entire concentration range studied suggests a homogeneous surface for the carbonaceous resins, which would differ from the heterogeneous surface of granular activated C. The polymeric XAD-8 resin was unable to adsorb low concentrations of FA and HA at normal soil pHs, but the carbonaceous resins functioned at all pH levels represented in the study. With carbonaceous resins, adsorption of FA increased with increasing temperature (13 - 50°C).

Values from thermodynamic calculations indicated a weak physical adsorption which is entropy driven, characteristic of a hydrophobic bonding process. The ability of carbonaceous resins to predict initial solution C concentration of both FA and HA after desorption using 2 N NaOH as the stripping solution was highly significant. This

indicates one potential of the use of carbonaceous resin capsules for quantitative environmental analysis and *in situ* monitoring. The results suggest that carbonaceous resin capsules have the ability to adsorb organic compounds under conditions normally found in natural soils and waters.

Results of soil LC adsorption by resin capsules over time indicated that intraparticle diffusion was adsorption rate-limiting. This supported results from solution adsorption of FA and HA in the resin characterization study. Increased adsorption of LC with increased temperature suggested entropy driven adsorption in soils.

In both MT and PA soils, 64-94 percent of LC fraction was composed of molecular weight less than 1000 daltons, with all molecular weights less than 10,000 daltons. Labile C was highly correlated to total soil C, Kjeldahl N, organic P, and organic S. Linear regressions of LC with these soil parameters indicated very significant ($P < .001$) relationships. Regressions were made by the statistically appropriate linear calibration of LC (Y values) on the various soil parameters (X values). The use of the resin Ambersorb XEN-564 resulted in the highest calibration with MT soils and a Carboxen-Carbotrap resin mixture was the highest in PA soils. One use of these calibrations would be for determining C and organic N, P, and S in soils, and all simultaneously.

Results from this study suggest that a partition-like mechanistic behavior exists between the LC fraction and solid C phase. The carbonaceous adsorbents used are generally non-ionic specific and it is proposed that their adsorption of LC actually modeled the behavior of the solid soil C phase.

Results also indicate that the methodology can be developed for the characterization and identification of humic and other organic compounds in soils. In these studies, the LC fraction contained aliphatic and aromatic structures, as well as carbohydrates and amino groups. The soluble C adsorbed by these resins strongly resembled the fulvic acid fraction of soils, based on results from nuclear magnetic resonance and infrared spectroscopy. This LC fraction was more aliphatic in character than aromatic, in agreement with previous studies dealing with soil FA and HA fractions. Organically complexed metals were found also. The resins adsorbed Cu, Fe, Mn, and Zn, apparently as complexes. The concentrations in the resultant resin extracts were 100 to 1000 fold higher than those found naturally in soil solutions. These analytical levels would overcome restrictions commonly encountered in the evaluation of organically complexed metals.

The methodology offers several unique advantages over current soil testing. Adsorption of measurable amounts of soil organic constituents occurred across a range of soil pHs. Adsorption was from saturated soil samples, and with no stirring or mixing. Adsorption at lower and variable soil moisture contents, such as *in situ* soil environments, would probably be sufficient for analysis if adequate time was allowed. Further development of the resin capsule technology for soil testing could provide the basis for simultaneous determination of both organic and inorganic soil components. One advantage with environmental implications would be the determination of soil C without the generation of toxic dichromate waste such as with the Walkley-Black method.

These carbonaceous resins were engineered for contaminant adsorption and have

been used successfully in laboratory studies to test soil and water samples for BXTs and other petroleum hydrocarbons (Hazard et al., 1991). Our results further indicate that the method allows for a non-destructive extraction of indigenous soil organic compounds for characterization and identification. Therefore, it is highly probable that carbonaceous resin capsules could be used for field monitoring of soil environmental pollutants, as well as for adsorption of naturally occurring organics *in situ*. Similar resins have also been used for trapping herbicides or other organics in air (Betz et al., 1989), so it is possible that the resins can act as a multi-phase extractor including the soil vapor phase. Development for use as an *in situ* monitoring device could eliminate the need to take repetitive, costly soil or water samples to detect leaking underground storage tanks, or for a myriad of other environmental applications.

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