⊛EPA ENVIRONMENTAL RESEARCH BRIEF

Characterization of Organic Matter in Soil and Aquifer Solids

M.J. Barcelona,[a] M.E. Caughey,[b] R.V. Krishnamurthy,[c] D.M. Shaw,[c] and K. Maas[c]

Abstract

The focus of this work was the evaluation of analytical methods to determine and characterize fractions of subsurface organic matter. Major fractions of total organic carbon (TOC) include: particulate organic carbon (POC) in aquifer material, dissolved organic carbon (DOC) and both volatile (VOC) and non-volatile (NVOC) organic carbon sub-fractions.

POC makes up the bulk of TOC in contaminated and uncontaminated subsurface soils and aquifer materials. The volatile subfraction of POC can be determined quantitatively when minimally disturbed sub-cores are preserved immediately in the field. Methanol and acid addition (i.e. , HCl, $NaHSO_4$) to pH 2 are adequate preservatives for specific volatile organic compound determinations. An interlaboratory round-robin test to improve acidification and removal methods for carbonates in total carbon using sulfurous acid (H_2SO_3) showed sensitivity to several factors. These factors include: operator care, acid strength and carbon content, and particularly, the incomplete removal of inorganic carbon at high total carbon to organic carbon ratios.

Stable isotopic characteristics of NVOC from fuel contaminated and organic-enriched environments were found to be quite sensitive to the stable isotopic signatures of natural organic matter. The extractability of POC by a range of high to medium polarity solvents resulted in the observations that relatively little POC was extractable and water extracted comparable amounts to 1:1 mixtures of 0.01M KOH in methanol:toluene.

Introduction

Organic matter in subsurface systems is a complex mixture of natural organic substances, fossil fuels and a variety of synthetic compounds. The transport and fate of organic contaminants is quite dependent on the nature and distribution of organic carbon in general.

Dispersion, sorption and degradation are processes which affect organic compound transport and fate. The estimation of the influence of these processes depends heavily on the quantitative determination of fractions of organic carbon in soils and aquifer materials (Powell et al., 1989). Conventional contaminant analytical methods have focused on constituents in fuels and synthetic mixtures (e.g., solvents, plasticizers and other chemicals) (Keith, 1991). Methods for determining volatile and non-volatile organic carbon (i.e., VOC and NVOC) in dissolved (DOC) and particulate (POC) fractions have seen relatively little attention in the literature or practice of subsurface environmental chemistry (Thurman, 1985).

Methods for the determination of major carbon subfractions, as well as the specific organic compounds of which they are composed, must be based on quantitative preservation, separation, and analytical methods which lend themselves to routine practice. In this way, the roles, identity, and fates of specific organic contaminants may be incorporated into process-level hydrogeological investigations.

[a]Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI 48109-2099.
[b]Office of Environmental Chemistry, Illinois State Water Survey, Champaign, IL 61820.
[c]Departments of Geology and Chemistry, Western Michigan University, Kalamazoo, MI 49008.

The present study was organized around the analytical determination of organic carbon fractions. Each fraction was related to the matrix it was associated with given its volatility, extractability/ polarity and its probable origin as identified by the stable isotopic characteristics of the carbon.

This operational categorization of total carbon is shown in Figure 1. Corresponding separation and analytical methods to selected categories in Figure 1 are shown in Table 1.

The primary objectives of the study address aspects of Figure 1 and Table 1 which are central to the routine application of carbon fractionation methods. These objectives were:

1) Refinement of the acidification step (i.e., TIC removal) techniques for the quantitative determination of non-volatile organic carbon ($NVOC_p$) in aquifer materials. Testing of the methodology in an interlaboratory round-robin trial. This objective addresses problems associated with Category 1 and 2 analyses.

2) Evaluation of in-field preservation techniques for sub-cores of split-spoon or piston cores of subsurface materials coupled with methods to determine VOC_p and $NVOC_p$ at the elemental and specific compound level. This objective addresses issues involved in Category 3.

3) Initial development of an extractability procedure to characterize the leachability of various fractions of organic matter by varying polarity solvents as shown in Category 4. and,

4) Evaluation of established stable carbon isotope methods to determine their potential to distinguish contaminant vs *natural* organic carbon in subsurface materials on the basis of $^{13}C/^{12}C$ ratios. These experiments pertain to the origin of organic fractions in Category 5.

The approach to these objectives focused on aquifer materials from reasonably well characterized fuel, solvent or organic leachate contaminated as well as uncontaminated sites. Most of these sites exhibited glacial or fluvioglacial geologic materials of low organic carbon content. Volatile organic compounds are among the most common ground-water contaminants and represent significant problems in quantitative sampling and analysis.

Experimental Procedures

Site Descriptions

The sites from which aquifer solid or ground-water samples were collected are listed in Table 2. Most of the samples were collected by opportunity in the course of collaboration with other researchers.
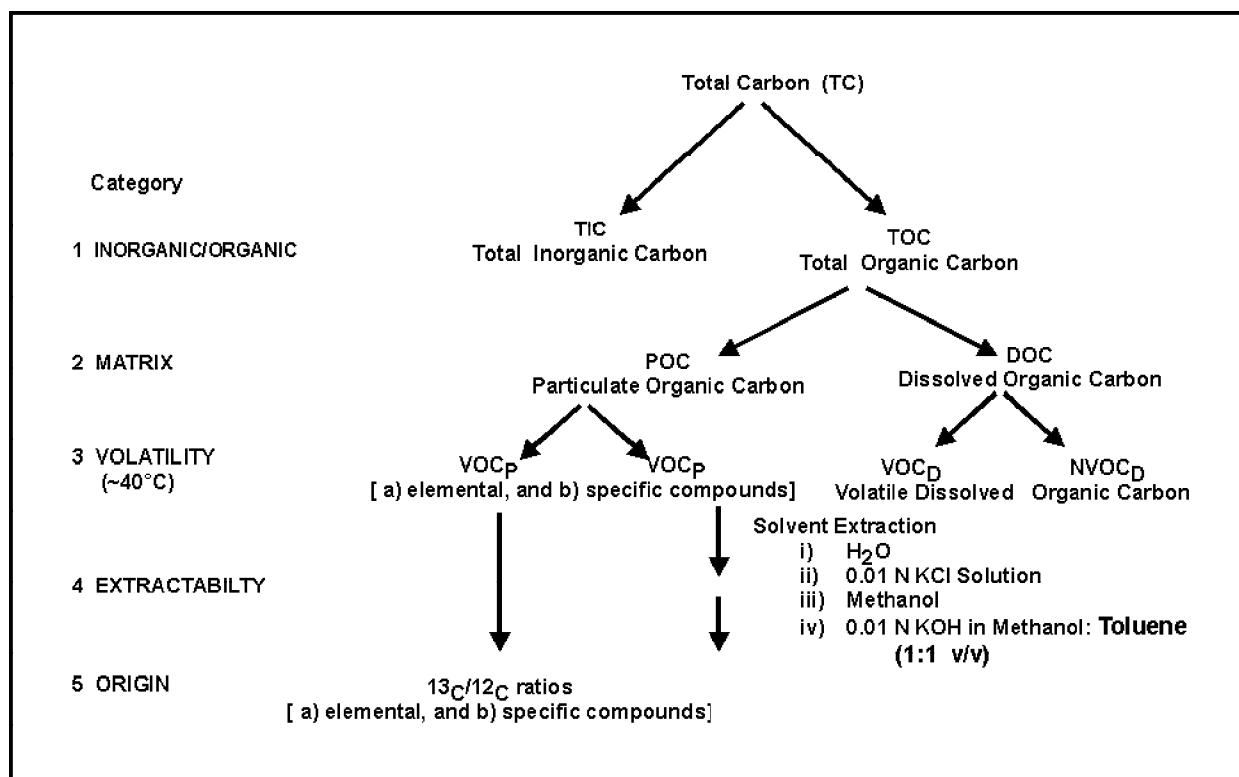

Figure 1. *Operational categories of subsurface carbon.*

Table 1. *Separation and Analytical Methods Corresponding to Selected Particulate Carbon Fractions*

Category	Carbon Fraction	Subfraction	Separation	Analysis
1	TIC		CO_2 removal by acidification of TC[1,2]	CO_2 by infrared spectrometry or coulometry
2	POC		Combustion of residue on acidification of TC to release CO_2[1,2]	(as above)
3	VOC_P $NVOC_P$		Infield preservation of sub-cores[3,4]	
	a) VOC_P (elemental)		Volatilization at $>40^O C$	Combustion of off-gases O_2 to CO_2 (CO_2 as above)
	b) VOC_P (specific compounds)		Volatilization at $>40^O C$	Dynamic or static head-space GC with selective detectors
	a) $NVOC_P$ (elemental)		POC as above	POC as above
	b) $NVOC_P$ (specific compounds)		Extraction of solid sub-core with organic solvents[5]	Various gas or liquid chromatographic methods
4	$NVOC_P$	i) weakly-sorbed room temperature (extraction solvent)	H_2O	Combustion of dried sample extract at $950^O C$ to CO_2 with CO_2 as determined in 1 above
		ii) weakly-sorbed/ ion-exchangeable	0.01NKCl solution	
		iii) strongly sorbed/ Hydrogen-bonded	Methanol	
		iv) bound/occluded[5,6]	0.01NKOH in Methanol:Toluene (1:1 v/v)	
5	VOC_P (a) (elemental)		Volatilization at $>40^O C$ off-gas combustion in O_2 to CO_2	Isotope-ratio mass spectrometry of CO_2
	$NVOC_P$ (a) (elemental)		Combustion of residue from volatilization in O_2 to CO_2	Isotope-ratio mass spectrometry of CO_2 [7]
	VOC_P (b) (specific compound)		GC separation of off-gas from volatilization step followed by on-line combustion in O_2 to CO_2	Isotope-ratio mass spectrometry of CO_2
	$NVOC_P$ (b) (specific compound)		GC separation of solvent extraction from 3 or 4 above followed by on-line combustion in O_2 to CO_2	Isotope-ratio mass spectrometry of CO_2

GC = Gas Chromatography

[1] Powell et al. (1989).
[2] Caughey et al. (1995).
[3] Hewitt et al. (1992).
[4] Siegrist and Jenssen (1990).
[5] Barcelona et al. (1995).
[6] Modified from Cheng (1990).
[7] Waasenaar et al. (1991).

Sampling Methods

Samples of aquifer solids and ground water were collected from six sites contaminated with mixed organic wastes or petroleum fuel mixtures. Water samples were collected by pumping or bailing existing monitoring wells at three underground storage tank (UST) sites in Houston, Texas; the former site of Casey's Canoe Livery at Sleeping Bear Dunes State Park in Empire, Michigan; an anaerobic treatment impoundment of meat processing wastes in Beardstown, Illinois; a clean site at Sand Ridge State Park in Illinois; and, a fire-training area at decommissioned Wurtsmith AFB in Oscoda, Michigan. The sampling sites were all in shallow unconfined aquifers which had experienced contamination over extended time periods (i.e., >minimum 5 years). With the exception of the Beardstown and Sand Ridge sites, the other sites had known BTEX (benzene, toluene, ethylbenzene and xylenes) contamination in the ground water.

The water samples at the UST sites were collected by a private consultant under the direction of Dr. Joseph Salanitro, Shell Development Co. Aquifer solid samples were subsampled from rig drilled cores at the Sleeping Bear Dunes site. All samples were refrigerated at $4^{\circ}C$ after collection and water samples were preserved by adjustment to pH 10 with KOH. Samples for BTEX determinations were preserved in the field with HCl to pH 2 prior to refrigeration and transported to the laboratory.

Analytical Methods

The common elements in analytical determinations which were accomplished on categories 1, 2, 3a $NVOC_p$, 4, and 5a, are that they could be referenced to verifiable primary standards. These include: National Institute of Standards Dolomite Standard Reference Material (SRM) #88 and potassium hydrogen phthalate. The determinations of volatile fractions 3b) VOC_p and $NVOC_p$ were straightforward applications of U.S. EPA Methods 601/602 (Keith, 1991) for which there are well-referenced standards. Elemental carbon determinations on VOC fractions were done on a compound specific basis (i.e., carbon content per compound) by static headspace capillary gas chromatography using EPA 601/602 methods with simultaneous photoionization and electrolytic conductivity detectors. Unknown compounds were quantified as dichloroethylene for chlorinated aliphatics or benzene for aromatic compounds. In all cases VOC_P samples were collected as cut-off syringe subcores (Hewitt, 1995) preserved with 50:50 methanol:H_2O or 1% $NaHSO_4$ solution.

The details of the acidification and analysis steps for $NVOC_p$ determinations were modified from Acton and Barker (1992) and are reported in Caughey et al. (1995). Four aquifer material *standards* of varying TOC/TC ratios were ground to pass 200 mesh. Along with National Institute of Standards SRM 88b-Dolomite, the ground solid samples were distributed to eight laboratories. These test materials are described in Table 3.

Table 2. *Description of Study Sites*

Site/(Location)	Contaminant Mixture	Geologic Materials
Asylum Lake (Kalamazoo, MI)	None	Glacial outwash sand/gravel-postglacial alluvium[1]
Beardstown/Sand Ridge State Park (Central Illinois) Leachate	Meat processing treatment impoundment	Glacial sands with some interbedded gravels[2]
Kalamazoo-Battle Creek Airport	Fuels and solvents from aircraft maintenance	Glacial sands and gravels with fill material[1]
Service Station Sites (Houston, TX)	Motor fuels from underground tanks	Low permeability silty sands/clays[3]
Sleeping Bear Dunes State Park (Empire, MI)	Motor/heating fuels from underground tanks	Coastal lacustrine sand-dunes[4]
Wurtsmith AFB (Oscoda, MI)	Jet fuel, chlorinated solvents from fire-training exercises	Fluvioglacial sands/gravels with aeolian dune deposits[5]

[1]Hydrogeology Field Course, Western Michigan University, Summer, 1992.

[2] Barcelona et al., 1989.

[3]Personal Communication, Dr. Joseph Salanitro, Shell Research, Houston, TX.

[4]West et al., 1994.

[5]Cummings and Twenter, 1986.

Overall, they covered a wide range of TIC at low TOC contents. The TIC in the samples was contributed by dolomite (e.g., 99.5% for Test Material #1 (TM1) to mixed calcite and dolomite mineralogy. Reagent grade 6% H_2SO_3 from the same lot was also sent to each lab after the carbon content of the acid was measured and confirmed to be less than 1 µg-C/ml. Round-robin participating laboratories were instructed to use the identical acidification procedure employing individual samples of >0.1g for five replicates on each of the five test materials.

Solid samples for parallel (i.e., duplicate solid portions for each solvent) or sequential (i.e., one set of duplicate solid portions for successive extraction by all solvents) extraction by the four solvents were air dried, and extracted at a 2:1 ratio of solid:extractant (i.e., ~100g/50ml) in amber glass jars with PTFE (polytetrafluoroethylene) lids. Extractions were conducted at room temperature for eight hours on a reciprocating shaker. The slurries were then centrifuged at ~2000g for an hour and then decanted. The extractions were repeated, combined with the previous decantate, volume adjusted and handled as water samples for NVOC or specific organic compound determinations.

Stable carbon isotope determinations on $NVOC_p$ and TIC samples were done by the method of Epstein et al., (1987) and CO_3^{2-} equilibration methods, respectively. Results were expressed in conventional per mille (0/00) del (d) notation relative to the Pee Dee Belemnite standard.

Results and Discussions
The full details of the results on each of the primary objectives of the work are contained in literature publications. The major highlights of the results are discussed below with reference to the publications.

Quantitative Determination of Non-Volatile Organic Carbon (NVOC)
Seven of the eight laboratories (designated A through G) fully participated in the round-robin study of TIC removal methods of NVOC determinations (Caughey et al., 1995). The details of their execution of the round-robin procedures are summarized in Table 4. Initially it was planned that mean reported TOC values would be used as the target values with which laboratory accuracy would be compared. However, the errors in the datasets were systematically biased rather than random and this was not possible. The pooled Total Carbon (TC), TIC and TOC (i.e., NVOC) results for the study are shown in Table 5. Interlaboratory agreement was best for TC and TIC for all five test materials. These results underscore the excellent accuracy and precision of combustion and coulometric endpoints for CO_2 quantitation. The TOC results showed significant scatter, however, particularly at high TIC to TOC ratios.

This study confirmed the results of previous literature contributions citing incomplete TIC removal as the most significant source of error in NVOC determinations. Clearly, the use of commercial sulfurous acid does not represent the answer to this problem. This work and more recent efforts (Heron et al., 1996) commends the use of strong non-oxidizing mineral acid (e.g., H_3PO_4, HCl etc.) for TIC removal from aquifer solids. The grinding of samples to grain sizes less than 0.063 mm and below is also recommended, provided a shatterbox rather than a high speed rotary grinder can be used. The principal journal publication from this work (Caughey

Table 3. *Test Material Descriptions*

Test Material	Description (depth interval)	Major Mineral by x-ray Diffraction XRD (Percentages)	Approximate Values		
			TC (mg g⁻¹)	TOC (mg g⁻¹)	TIC (mg g⁻¹)
1	NIST SRM 88b	Dolomite, 99.5; quartz, 0.5	126.5	0.5	125.9
2	Aquifer material core A (76-98 cm)	Quartz, 63.1; dolomite, 18.0; feldspars, 13.6; calcite, 5.2	28.8	1.7	27.2
3	Aquifer material core A (262-284 cm)	Quartz, 87.0; feldspars, 5.9; dolomite, 5.5; calcite, 1.6	12.8	2.1	10.0
4	Aquifer materials core SC (317-415 cm)	Quartz, 54.5; dolomite, 28.9; calcite, 9.4; feldspars, 7.2	48.2	0.6	46.9
5	Aquifer material core 40 (60-125 cm)	Quartz, 91.6; feldspars, 5.2; dolomite, 2.6; calcite, 0.5	19.6	13.5	4.6

Table 4. Method Details for Seven Participating Laboratories

Lab ID	Replicate Weight (mg)	Total Acid Used (ml)	TOC Instrument	Comments
A	30-90	9	UIC 5000	Samples were acidified before transfer to combustion boats
B	20-30	12	LECO WR-112	Porous combustion crucibles leaked acid
C	20-50	3-18	UIC 5000	
D	20-30	3-18	UIC CM 120	Salt crust hindered sample acidification
E	400-800	5-9	LECO CS-225; Dohrmann DC1800	Used 2M HNO_3 for acidification; determined TOC as ASOC + AIOC
F	250-500	9-12	LECO CS-444	Did not determine TIC
G	80-130	9	UIC	

Table 5. Pooled Round-Robin Test Results for Carbon Determinations

Parameter (units)	TM 1	TM 2	Test Material TM 3	TM 4	TM 5
Pooled TOC mean ($mg\ C\ g^{-1}$)	50.99* (35.85) [70%]	5.07* (5.79) [114%]	2.75 (2.04) [74%]	11.87* (13.84) [117%]	13.52 (2.16) [16%]
Pooled TC mean ($mg\ C\ g^{-1}$)	126.70 (1.84) [1.5%]	28.84 (1.43) [4.9%]	12.83 (0.78) [6.1%]	48.54 (2.17) [4.4%]	19.63 (0.96) [4.9%]
Pooled TIC mean ($mg\ C\ g^{-1}$)	125.67 (0.37) [0.3%]	27.18 (0.74) [2.7%]	9.97 (0.45) [4.5%]	46.91 (1.00) [2.1%]	4.55 (0.92) [20.3%]
TOC_{EST} ($mg\ C\ g^{-1}$)	1.03	1.66	2.86	1.63	15.08
TIC/TOC_{EST}	122	16	3.5	29	0.30

NOTE: Asterisks indicate biased values where the estimated error was greater than 100%. Values in parentheses are standard deviations; values in brackets are relative standard deviations.

et al., 1995) provides a detailed description of the procedural recommendations.

It should be noted that TOC errors of a factor of two or more would have a significant impact on the value of K_{OC} input to an estimation of retardation coefficients. This level of error may be routinely observed in samples with high TIC to TOC ratios (i.e., >10) and dolomite percentages above 15%. Practically, these analytical problems may be expected in studies involving glacial or carbonate aquifer solid samples.

Evaluation of In-field Aquifer Solid Preservation Techniques for VOC Determinations

There has been a great deal of recent concurrent work on the preferred means of preservation of VOC samples. The results of this work reported along with those of other groups (Siegrist and van Ee, 1994) and (Wisconsin DNR, 1994) strongly support the following:

1) Immediate field preservation of core material in 40 ml of headspace vials with mineral acid, methanol, or sodium bisulfate is necessary to perform accurate VOC determinations;

2) Syringe sub-sample collection from cores minimizes sample disturbance and handling time which leads to higher and more reproducible recoveries;

3) Negative bias (i.e., low results) levels are greater for compounds which are more volatile and less strongly sorbed; and

4) Bulk jar sampling of core materials without preservation other than refrigeration leads to gross negative bias in VOC determinations.

The limited results of the present study were in close agreement with those of more systematic investigations reported above. The primary references including Barcelona et al., 1993 and Barcelona et al., 1995 should be consulted for complete details.

Extractability of NVOC by Solvents of High to Medium Polarity

Fifteen samples of aquifer materials from several sites were taken in parallel (i.e., individual solid samples for each extraction solution) and sequentially (i.e., single solid samples taken through the series of extractions). The extracting solutions and the operational leachability fraction they represent included:

Extractant	*Leachability Fraction*
1. Distilled H_2O	Weakly Sorbed
2. 0.01N KCl	Weakly Sorbed/Ion Exchangeable
3. Methanol (MeOH)	Strongly Sorbed/Hydrogen Bonded
4. MeOH-0.01N (KOH/Toluene) (1:1 V/V)	Bound/Occluded

The results of these extractions are shown in Tables 6 and 7 for the parallel and sequential methods, respectively. In general, MeOH and the MeOH-KOH/toluene extracted more of the total extractable carbon than the aqueous solvents (e.g., H_2O and KCl solution). For both contaminated and uncontaminated solids, the percent carbon extractable by the aqueous based solvents, which might be leached easily, was less than 50% of the total. Parallel extraction tended to extract more total carbon than the sequential method. This might be explained by the full rehydration of the solid samples by the preceding aqueous extractions in the sequential case which reduced the effectiveness of *stronger* solvents.

The extractability of carbon from the Sleeping Bear Dunes samples is shown graphically in Figure 2. There was a clear trend in apparent leachability as a function of position in the flow field. That is, *source* zone organic matter was less extractable than background or downgradient samples. This may be expected due to lower hydraulic conductivity and perhaps interconnected pore space near fuel product masses. It was unresolved why methanol and the alkaline methanol:toluene differed greatly in their extractability of the hydrocarbon contaminants.

Evaluation of Stable Carbon Isotope Characteristics of Major Carbon Fractions

In this portion of the work it was anticipated that significant differences could be observed in the stable carbon isotopic ratios (i.e., $^{13}C/^{12}C$) between TIC and TOC fractions. This was because of their likely carbonate mineral and plant matter origins, respectively. Mineral carbonates typically show $d^{13}C$ values of ~0 o/oo relative to the Pee Dee Belemnite standard. Organic carbon from fossil fuels and plants exhibit $d^{13}C$ values -20 to -28 o/oo. In the d notation, this reflects depletion of ^{13}C relative to the standard in parts per thousand and is termed isotopically depleted (lighter). It was also hoped that petroleum contaminated samples would differ significantly in $^{13}C/^{12}C$ ratios from both of the above end members and isotopic shifts (Suchomel et al., 1990) or in PIC or POC fractions from transformation of the contaminants.

The samples for this part of the study were collected from the Sleeping Bear Dunes, Beardstown and Sand Ridge sites which were petroleum or meat processing contaminated and uncontaminated, respectively.

The limited selection of sampling sites and types of contamination did not permit a comprehensive conclusion to be drawn on the utility of stable carbon isotope determinations to differentiate natural organic carbon from fuel hydrocarbons in aquifer solids. A summary of the overall data set (Table 8) suggests that distinct differences in the $d^{13}C$ signatures of NVOC and PIC exist between both the saturated and unsaturated zones at contaminated and uncontaminated sites. Unsaturated zone $d^{13}C$ natural NVOC was ~6 o/oo heavier than that in the saturated zone possibly reflecting transformation of the original organic mixture. A recent study by Landmeyer et al. (1996) should be consulted for the use of $d^{13}C$ signatures as a function of the redox environment in which transformations proceed.

The petroleum contaminated samples from the Sleeping Bear site were intermediate between these values. This indicated that the weathered fuels at this site were quite close to plant-derived organic matter in stable carbon isotope characteristics. In general, fossil liquid hydrocarbon mixtures as well as refined products

Table 6. *Average Organic Carbon In Parallel Extracts of Aquifer Solids*

	Sample	Total C (mg/g)	H_2O	Extracts KCl (mg C/g)	Methanol	KOH/ methanol toluene	Total Extract (mg C/g)	Percent Extractable
1001	SB Background 54E 5.5-6.0	770	82.3	47.9	114	187	431	56
1002	WMU AP/NPWH Airport Spill	1730	180	123	377	326	1006	58
2	SB-40' Cluster 4.9-7.4'	4600	54.7	15.0	146	230	446	10
3	Carson City Ref. 16'	722	21.3	32.0	80.2	201	335	46
4	SB-90' Cluster 5.0-7.8'	1111	31.0	18.7	48	135	233	21
5	SB-90' Cluster 2.0-4.7'	2433	73.6	47	<1.0	<1.0	121	5
6	SB-40' Cluster 4.8-6.9'	658	45.1	110	31.3	37.9	224	34
7	SB-40' Cluster 2.0-4.1'	8322	87	43.5	45.9	229	405	5
8	SB-Source Cluster 10.6-13.6'	1020	14.7	<1.0	129	21.0	165	16
9	SB-Source Cluster 7.4-10.5	1162	<1.0	57	12.5	37.6	107	9
	<u>ASYLUM LAKE</u>							
10	AL-5'	1223	2.7	<1.0	11.7	51.2	66	5
			0	5.8	5.9	61.2	72.9	6*
11	AL-15'	615	11.4	28.6	31.4	119	190	31
			34.8	51.3	65.7	163	314	51*
12	AL-25'	317	16.6	61.3	37.8		116	37
13	AL-35'	806	-	-	-	-	-	-
14	AL-45'	123	-	-	-	-	-	-
15	AL-55'	123	17.2	112	36.4	34.0	199.6	162

- = samples too low for quantitation
* replicate determinations (other chemists)
SB samples = Sleeping Bear Dunes, Empire, Michigan

range between -24 to -30 o/oo d[13]C. Contaminated ground water and soil gas samples from this site were somewhat heavier -22.3 o/oo (n=1) and -22.9 ± 0.1 (n=4), respectively. These samples reflect an isotopic shift towards heavier isotopic signatures which could be expected from microbial remineralization of either natural plant or petroleum-related organic carbon.

It was clear from these data that though the stable isotopic differences between plant and weathered-petroleum product organic carbon were not overwhelming they were significant and measurable. The work of Suchomel et al. (1990) incorporated ^{14}C determinations into the interpretation of stable carbon ratios and

the origin of organic matter. Their approach should be valuable in identifying the contribution of recent or synthetic carbon in NVOC mixtures in aquifer solids.

Conclusion
The focus of this work was the evaluation of analytical methods to determine and characterize fractions of subsurface organic matter. Major fractions of total organic carbon (TOC) include: particulate organic carbon (POC) in aquifer material, dissolved organic carbon (DOC) and both volatile (VOC) and non-volatile (NVOC) organic carbon subfractions.

Table 7. *Average Organic Carbon In Sequential Extractions of Aquifer Solids*

|	Sample	Total C (mg/g)	Extracts H₂O	KCl (mg C/g)	Methanol	KOH/ methanol toluene	Total Extract (mg C/g)	Percent Extractable
1001	SB Background 54E 5.5-6.0'	770	91.7	13.9	104	4.6	214	27.8
1002	WMU AP/NPWH Airport Spill	1730	60.6	59.1	75.2	66.4	261	15.1
2	SB-40' Cluster 4.9-7.4'	4600	0	6.4	17.2	7.5	31.1	0.7
3	Carson City Ref. 16'	722	5.7	0	6.0	0	11.7	1.6
4	SB-90' Cluster 5.0-7.8'	1111	30.5	6.2	65.2	57.4	159	14.3
5	SB-90' Cluster 2.0-4.7'	2433	22.6	64.7	82.4	36.5	206	8.5
6	SB-40' Cluster 4.8-6.9'	658	4.0	0	32.4	30.2	66.6	10.1
7	SB-40' Cluster 2.0-4.1'	8322	9.3	0	46.0	24.2	79.5	1.0
8	SB-Source Cluster 10.6-13.6'	1020	0	35.6	53.5	41.0	130	12.8
9	SB-Source Cluster 7.4-10.5	1162	16.6	82.5	45.0	60.3	204	17.6
	ASYLUM LAKE							
10	AL-5'	1223	-	-	-	-	-	-
11	AL-15'	615	-	-	-	-	-	-
12	AL-25'	317	52.6	58.6	67.1	53.4	232	73.0
13	AL-35'	806	0.9	6.8	44.4	16.6	68.7	8.5
14	AL-45'	123	11.7	22.5	110	31.7	175.9	143
15	AL-55'	123	25.6	162	54.5	51.6	294	239

- = samples too low for quantitation.
SB = Sleeping Bear Dunes, Empire, Michigan.

POC makes up the bulk of TOC in contaminated and uncontaminated subsurface soils and aquifer materials. The volatile subfraction of POC can be determined quantitatively when minimally disturbed subcores are preserved immediately in the field. Methanol and acid addition (i.e., HCl, $NaHSO_4$) to pH 2 are adequate preservatives for specific volatile organic compound determinations. An interlaboratory round-robin test to improve acidification and removal methods for carbonates in total carbon using sulfurous acid (H_2SO_3) showed sensitivity to several factors. These factors include: operator care, acid strength and carbon content, and particularly, the incomplete removal of inorganic carbon at high total carbon to organic carbon ratios.

The extractability of POC by a range of high to medium polarity solvents resulted in the observations that relatively little POC was extractable and water extracted comparable amounts to 1:1 mixtures of 0.1M KOH in methanol:toluene. Stable isotopic characteristics of NVOC from fuel contaminated and organic-enriched environments were found to be quite sensitive to the stable isotopic signatures of natural organic matter.
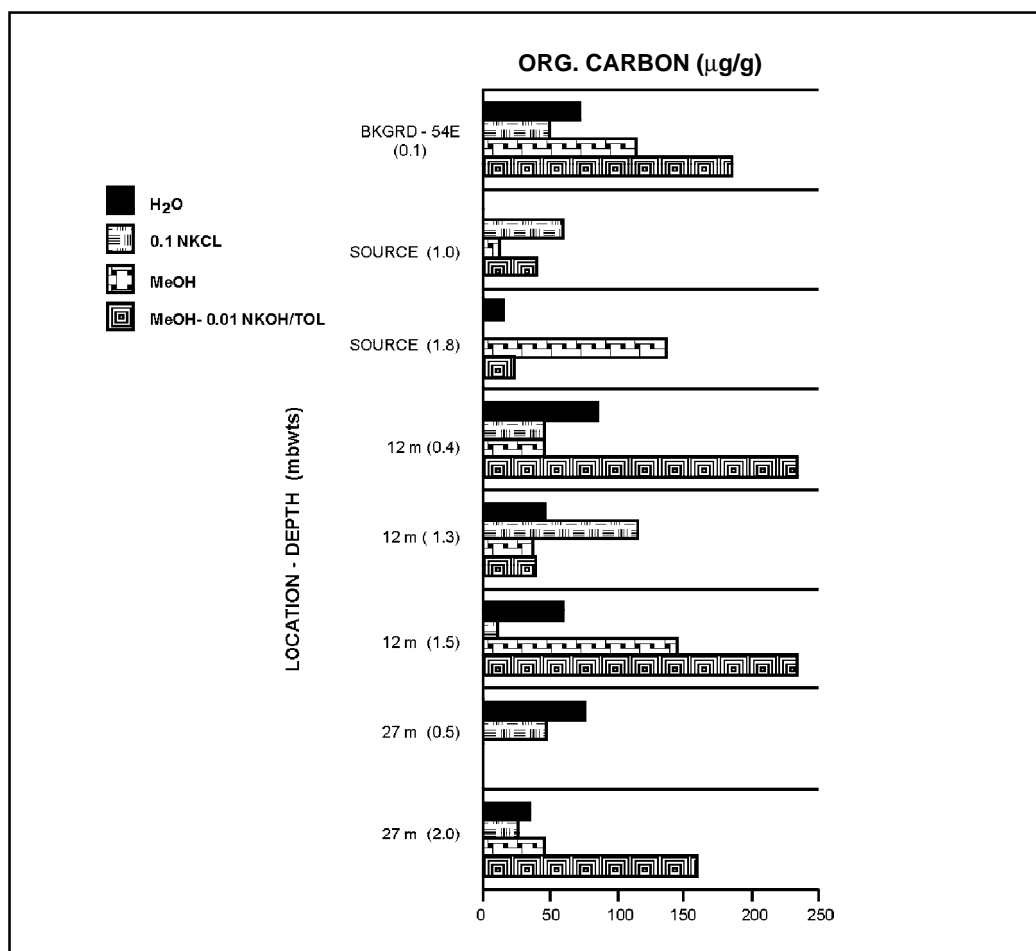
Figure 2. *Average Extractable Organic Carbon for Selected Sleeping Bear Dunes Samples (mg/g). Locations are designations: background, in source area, and 12m and 27m downgradient from source, respectively. Parentheses denote depth in meters below land surface at each location.*

Table 8. *Summary of Average $^{13}C/^{12}C$ (d o/oo) Ratios in Non-Volatile Carbon Fractions*

		Organic Carbon		n	Inorganic Carbon	n
(parentheses denote relative standard derivations)						
Uncontaminated						
Unsaturated Zone	SR	-21.5	(17%)	4	-15.7 (25%)	3
	BTU	-22.5	(11%)	2	-19.2	1
	BTD	-22.1	(5%)	6	-22.1 (9%)	6
Saturated Zone	SR	-27.6	(1.5%)	3	0.8	1
	BTU	-28.2	(1.4%)	10	-14.1 (28%)	3
Contaminated						
Saturated Zone	BTD	-27.1	(6.3%)	4	0.5	1
	SB	-25.5	(0.1%)	6	0.0	1

SR   *Sand Ridge.*
SB   *Sleeping Bear.*
BTU   *Beardstown Upgradient.*
BTD   *Beardstown Downgradient.*

References

Acton, D.W. and J.F. Barker (1992). In-Situ Biodegradation Potential of Aromatic Hydrocarbons in Anaerobic Ground-Water. J. Contam. Hydrol., 9: 325-352.

Barcelona, M.J., T.R. Holm, M.R. Schock, and G.K. George (1989). Spatial and Temporal Gradients in Aquifer Oxidation-Reduction Conditions. Water Resour. Res., 25 (5): 991-1003.

Barcelona, M.J., J. Lu and D.M. Tomczak (1995). Organic Acid Derivatization Techniques Applied to Petroleum Hydrocarbon Transformations in Subsurface Environments. Ground Water Monit. Remediat., 15(2):114-124.

Barcelona, M.J., D.M. Shaw, J. Lu, D. Tomczak and C. Virkhaus (1993). Volatile Organics In Soil Symposium, Eds: Robert L. Siegrist and J. Jeffrey Van Ee, Las Vegas, NV, Jan. 1993.

Caughey, M.E., M.J. Barcelona, R.M. Powell, R.A. Cahill, C. Gron, D. Lawrenz, P.L. Meschi (1995). Interlaboratory Study of a Method for Determining Nonvolatile Organic Carbon in Aquifer Materials. Environ. Geol., 26: 211-219.

Cheng, H.H. (1990). Organic Residues in Soils, Mechanisms of Retention and Extractibility. Int. J. Environ. Anal. Chem., 39: 165-171.

Cummings, T.R. and E.R. Twenter (1986). Assessment of Ground Water Contamination at Wurtsmith, AFB, Michigan. U.S. Geological Survey Water Resource Investigations Report 8C-4188.

Epstein, S., R.V. Krishnamurthy, J.R. Cronin, S. Pizzarello, G.V. Yuen (1987). Unusual Stable Isotopic Ratios in Amino Acids and Carboxylic Acid Extracts from the Murchison Meteorite. Nature, 326: 477-479.

Heron, G., M.J. Barcelona, M.L. Andersen, T.H. Christensen, (1996). Determination of Non-Volatile Organic Carbon in Aquifer Solids Carbonate Removal by Sulfurous Acid. Ground Water, *in press.*

Hewitt, A.D., P.H. Miyares, D.C. Leggett and T.F. Jenkins (1992). Comparison of Analytical Methods for Determination of Volatile Organic Compounds in Soils. Environ. Sci. Technol., 26(10): 1932-1938.

Hewitt, A.D. (1995). Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil. American Environmental Laboratory, February 1995: 25-28.

Hydrogeology Field Course (1992). Department of Geology, Western Michigan University, Kalamazoo, MI (unpublished reports).

Keith, L.H. (1991). Compilation of EPA's Sampling and Analysis Methods. Lewis Publishers, Chelsea, MI, 803 pp.

Landmeyer, J.E., D.A.Vroblesky, F.H. Chapelle (1996). Stable Carbon Isotope Evidence Biodegradation Zonation in a Shallow Jet-Fuel Contaminated Aquifer. Environ. Sci. Technol., 30(4): 1120-1128.

Powell, R.M., B.E. Bledsoe, G.P. Curtis, and R.L. Johnson (1989). Interlaboratory Methods Comparison for the Total Organic Carbon Analysis of Aquifer Materials. Environ. Sci. Technol., 23(10): 1246-1249.

Siegrist, R.C. and P.D. Jenssen (1990). Evaluations of Sampling Method Effects on Volatile Organic Compound Measurements in Soils. Environ. Sci. Technol., 24(9): 1387-1392.

Siegrist, R.C. and J.J. Van Ee (1993). Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs, A Symposium Summary. U.S. EPA, Washington, D.C. EPA/540/R-94/506.

Suchomel, K.H., Kreamer, D.K., Long, A. (1990). Production and Transport of Carbon Dioxide in a Contaminated Vadose Zone: A Stable and Radioactive Carbon Isotope Study. Environ. Sci. Technol., 24(12): 1824-1831.

Thurman, E.M. (1985). Organic Geochemistry of Natural Waters. Dordrecht, The Netherlands, Martinus Nijhoft/Dr. W. Junk Publishers.

Waasenaar, L.I., R. Aravena, P. Fritz, and J.F. Barker (1991). Controls on the Transport and Carbon Isotopic Composition of Dissolved Organic Carbon in a Shallow Groundwater System. Chem. Geol. (Isotope Geoscience Section) 87: 39-57.

West, C.C, W.G. Lyon, D.L. Ross, and L.K. Pennington (1994). Investigation of Vertical Distribution and Morphology of Indigenous Organic Matter at Sleeping Bear Site, Michigan. Environ. Geol., 24: 176-187.

Wisconsin DNR (1994). Methanol Preservation Required for All Soil VOC Samples. Release News, July 1994, 4(3): 1-4.

Acknowledgement

Disclaimer

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

EPA/600/S-97/001