01.01-10/18/99-02371 DUP

NORTH CAROLINA DEPARTMENT OF
ENVIRONMENT AND NATURAL RESOURCES
DIVISION OF WASTE MANAGEMENT

NCDENR

JAMES B. HUNT JR.
GOVERNOR

WAYNE MCDEVITT
SECRETARY

WILLIAM L. MEYER
DIRECTOR

October 18, 1999

Commander, Atlantic Division
Naval Facilities Engineering Command
1510 Gilbert Street (Building N-26)
Norfolk, Virginia 23511-2699

Attention: Ms. Katherine Landman
Navy Technical Representative
Code 1823

Commanding General
Marine Corps Base
PSC Box 20004
Camp Lejeune, NC 28542-0004

Attention: AC/S, EMD/IRD

RE: Draft Sample Strategy Plan
Phase II SWMU
Confirmatory Sampling Investigation
MCB Camp Lejeune, North Carolina

Dear Ms. Landman:

Superfund and Hazardous Waste Sections have reviewed the Draft Plan for the Phase II Confirmatory Sampling Investigation and submit the attached comments. We appreciate the opportunity to review this document. If you have any questions or comments, please call Patrick Watters or me.

Sincerely,

David J. Lown, LG, PE
Geological Engineer
Superfund Section

cc: Neal Paul, MCB Camp Lejeune
Gena Townsend, US EPA Region IV
Kathy Chavara, Baker Environmental

401 OBERLIN ROAD, SUITE 150, RALEIGH, NC 27605
PHONE 919-733-4996 FAX 919-715-3605
AN EQUAL OPPORTUNITY / AFFIRMATIVE ACTION EMPLOYER - 50% RECYCLED/10% POST-CONSUMER PAPER

North Carolina Division of Waste Management Comments
Draft Sample Strategy Plan
Phase II SWMU
Confirmatory Sampling Investigation
MCB Camp Lejeune, North Carolina

1. SWMU-Specific Recommendations

Table 1 lists some of our recommendations for the SWMU investigations. In addition to sampling for contamination, it is important to collect site information to calculate SWMU-specific screening values. Details about Table 1 are discussed below. Generally the results of the Phase II sampling will be improved by collecting information to determine site-specific partitioning coefficients (K_d). This usually means fraction of organic carbon (f_{oc}) and/or pH. Also, arsenic background levels need to be determined and properly evaluated.

2. Groundwater Flow Direction

A minimum of three groundwater levels is usually needed to determine groundwater flow directions. Several SWMUs are being sampled for groundwater, but there are less than three water level determinations. Additional information on the groundwater flow direction will be needed at any site where groundwater samples are taken. If the flow direction cannot be confirmed, additional groundwater sampling may be needed.

3. Soil-to-Groundwater Screening Levels

EPA's *Soil Screening Guidance* documents (EPA/540/R95/128 and EPA/540/R-96/018) were used by North Carolina to calculated the soil-to-groundwater screening values. This is a conservative approach with several conservative assumptions. Site-specific data can be used to calculate new screening values.

One assumption, used in the EPA Guidance, is that a half-acre area is contaminated at the screening level from the land surface to the top of the water table. If there is adequate sample density and the average contaminant level is below the screening level for an area smaller than a half-acre, then additional work may not be required. If some of the soil samples contain greater than twice the screening level, additional investigation may be necessary before the SWMU can be closed.

As mentioned above, site-specific information can be used to calculate SWMU-specific screening levels. Attached (Attachment 1) is some guidance prepared by the NC Hazardous Waste Section on the calculation of contaminant screening levels. To calculate a K_d for organic compounds the following equation is used

$$K_d = K_{oc} f_{oc}$$

Where K_{oc} is the soil organic carbon-water partition coefficient and f_{oc} is the fraction of organic carbon in subsurface vadose soils. (Note that K_d for organic compounds is referred to as K_s in the NC Hazardous Waste Guidance.) The default f_{oc} level (.001) for calculating the generic screening levels for North Carolina is probably low for Camp Lejeune. Site-specific samples should be collected to determine a realistic f_{oc} for each individual SWMU.

It is important to carefully consider how the f_{oc} analysis will be done. Attached (Attachment 2) is an EPA Environmental Research Brief entitled, "Characterization of Organic Matter in Soil and Aquifer Solids." Consultant, Michael Barden, and owner of Geoscience Resource Ltd. in Albuquerque, New Mexico brought this document to our attention. Mr. Barden teaches the National Ground Water Association Short Course, "Transport and Fate Principles and Parameter Estimation – Use in Modeling for Risk-Based Evaluation and Screening of Soil Contamination." Mr. Barden recommends using an agricultural lab rather than an environmental lab to analyze for f_{oc}. We do not have a preference on how f_{oc} is determined, but recommend that you carefully consider how the determination is made.

Recent EPA documents discussing the determination K_d can be found at the following Internet address: http://www.epa.gov/radiation/technology/partition.htm. (The title of these documents are *Understanding Variations in Partition Coefficient Values, Volumes 1 and 2*.) These documents discuss several methods for determining K_d, including the K_{oc} Method (which is used in the calculation of the North Carolina soil-to-groundwater screening levels) and the Laboratory Batch Method (LBM). Under most circumstances the K_{oc} Method is probably easier to determine and less costly than the LBM. However, in situations were the K_{oc} Method does not produce realistic numbers, or the site has some geologic condition that might cause more sorption of contaminants than might be expected (e.g. high clay content or high pH), it is might be good to invest in the LBM test.

As indicated in the EPA *Soil Screening Guidance*, most inorganic contaminants, and a few organic compounds are highly sensitive to site pH. Table 1 shows the SWMUs where we believe that determination of pH may be important.

4. Determination of Background Levels

Several sites have arsenic levels above the Region III RBC. The high level may not be related to the SWMU. Additional information on background levels for arsenic is needed. We suggest collecting background samples near, but outside the influence of the SWMU being tested. Statistics should be applied to determine the characteristics of the background population. Attached (Attachment 3) is guidance on statistics used by the State of Ohio to determine background. The guidance was developed specifically for background-based remediation levels, but should be

applicable to developing background levels during the site characterization. North Carolina Hazardous Waste Section is aware of this approach and will consider its application at Lejeune. Further information on this subject can be found in the Hazardous Waste Section Guidance on risk-based cleanup levels (Attachment 1).

5. Remedial Action Recommended in the Phase I Report

Removal actions (SWMU 291 and 310) as well as additional engineering and/or institutional controls (SWMUs 299 and 310) were recommended in the Phase I report. These were not reiterated in Phase II sampling plan; however, we assume that they will be implemented or addressed appropriately.

6. Site 339

Controls are needed at SWMU 339 to prevent the migration of contaminated sand and grit to the storm-water collection system.

Table 1. Recommendations for Additional Data Collection Phase II Sampling Plan, MCB Camp Lejeune

SWMU	K_d	pH	Background Sample	Comments
43	X		As	Kd information is necessary to determine remediation levels. Flow direction of the drainage ditch is not apparent.
46		X	As	
53 & 296			As	
89	X			
253			As	
254	X		As	
255	X	X	As	A Laboratory Batch Test for leachable pentachlorophenol may be needed. Flow direction of the drainage ditch is not apparent. Two soils have elevated As levels of 13.4 and 7 mg/kg.
256	X			
258	X	X		
261/297		X	As	Non-detect limit for VOAs is greater than screening criteria by an order of magnitude
262			As	
264	X	X	As	Pentachlorophenol is present.
265	X			
269			As	
272	X	X	As	Pentachlorophenol is present. Several compounds detected, most below the RBCs, but above SSL. Might be a good candidate for Laboratory Batch Test for Kd.
273			As	
279	X		As	
280			As	High As level, 8.6 ppm.
284			As	
285	X		As	
286			As	
291	X	X	As	One sample has PCE at 8.4 µg/kg and one has chromium at 43.3 mg/kg.
293				NFA? - Lead slightly greater than SSL in one sample. If the average is considered, probably not a problem.
295	X			
299	X	X	As	Several contaminants above screening levels, including SVOCs and lead.
300	X		As	Benzo(a)pyrene is at 5000 µg/kg.
301			As	
302	X	X		

SWMU	K_d	pH	Background Sample	Comments
303	X		As	Cr is probably not a problem if the average concentration over the area is considered.
304			As	
305			As	
306		X	As	
307			As	
308	X			
309			As	
310			As	
311	X	X	As	Lead is high at 1110 mg/kg.
312			As	Benzo(a)pyrene is just above SSL in one sample.
313		X		
314	X			
315	X	X		Pentachlorophenol
316	X			
317				
318	X	X	As	One sample has arsenic at 14.3 mg/kg and elevated SVOCs.
319	X			
339				Confirm that acetone is not a problem.

ATTACHMENT 1

North Carolina Hazardous Waste Section

Establishing Risk-Based Cleanup Levels at
RCRA Hazardous Waste Sites, September 1998

Facility Management Branch Guidance

DRAFT

ESTABLISHING RISK-BASED CLEANUP LEVELS AT RCRA HAZARDOUS WASTE SITES

FACILITY MANAGEMENT BRANCH GUIDANCE

The development of risk-based cleanup levels or the performance of a site-specific risk assessment by a facility (or the Facility Managment Branch) must be completed in a manner consistent with the policies and procedures of both the Facility Management Branch (FMB) and the Occupational and Environmental Epidemiology Section (OEES). It is the responsibility of the FMB project manager to facilitate the transfer of information between the facility and the OEES.

When establishing soil and groundwater cleanup levels at RCRA sites, keep the following in mind:

- In North Carolina, institutional controls are not enforceable under RCRA except through a permit or Administrative Order on Consent. If you or the facility have any questions concerning the use of institutional controls to restrict land use contact Kathleen Waylett of the Attorney General's Office at 919/716-6600.
- North Carolina has State groundwater standards which are enforceable under the 2L rules. While we have a mechanism in RCRA to approve alternate concentration levels, if these levels are above the 2L standards the facility would still be subject to the 2L rules. Corrective action alternatives for groundwater are set out in .0106 of the 2L rules. The variance process is set out in .0113 of the 2L rules.
- Soil and groundwater cleanup levels may be established by OEES at values less than those established in accordance with this guidance when two or more substances exist in combination. In the absence of information to the contrary, the carcinogenic risks associated with carcinogens shall be considered additive and the toxic effects of non-carcinogens present shall also be considered additive.

PREREQUISITE FOR CONSIDERATION OF RISK-BASED CLEANUP LEVELS

A RCRA Facility Investigation (RFI) or the applicable portion of the RFI must be completed prior to the FMB and OEES considering the establishment of risk-based cleanup levels or evaluating a site-specific risk assessment. Completion of the RFI includes a determination of the nature and extent of releases from Solid Waste Management Units (SWMUs) and Areas of Concern (AOCs):

INFORMATION NEEDED TO EVALUATE RISK-BASED CLEANUP LEVELS

The following information must be provided to the FMB and the OEES along with the proposed risk-based cleanup levels.

1. Confirmation from the project manager that adequate sampling and analysis has been

completed to define the extent of contamination. State the sources of contamination and whether or not they are currently controlled.

2. List of the highest constituent concentrations for each medium (soil, groundwater, surface water, etc.) within each area of concern.

3. Current and future (if known) land use(s) of the areas of concern and surrounding areas.

4. Distance from area(s) of concern to nearest residential area.

5. Distance and likelihood of impact of contamination to public and/or private wells.

6. Accessibility of the area(s) of concern and surrounding areas to a public water supply .

7. Distance and likelihood of impact of contamination to surface water.

8. Contact and phone number of consultant conducting the sampling.

GROUNDWATER CLEANUP LEVELS

The maximum concentration of each groundwater constituent, located within the contaminant plume (onsite or offsite), is compared to the 15A NCAC 2L Groundwater Quality Standard, an interim maximum allowable concentration (IMACs), or an OEES recommended standard. The maximum concentration should be less than or equal to the NC Groundwater Quality Standard, IMAC, or OEES recommended standard. For constituents that do not have a level specified in 2L or an IMAC, a request for a determination of an interim maximum allowable concentration can be made to the DWQ Groundwater Section. Contact David Hance at 919/ 715-6189 for information concerning interim concentration requests.

An alternate concentration limit (ACL), or cleanup level, may be requested by a facility if the constituent concentration will not pose a present or future adverse impact to human health or the environment. The authority and criteria used for granting ACLs under RCRA is found at 40 CFR 264.94(b) as adopted by 15A NCAC 13A.

If an ACL is approved by the FMB, the facility will have to file an application with the Division of Water Quality Groundwater Section requesting a variance to the 2L rules (or the facility may want to contact the DWQ Groundwater Section for other Corrective Action options under the 2L rules). The variance application requirements are found in 15A NCAC 2L .0113.

NOTE: The NC 2L rules state that "where the standard for a substance is less than the practical quantitation limit (PQL), the detection of that substance at or above the PQL shall constitute a violation of the standard" and that "...substances which are not naturally occurring and for which no standard is specified shall not be permitted in detectable concentrations...".

DRAFT

SOIL CLEANUP LEVELS

Two potential soil cleanup levels must be determined for each constituent detected at a site. These two cleanup levels include a residential cleanup level based on ingestion of soil and a cleanup level to protect groundwater referred to as a soil-to-groundwater cleanup level. When both clean up levels apply to a site, the lesser of the two will become the cleanup level. The following paragraphs describe how each of these cleanup levels can be determined:

Residential Soil Cleanup Levels

For all sites, the maximum concentration of each constituent detected in the surface soil is compared to the most current EPA Region III Risk-Based Concentration (RBC) for Residential Ingestion. Typically, surface soil samples should be taken from the upper 6 inches (USEPA Soil Screening Guidance) to the upper 12 inches (EPA Region IV Guidance) of the soil surface.

Soil- to- Groundwater Cleanup Levels

The soil-to-groundwater cleanup level should be determined using the following approaches:

1. The maximum concentration of each constituent detected in the soil is compared to the North Carolina Soil Screening Levels (NCSSLs) for soil-to-groundwater in the attached Table 1. NCSSLs have been determined for constituents which have a NC Groundwater (GW) Quality Standard (15A NCAC 2L), a recommended interim maximum allowable concentration, or an OEES recommended standard. The NC soil- to- groundwater SSLs were calculated using the equations found in Figure 1 which were taken from the Draft NC Risk Analysis Framework (November 1996). The maximum soil concentration at the site should be less than or equal to the NCSSL for soil-to-groundwater.

2. The second approach involves the calculation of a site-specific soil- to- groundwater target concentration using the equations found in Figure 1 and site-specific parameter values. The NC Groundwater Quality Standard, found in 15A NCAC 2L, a proposed interim maximum allowable concentration, or an approved alternate standard is the applicable groundwater target concentration (C_{gw}) that should be used in Equation 1. The maximum soil concentration at the site should be less than or equal to the soil target concentration for soil-to-groundwater as determined using the equations in Figure 1.

3. When it is not possible to calculate a soil-to-groundwater SSL, the maximum concentration of each constituent in the soil, as analyzed by an approved method for total analyte concentrations, is compared to ten (10) times the NC Groundwater Quality standard. The maximum soil concentration should be less than or equal to ten (10) times the NC Groundwater Quality Standard or IMAC for that constituent.

DRAFT

SURFACE WATER CLEANUP LEVELS

When surface water is being impacted, the 15A NCAC 2B Classifications and Water Quality Standards Applicable to Surface Waters of NC are used to evaluate contaminate concentrations in surface water. The concentrations of contaminants, measured or modeled, are compared to the appropriate surface water standard for protection of the applicable surface water classification. At a minimum, at least one surface water and one sediment sample should be collected immediately upstream and downstream of the area(s) of concern. Questions concerning surface water should be directed to Dianne Reid, DWQ, at 919/733-5083 extension 568.

USE OF BACKGROUND LEVELS

For naturally occurring substances found in soil, groundwater, surface water, or sediment (as determined by proper background sampling), compare onsite maximum detected media concentrations to two (2) times the mean site-specific background concentration. The maximum media concentration should be less than 2 times the mean site-specific background. Approved statistical methods may also be used.

MEMO TO OEES

A memo outlining the risk-based cleanup level request, along with the information needed to evaluate the request, should be prepared by the project manager and forwarded to the Unit Supervisor and to the Chemical Technical Advisor for review. The Chemical Technical Advisor will make the determination that the information is complete and forward it to OEES for approval and/or further evaluation.

REFERENCES

15A NCAC 13A NC Hazardous Waste Management Rules.

15A NCAC 2L Classifications and Water Quality Standards Applicable to the Groundwaters of North Carolina. Division of Water Quality website address: http://h2o.ehnr.state.nc.us

15A NCAC 2B Classifications and Water Quality Standards Applicable to Surface Waters of North Carolina. Division of Water Quality website address: http://h2o.ehnr.state.nc.us

NC Risk Analysis Framework. Methods for determining contaminant target concentrations in soil & groundwater. November, 1996. Draft. Website address: http://www.ehnr.state.nc.us/EHNR/files/docs.htm

RCRA Facility Investigation (RFI) Guidance. EPA 530/SW-89-031

RCRA Ground Water Monitoring Draft Technical Guidance. EPA 530-R-93-001.

DRAFT

US EPA Region III "Risk-Based Concentrations" table can be found on the internet at http://www.epa.gov/reg3hwmd/risk/riskmenu.htm

US EPA Region IV guidance documents can be found on the internet at http://www.epa.gov/region4/wastepgs/oftecser/ostinfo.htm.

US EPA Soil Screening Guidance: Technical Background Document. EPA/540/R-95/128.
US EPA Soil Screening Guidance: User's Guide. EPA/540/R-96/018. Website address: http://www.epa.gov/superfund/oerr/soil/index.html

Updated List of Groundwater Quality Standards and List of Recommended Changes to Groundwater Quality Standards for Distribution. April 15, 1998 Memo from Luanne K. Williams, OEES to Jimmy Carter, HW Section Chief.

CONTACTS

Luanne Williams, Toxicologist, OEES, (919) 715-6429
Dianne Reid, DWQ, (919) 733-5083 ext. 568 (For information on SW Quality Standards)
David Hance, DWQ, (919) 715-6189 (For information on GW Quality Standards)
Sandra Moore, DWM, (919) 733-2178 ext. 231 (Hazardous Waste Section)

Figure 1

DRAFT

Transport Model For Calculation of S-3 Soil Target Concentrations

Equation 1 - General Formula for S-3 Soil Concentrations Protective of Groundwater:

$$C_{soil} = C_{gw} \left[k_s + \frac{(\theta_w + \theta_a H')}{P_b} \right] df$$

	Parameters	Default Values	Units
C_{soil}	Calculated Source Concentration for soil	not applicable	mg/kg - soil
C_{gw}	Applicable Groundwater Target Concentration (NC GW Std)	chemical-specific	mg/L - water
df	Dilution factor (see equation 2)	20 (0.5 acre source size)+*	unitless
k_s	Soil-water partition coefficient for organic constituents $k_s = k_{oc} f_{oc}$ for inorganic constituents $ks = k_d$	chemical-specific	L/kg
k_{oc}	Soil organic carbon-water partition coefficient	chemical-specific	L/kg
f_{oc}	Fraction of organic carbon in subsurface vadose soils	0.001 (0.1%)+	kg/kg
k_d	Soil-water partition coefficient for inorganics	chemical-specific (pH=5.5)	L/kg
θ_w	Water-filled soil porosity-vadose soils	0.3	L_{water}/L_{soil}
θ_a	Air-filled soil porosity-vadose soils	0.13	L_{air}/L_{soil}
P_b	Dry bulk density	1.5	kg/L
H'	Henry's Law constant-dimensionless where: H' = Henry's Law constant (atm-m^3/mole) x conversion factor of 41	chemical-specific	unitless

continued on next page

Figure 1 continued

DRAFT

Equation 2 - Derivation of Dilution Factor:

$$df = 1 + \frac{kid}{IL}$$

	Parameters	Units
df	Dilution factor	unitless
k	Aquifer hydraulic conductivity+	m/yr
i	Hydraulic gradient+	m/m
I	Infiltration rate of water through soil+	m/yr
d	Mixing zone depth (see equation 3)+	m
L	Source length parallel to groundwater flow+	m

Equation 3 - Estimation of Mixing Zone Depth:

$$d = (0.0112\,L^2)^{0.5} + d_a\left[1 - e^{\left(\frac{-LI}{kid_a}\right)}\right]$$

	Parameters	Units
d	Mixing zone depth	m
L	Source length parallel to groundwater flow+	m
I	Infiltration rate of water through soil+	m/yr
k	Aquifer hydraulic conductivity+	m/yr
i	Hydraulic gradient+	m/m
d_a	Aquifer thickness+	m

+Site-specific values for these parameters may be used.

DRAFT

*Facility Management Branch default value from Soil Screening Guidance: User's Guide (April 1996).

TABLE 1
NORTH CAROLINA SOIL SCREENING LEVELS
Protective of Groundwater Used for Drinking

DRAFT: Values in Table are subject to change. Contact the NC Hazardous Waste Section, Facility Management Branch for the most recent version.

COMPOUNDS	CAS #	Kd (L/kg)	Ref.	Koc (L/kg)	Ref.	HENRY'S LAW CONSTANT (unitless)	Ref.	See Footnotes	TARGET GROUNDWATER CONCENTRATION (2L, Interim 2L Recommended 2L, or MCLG) (mg/L)	NC SSL CONCENTRATIONS (mg/kg)
ACENAPHTHENE	83329			4900	a	0.00636	a	1	0.08	8.16
ACENAPHTHYLENE	208968			2500	c	0.05945	c	1	0.21	11.4
ACETONE	67641			0.575	a	0.00159	a		0.7	2.81
ACRYLAMIDE (PROPENAMIDE)	79061			0	e	1.2423E-07	e	2	0.000008	0.000032
ANTHRACENE	120127			23500	a	0.00267	a	1	2.1	995
ANTIMONY	7440360	45	d					3	0.006	5.42
ARSENIC	7440382	26	a					2	0.00002	0.0105
ATRAZINE	1912249			200	f	0.000000086	j	1	0.003	0.024
BARIUM	7440393	21	a						2	848
BENZENE	71432			61.7	a	0.2255	c		0.001	0.00562
BENZOIC ACID	65850			1.94	a	0.0000631	a	2	28	113
BENZO (A) ANTHRACENE	56553			358000	a	0.000137	a	1	0.0000479	0.343
BENZO (A) PYRENE	50328			969000	a	0.0000463	a	1	0.0000047	0.0911
BENZO (G,H,I) PERYLENE	191242			1600000	c	0.000005904	c	1	0.21	6720
BERYLLIUM	7440417	42	a					3	0.004	3.38
BIS (2-CHLOROETHYL) ETHER	111444			75.9	a	0.000738	a	2	0.000031	0.000171
BIS (2-CHLOROISO-PROPYL) ETHER	396383329			61	c	0.004633	c			
BORON	7440428	3	d					2	0.315	20.2
BROMODICHLOROMETHANE	75274			55	a	0.0656	a	1	0.00056	0.00292
BROMOFORM (TRIBROMOMETHANE)	75252			126	a	0.0219	a	2	0.00443	0.0291
BROMOMETHANE	74839			5.9	c	8.077	c			
BUTYL BENZYL PHTHALATE	85687			13700	a	0.0000517	a		0.1	27.8
CADMIUM	7440439	27	a					2	0.00175	0.952
CAPROLACTAM	105602				cd		cd	1	3.5	
CARBOFURAN	1563662			158	e	1.5908E-06	e	2	0.035	0.251
CARBON DISULFIDE	75150			45.7	a	1.24	a	1	0.7	4.94

1 - Interim 2L Standard
2 - Recommended 2L Standards per 4/15/98 or 12/14/98 OEES Memorandum
3 - No 2L Std; MCLG/proposed MCLG used instead

TABLE 1

NORTH CAROLINA SOIL SCREENING LEVELS

Protective of Groundwater Used for Drinking

DRAFT: Values in Table are subject to change. Contact the NC Hazardous Waste Section, Facility Management Branch for the most recent version.

COMPOUNDS	CAS #	Kd (L/kg)	Ref.	Koc (L/kg)	Ref.	HENRY'S LAW CONSTANT (unitless)	Ref.	See Footnotes	TARGET GROUNDWATER CONCENTRATION (2L, Interim 2L Recommended 2L, or MCLG) (mg/L)	NC SSL CONCENTRATIONS (mg/kg)
CARBON TETRACHLORIDE	56235			152	a	1.2013	c	2	0.00026	0.0237
CHLORDANE	57749			51300	a	0.00199	a	2	0.0000269	0.0277
CHLOROBENZENE	108907			224	a	0.16113	c		0.05	0.438
CHLOROETHANE	124481			3.24	e	0.4551	e	1	2.8	13.6
CHLOROFORM (TRICHLOROMETHANE)	75003			52.5	a	0.13899	c	2	0.0057	0.0302
CHLOROPHENOL 2-	95578			397	a	0.016	a	2	0.0350	0.419
CHROMIUM	7440473	27	a					2	0.00175	0.952
CHRYSENE	218019			398000	a	0.00388	a	1	0.00479	38.1
COPPER	7440508	35	d						1.0	704
CYANIDE	57125	9.9	a					2	0.07	14.1
4,4' - DDD	72548			4.58E+04	a	1.64E-04	a	1	0.00014	0.129
4,4' - DDT	50293			6.78E+05	a	3.32E-04	a	1	0.0001	1.36
DIBENZ (A,H) ANTHRACENE	53703			1.79E+06	a	6.03E-07	a	1	0.0000047	0.168
DI (OR BIS) 2-ETHYLHEXYL PHTHALATE (DEHP)	117817			111000	c	0.0000418	c	2	0.0025	5.56
DI-N-BUTYL (OR DIBUTYL) PHTHALATE (DBP)	84742			1570	a	3.85E-08	a		0.7	24.8
DI-N-OCTYL PHTHALATE	117840			83200000	a	0.00274	a		0.14	233000
DIBROMOCHLOROMETHANE (CHLORODIBROMOMETHANE)	124481			6.31E+01	a	0.03210	a	2	0.00041	0.00171
DIBROMO-3-CHLOROPROPANE 1,2-	96128			98	b	0.01275	b		0.000025	0.00015
DICHLOROBENZENE 1,2 (O-DCB)	95501			379	a	0.07954	c	2	0.024	0.281
DICHLOROBENZENE 1,3 (M-DCB)	541731			1700	c	0.10783	c	2	0.63	24.1
DICHLOROBENZENE 1,4 (P-DCB)	106467			616	a	0.11152	c	2	0.011	0.182
DICHLORODIFLUOROMETHANE (FREON-12; HALON)	75718			58	b	123	e		1.4	306
DICHLOROETHANE 1,1	75343			53.4	a	0.22345	c	2	0.07	0.382
DICHLOROETHANE 1,2 (ETHYLENE DICHLORIDE)	107062			38	a	0.0451	c		0.00038	0.00184
DICHLOROETHENE 1,2 (CIS)	156592			35.5	a	0.167	a		0.07	0.350
DICHLOROETHENE 1,2 (TRANS)	156605			38	a	0.385	a	2	0.1	0.543
DICHLOROETHYLENE 1,1 (VINYLIDENE CHLORIDE)	75354			65	c	0.6109	c	2	0.000058	0.000369
DICHLOROPHENOXY ACETIC ACID 2,4 (2,4-D)	94757			20	b	0.007708	b		0.07	0.309

1 - Interim 2L Standard
2 - Recommended 2L Standards per 4/15/98 or 12/14/98 OEES Memorandum
3 - No 2L Std; MCLG/proposed MCLG used instead

TABLE 1

NORTH CAROLINA SOIL SCREENING LEVELS

Protective of Groundwater Used for Drinking

DRAFT: Values in Table are subject to change. Contact the NC Hazardous Waste Section, Facility Management Branch for the most recent version.

COMPOUNDS	CAS #	Kd (L/kg)	Ref.	Koc (L/kg)	Ref.	HENRY'S LAW CONSTANT (unitless)	Ref.	See Footnotes	TARGET GROUNDWATER CONCENTRATION (2L, Interim 2L Recommended 2L, or MCLG) (mg/L)	NC SSL CONCENTRATIONS (mg/kg)
DICHLOROPROPANE 1,2-	78875			47	a	0.11562	c	2	0.00051	0.00262
DICHLOROPROPENE 1,3 (CIS AND TRANS)	542756			27.1	a	0.1435	c	1	0.00019	0.00091
DIELDRIN				25500	a	0.000619	a	1	0.0000022	0.00113
DIETHYLPHTHALATE (DEP)	84662			82.2	a	0.0000185	a		5	28.2
DINOSEB (DNBP) (2-SEC-BUTYL-4,6-DINITROPHENOL)								3	0.007	
2,4-DIMETHYLPHENOL	105679			209	a	0.000082	a	1	0.140	1.15
DIOXANE 1,4	123911			3.47	e	0.00020008	e	2	0.00318	0.0129
DIOXIN: 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN (TCDD)	1746016			3300000	b	0.1476	b		0.00000000022	0.0000145
DIPHENYL (BIPHENYL)	92524			1072	e	0.007913	e	1	0.35	8.91
DIUNDECYL PHTHALATE (SANTICIZER 711)	3648202				cd		cd		0.14	
ENDRIN	72208			10800	a	0.000308	a	1	0.002	0.440
EPICHLOROHYDRIN (1-CHLORO-2,3-EPOXYPROPANE)	106898			10	b	0.0013079	b		0.00354	0.0149
ETHYLBENZENE	100414			204	a	0.14063	c	2	0.7	5.83
ETHYLENE DIBROMIDE (EDB, 1,2-DIBROMOETHANE)	106934			44	c	0.027593	c		0.0000004	0.00000197
ETHYLENE GLYCOL	107211			0.0127	g	9.594E-09	k	2	14	56.0
FLUORANTHENE	206440			49100	a	0.00066	a	1	0.28	276
FLUORENE	86737			7710	a	0.00261	a		0.28	44.3
FLUORIDE	7782414		cd					2	1	
HEPTACHLOR	76448			9530	a	60.7	a	2	0.0000078	0.00234
HEPTACHLOR EPOXIDE	1024573			83200	a	0.00039	a	2	0.0000038	0.00634
HEPTANE	142825			5870	h	83.435	e	2	0.42	112
HEXACHLOROBENZENE (PERCHLOROBENZENE)	118741			80000	a	0.0541	a		0.00002	0.0321
HEXACHLOROCYCLOPENTADIENE	77474			200000	a	1.1	a	3	0.05	200
IRON	7439896	25	d						0.3	151
INDENO (1,2,3-CD) PYRENE	193395			3.47E+06	a	6.56E-05	a	1	0.000047	3.26
ISOPHORONE	78591			46.8	a	0.000272	a	1	0.0368	0.182
ISOPROPYL ETHER (DIISOPOROPYL ETHER)	108203			31.22	g	0.40877	e	1	0.07	0.373
LEAD	7439921	900	d						0.015	270

1 - Interim 2L Standard
2 - Recommended 2L Standards per 4/15/98 or 12/14/98 OEES Memorandum
3 - No 2L Std; MCLG/proposed MCLG used instead

TABLE 1

NORTH CAROLINA SOIL SCREENING LEVELS

Protective of Groundwater Used for Drinking

DRAFT: Values in Table are subject to change. Contact the NC Hazardous Waste Section, Facility Management Branch for the most recent version.

COMPOUNDS	CAS #	Kd (L/kg)	Ref.	Koc (L/kg)	Ref.	HENRY'S LAW CONSTANT (unitless)	Ref.	See Footnotes	TARGET GROUNDWATER CONCENTRATION (2L, Interim 2L Recommended 2L, or MCLG) (mg/L)	NC SSL CONCENTRATIONS (mg/kg)
LINDANE (GAMMA-BHC)	58899			1350	a	0.000574	a		0.0002	0.00620
MANGANESE	7439965	65	d						0.05	65.2
MERCURY	7439976	0.46	a			0.467	a	2	0.00105	0.0147
METHANOL	67561			2.75	e	0.00018204	e	1	3.5	14.2
METHOXYCHLOR	72435			80000	a	0.000648	a		0.035	56.1
METHYL ETHYL KETONE (MEK; 2-BUTANONE)	78933			3.5	c	0.0011234	c	2	4.2	17.1
METHYL ISOBUTYL KETONE (MIBK)	108101			3.1	c	0.005658	c			
METHYL TERT-BUTYL ETHER	1634044			27	c	0.024231	c	2	0.07	0.321
METHYLENE CHLORIDE (DICHLOROMETHANE)	75092			10	a	0.13079	c	2	0.0046	0.0203
N-HEXANE	110543			1468	h	31.488	e		0.42	36.9
NAPHTHALENE	91203			1190	a	0.0198	a		0.021	0.585
NICKEL	7440020	28	a						0.1	56.4
NITRATE (AS N)	14797558		cd						10	
NITRITE (AS N)	14797650		cd						1	
OXAMYL	23135220			2.24	l	0.0000902	l		0.175	0.708
PENTACHLOROPHENOL	87865			3650	a	0.000001	a	2	0.00029	0.0223
PHENANTHRENE	85018			14000	c	0.0016113	c		0.21	59.6
PHENOL	108952			91	c	0.0000163	a		0.3	1.75
POLYCHLORINATED BIPHENYLS; PCBs										
PYRENE	129000			68000	a	0.000451	a	1	0.21	286
SELENIUM	7782492	12	a						0.05	12.2
SILVER	7440224	0.42	a					2	0.0175	0.217
SILVEX (2,4,5-TP)	93721			2570	i	3.444E-09	i		0.05	2.77
SIMAZINE	122349			138	l	1.394E-07	l	1	0.0035	0.0237
STYRENE (ETHENYLBENZENE)	100425			912	a	0.10701	c		0.1	2.24
SULFATE	4808798		cd						250	
TETRACHLOROETHANE 1,1,1,2-	630206			54	c	0.451	c			
TETRACHLOROETHANE 1,1,2,2-	79345			79	a	0.0141	a	2	0.00017	0.000953

1 - Interim 2L Standard
2 - Recommended 2L Standards per 4/15/98 or 12/14/98 OEES Memorandum
3 - No 2L Std; MCLG/proposed MCLG used instead

TABLE 1

NORTH CAROLINA SOIL SCREENING LEVELS

Protective of Groundwater Used for Drinking

DRAFT: Values in Table are subject to change. Contact the NC Hazardous Waste Section, Facility Management Branch for the most recent version.

COMPOUNDS	CAS #	Kd (L/kg)	Ref.	Koc (L/kg)	Ref.	HENRY'S LAW CONSTANT (unitless)	Ref.	See Footnotes	TARGET GROUNDWATER CONCENTRATION (2L, Interim 2L Recommended 2L, or MCLG) (mg/L)	NC SSL CONCENTRATIONS (mg/kg)
TETRACHLOROETHYLENE (PERCHLOROETHYLENE; PCE)	127184			265	a	0.754	a		0.0007	0.00742
THALLIUM	7440280	51	a					3	0.0005	0.512
TOLUENE (METHYLBENZENE)	108883			140	a	0.27388	c		1	7.27
TOXAPHENE	8001352			95800	a	0.000246	a		0.000031	0.0595
TRICHLOROBENZENE 1,2,4-	120821			1660	a	0.05822	c	3	0.07	2.61
TRICHLOROETHANE 1,1,1 (METHYL CHLOROFORM)	71556			135	a	0.9471	c		0.2	1.67
TRICHLOROETHANE 1,1,2-	79005			75	a	0.03731	c	3	0.003	0.0167
TRICHLOROETHYLENE (TCE)	79016			94.3	a	0.37392	c		0.0028	0.0183
TRICHLOROFLUORO-METHANE	75694			158	e	4.51	e		2.1	31.5
VINYL CHLORIDE (CHLOROETHYLENE)	75014			18.6	a	1.1398	c		0.000015	0.0000952
XYLENES (O-, M-, AND P-)	1330207			249	a	0.21607	c		0.53	4.96
ZINC	7440666	26	a					2	1.05	550

a USEPA, 1996, Soil screening guidance: Technical background document: EPA/540/R95/128

b USEPA, 1986, Superfund public health evaluation manual: Office of Emergency and Remedial Response

c Massachuesetts Department of Environmental Protection, 1994, Background documentation for the development of the MCP numerical standards

d Baes, C.F., III, R.D. Sharp, A.L. Sjoreen, and R.W. Shor, 1984, A review and analysis of parameters for assessing transport of environmentally released radionuclides through agriculture: Oak Ridge National Laboratory

e Montgomery, J.H., 1996, Groundwater chemicals desk reference: CRC Press, Inc.

f Lymen, W.J., W.F. Reehl, D.H. Rosenblat, 1990, Handbook of chemical property estimation methods: American Chemical Society

g Calculated using equation (70) in reference (a)

h Calculated using equation (71) in reference (a)

i Sims, R.C., J.L. Sims, and S.G. Hansen, 1991, Soil transport and fate database, version 2.0: USEPA Robert S. Kerr Environmental Research Laboratory

j Calculated using equation (63) in reference (a)

k ABDR Toxicity Profile, 1993

l Montgomery, J.H., 1993, Agrochemical desk reference environmental data: Lewis Publishers, Chelsea, MI

1 - Interim 2L Standard
2 - Recommended 2L Standards per 4/15/98 or 12/14/98 OEES Memorandum
3 - No 2L Std; MCLG/proposed MCLG used instead

ATTACHMENT 2

EPA Environmental Research Brief

Characterization of Organic Matter in Soil
and Aquifer Solids, April 1997

United States
Environmental Protection
Agency

National Risk Management
Research Laboratory
Ada, OK 74820

Research and Development

EPA/600/S-97/001 April 1997

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.

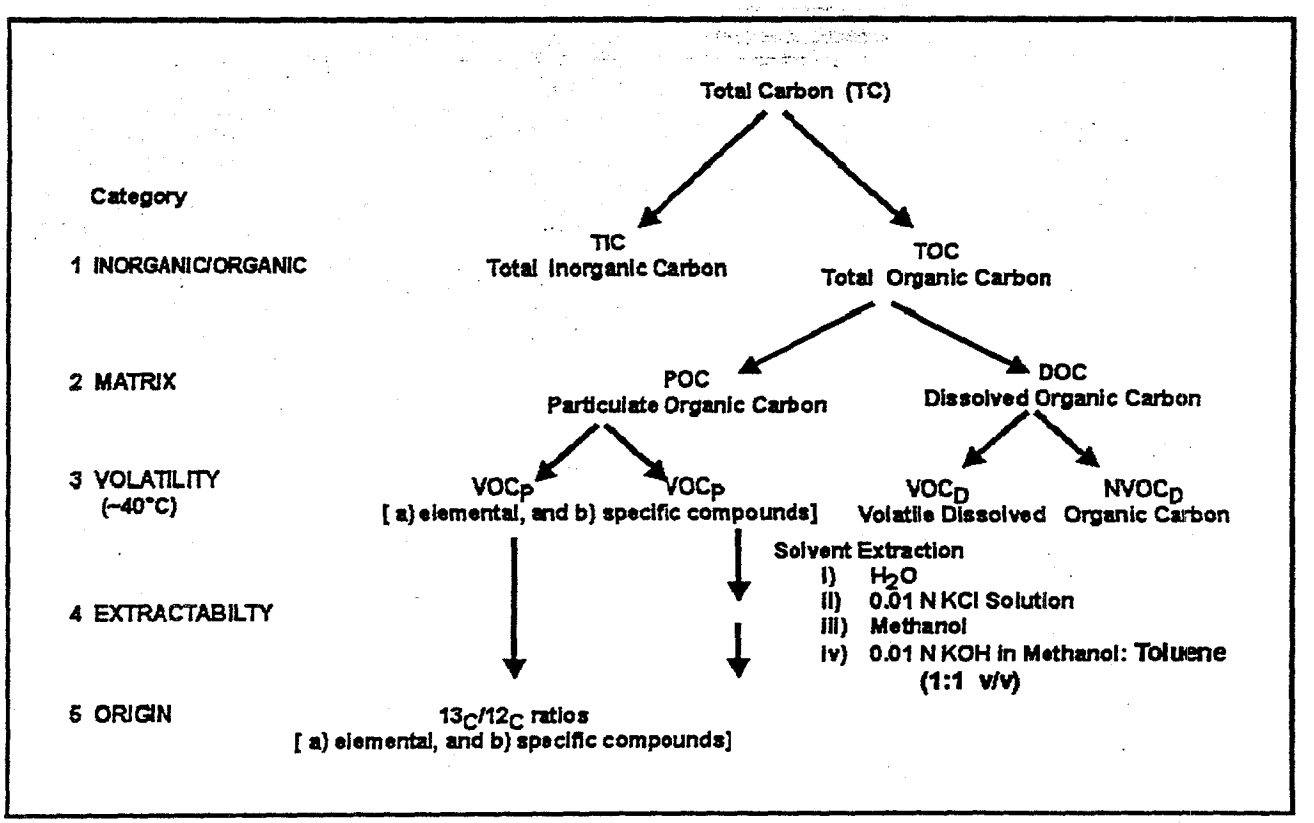


Figure 1. Operational categories of subsurface carbon.

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°C	Combustion of off-gases O_2 to CO_2 (CO_2 as above)
	b) VOC_p (specific compounds)		Volatilization at >40°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°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°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°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 (Caughe

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)	Test Material TM 1	TM 2	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 produc

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

	Sample	Total C (mg/g)	Extracts H_2O	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
	ASYLUM LAKE							
10	AL-5'	1223	2.7 0	<1.0 5.8	11.7 5.9	51.2 61.2	66 72.9	5 6*
11	AL-15'	615	11.4 34.8	28.6 51.3	31.4 65.7	119 163	190 314	31 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 $\pm$ 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 H_2O	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.

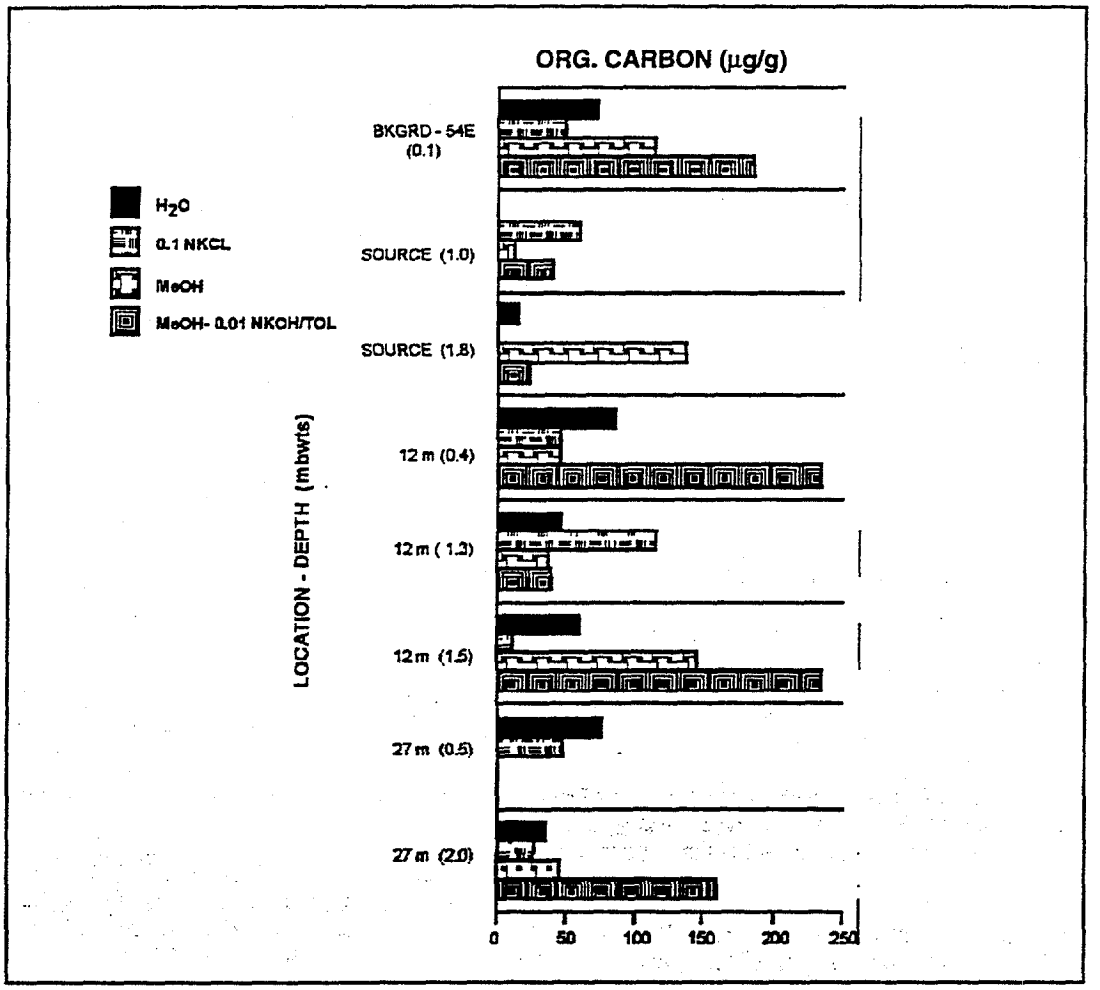


Figure 2. Average Extractable Organic Carbon for Selected Sleeping Bear Dunes Samples (mg/g). Locations are designations: background, in source area, and 12m and 27m downgradient from source, respectively. Parentheses denote depth in meters below land surface at each location.

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

(parentheses denote relative standard derivations)

		Organic Carbon		n	Inorganic Carbon	n
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

The authors wish to thank Ms. Bonnie Dube, Ms. Carolyn Virkhaus, and Mrs. Debbie Patt for their assistance in the work. The guidance and support of Candida C. West, the EPA Project Officer, is very much appreciated.

Disclaimer

The U.S. Environmental Protection Agency through its Office of Research and Development partially funded and collaborated in the research described here under Cooperative Agreement No. CR-817287 to Western Michigan University. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ATTACHMENT 3

Ohio EPA

Closure Plan Review Guidance for RCRA Facilities, March 1999

Section 3.12 Guidance for Statistical Evaluation of
Hazardous Waste Constituent Levels in Soils

3.12 Guidance for Statistical Evaluation of Hazardous Waste Constituent Levels in Soils

3.12.1 Introduction

When a clean closure of a hazardous waste management unit (unit) includes remediation of affected soil to the site specific background concentrations, the determination whether the soil has been successfully remediated always relies on some kind of statistical inference. In order to assist closure plan reviewers to decide whether the background-based remediation standards (BRS) were established properly and if the statistical analyses were applied correctly, some commonly used statistical procedures are discussed in the following text. In general, these procedures allow for comparison between selected observations in such a way that the result of comparison can be obtained with a specified (required) level of confidence (or significance).

In order to conduct a background-based clean closure process (closure), it is necessary to establish a BRS for each constituent of concern. For that purpose, an adequate number of background soil samples must be collected. While this number depends on many factors, the Ohio EPA believes that it should not be less than twelve (12). The concentrations of a constituent in the soil samples (determined through the laboratory analysis) form one "statistical sample" of all background concentrations - a "background data set". In addition, to complete (and certify) a closure, soil samples should be collected from under and/or around the unit (the affected area now assumed to be remediated) to prove that the constituent concentrations have been "sufficiently" lowered. These concentrations are data points which form a "confirmation data set". Unless all confirmation concentrations are below the BRS, a statistical test is necessary to demonstrate (in an objective manner) if a "sufficient" level of soil remediation has been attained. Depending on whether data is, or is not, normally distributed (or can/cannot be normalized with a transformation common to both data sets), two types of statistical methods are used. They are respectively called "parametric" and "nonparametric" methods. For the purpose of this guidance document, the more common parametric approach will be discussed in some detail, while a reference will be made to nonparametric methods whenever appropriate.

3.12.2 DETERMINATION OF THE NUMBER OF SAMPLES

Due to practical reasons and constraints, statistical analyses are frequently conducted on a limited number of observations. This limited number of observations represents a (statistical) sample (not to be confused with a "soil sample") extracted from a much larger group of values (called "population") in an attempt to estimate some statistical parameter(s) (such as a mean value of metal concentrations, for instance), or to conduct a statistical test, while staying within economical and technical limits. If the entire population could be taken into account, a statistical estimate would reflect a "true" value. Any lesser number of observations will probably introduce an error. In other words, how close and how reliably will a statistical parameter represent the truth, or how correct a conclusion drawn from a particular statistical test will be, depends largely on the number of observations that were chosen to represent the population. Determination of a smallest number of

observations (smallest sample size) that will still allow a certain satisfactory level of confidence in a statistical evaluation, is a common problem. Unfortunately, it does not have a straightforward answer. The following are some of the reasons:

- Different statistical methods for testing hypotheses, or for determination of estimators (mean, variance, quantiles, etc.), require a different number of observations (data points) in order to achieve desired accuracy and level of confidence (i.e., the kind of methods involved must be known up-front);

- Desired accuracy and confidence level have to be predetermined;

- An assumption about normality of data distribution has to be made before the data is actually collected;

- A guess has to be made about dispersion (variability) of data.

It is obvious that the above requirements lead to a somewhat arbitrary determination of a smallest acceptable number of observations. To facilitate the initial choice of a (statistical) sample size for the purpose of establishing background based remediation standards for soils, Ohio EPA recommends a minimum of 12 (twelve) soil samples to be collected from an appropriate soil type (as described under "Requirements for Background Soil Sampling and Data Management" Section 3.11.1.1). In statistical terms, these 12 data points allow for determination of a mean value with 95% probability that it will not exceed a true (population) mean by 50%. In other words, if soil sampling, analysis and the mean value calculations were done repeatedly, many times in the same manner, a chance of making an estimate of a mean value 50% greater than the true mean is only 5%. If, for example, a true mean of a metal concentration in soil is 145 mg/kg, then the estimated mean would be less than 217.5 mg/kg (true mean + 50% of the true mean) 95% of the time. This is correct only under the assumption that the soil samples (not correlated over time and space) were collected through a simple random sampling process, that the results of laboratory analysis (data) are normally distributed, and that the coefficient of variation (the ratio between the standard deviation and the mean of the collected data) is within 95%. (For more detailed explanation, see Gilbert, Chapter 4.)

The above discussion shows that the recommended minimum of 12 (twelve) soil samples offers somewhat limited accuracy in estimating the mean value (and may be inadequate for some other type of statistical inference). If a more accurate estimate of the mean concentration of a constituent in a given soil is required, or if any other requirement (statistical method) so dictates, the necessary number of background soil samples has to be increased.

It is also important to mention that all 12 (twelve) soil samples have to be valid (i.e., usable). To avoid additional sampling in case something goes wrong (lab error, outlier, etc.), it is considered a good practice to collect more than 12 soil samples initially.

Various methods on how to determine an appropriate (necessary) number of observations are presented in many statistical textbooks, papers and guidance documents (some of which are referenced at the end of this section).

3.12.3 Data Comparison

Under the assumption that the background and confirmation data are normally distributed (which needs to be demonstrated through appropriate tests for normality, i.e. probability plots, box and whiskers plots, Shapiro-Wilk test, and/or Kolmogorov-Smirnov test with Lilliefors critical values) a BRS is defined as a **mean value plus two standard deviations of the background data (i.e., concentrations).**

So defined, BRS represents the 97.72th percentile (or the 0.9772 quantile - quantiles are percentiles expressed as a fraction rather than percents) of the background distribution. In that case, the soil can be declared successfully remediated (for the metal of concern) when the 95% upper confidence limit for the mean of the confirmation data (which also has to be normally distributed for this purpose) is significantly smaller than the BRS. This can be demonstrated through a one sided 95% confidence (i.e., 0.05 significance) level t test. (If all confirmation data points are below BRS, there is no need for any formal statistical test.)

$$\frac{\overline{Y} - BRS}{S_y / \sqrt{m}} < -t_{m-1,\ 0.95}$$

or

$$\overline{Y} + t_{m-1,\ 0.95} \times (S_y/\sqrt{m}) < BRS$$

where:

$\overline{Y}$ - mean of confirmation data

S_y - standard deviation of confirmation data,

m - number of confirmation samples, and

$t_{m-1,\ 0.95}$ - 0.95th quantile of the t distribution with m-1 degrees of freedom

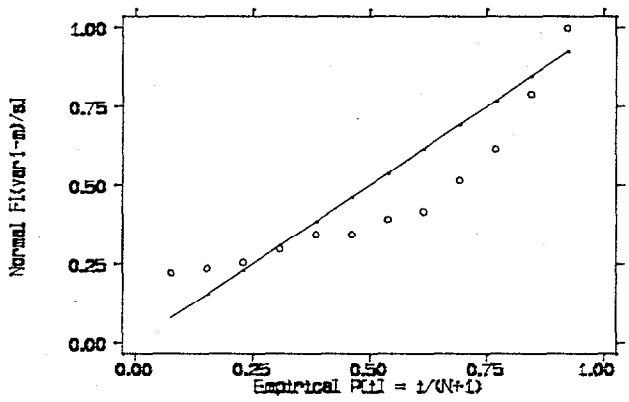
NOTE: When the background and confirmation data sets (both or either one) are not normal, and cannot be normalized, an appropriate nonparametric test (such as: Wilcox on Rank-Sum Test, test of proportions, etc.) should be utilized to prove that the soil has been satisfactorily remediated.

3.12.4 Test for Normality

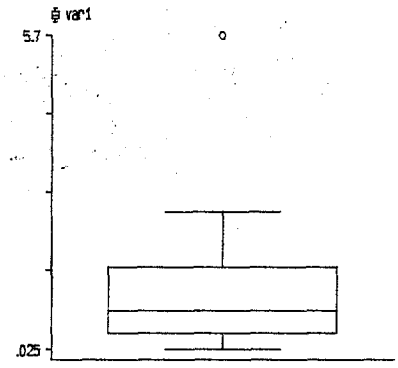
In order to correctly use a t test to demonstrate that the remaining contaminant concentrations do not significantly exceed the BRS, the background and confirmation data must be normally distributed, or transformed to normality using the same transformation. The demonstration of normality should be made graphically (through probability plots and box plots) and through either the Shapiro-Wilk test (also known as the *W*-test), or the Kolmogorov-Smirnov test with Lilliefors critical values. An explanation on how to perform the Shapiro-Wilk and Kolmogorov-Smirnov tests can be found in *Practical Nonparametric Statistics, 2nd Edition, W.J. Conover, 1980 (John Wiley & Sons); and Statistical Methods for Environmental Pollution Monitoring, R.O. Gilbert, 1987 (Van Nostrand Reinhold).*

As an example for graphical determination of normality, the data can be plotted as shown below;

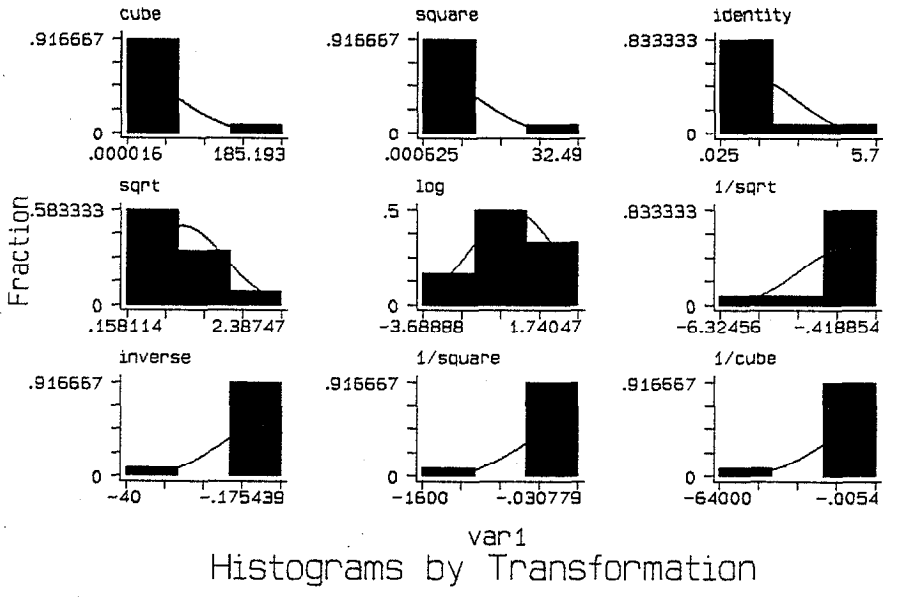
Normal Probability Plot



Box Plot

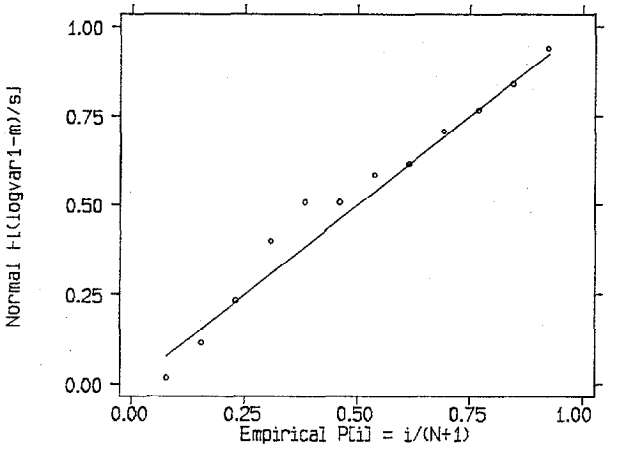


The graphs in this example tend to indicate that the data distribution is not normal. In the case of the probability plot graph, the closer the data points are to the line defining normality, the more likely the data are normally distributed. With the box plot graph, the more symmetrical the plot, the closer to normality the data distribution is. In order to proceed with the statistical analysis, the data set needs to be transformed to normality. Log or power transformations will often make a data set normally distributed. Some computer programs, as shown below, allow for a graphical comparison of several different transformations:

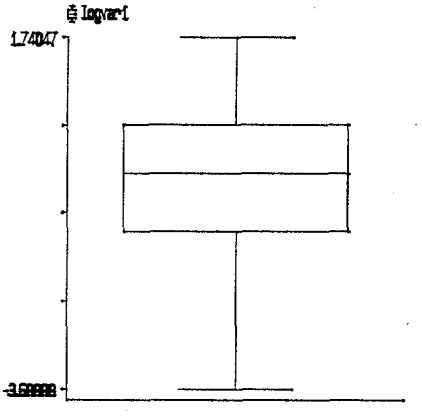


The graphs indicate that (in this case) a log transformation may be the best way to normalize the data. After transforming the data, a check with a probability plot and a box plot can be made to verify this indication.

Normal Probability Plot



Box Plot



A final check for normality should be made through the Shapiro-Wilk test, and/or Kolmogorov-Smirnov test with Lilliefors critical values.

It is important to note that, in order to conduct a t-test, the same kind of transformation must be applied to both, the background data set and the confirmation data set. In other words, to compare the 95% upper confidence limit for the mean of the confirmation data in the transformed scale, the remediation standard must be calculated from the background data set being transformed in the same manner.

If the data sets cannot be transformed to normality, an alternative method (one that does not rely on normality) must be used to prove that the soil has been successfully remediated. The two generally recommended (nonparametric) methods are the Wilcoxon Rank-Sum Test, and the Test of Proportions.

3.12.5 Test for Outliers

Prior to proceeding with statistical analysis, i.e., establishing a BRS from a normally distributed raw, or normalized (transformed) background data, a test for outliers should be conducted. This test is not required for the confirmation data set, but may be used for the screening purposes. Since, in this case, a discovery of an elevated concentration (above the BRS) usually indicates an incomplete remediation, additional soil removal (or treatment) consequently eliminates the outstanding concentration. One, or few slightly elevated concentrations in a confirmation data set may not necessarily require additional soil remediation - if an appropriate statistical test (such as t test) shows that the BRS has not been significantly exceeded. The following equations (Hoaglin et al, 1983) are used to determine whether there is statistical evidence that a background observation (constituent concentration) appears extreme and therefore does not fit the distribution of the rest of the data:

Upper cutoff = upper quartile + 1.5 (interquartile range) **Equation 1**

Lower cutoff = lower quartile - 1.5 (interquartile range) **Equation 2**

where:

Upper quartile ($Q_{.75}$ or Q3) equals an observation in the background data set which divides the data so that 25% of the data are greater than Q3 and 75% of the data are less than or equal to Q3;

Lower quartile ($Q_{.25}$ or Q1) equals an observation in the background data set which divides the data so that 75% of the data are greater than Q1 and 25% of the data are less than or equal to Q1; and

Interquartile range (IQR) equals the difference between the upper quartile and the lower quartile (i.e., IQR = Q3 - Q1).

Example for even number of background data:

Given the following data set consisting of twelve data points,

1.3 0.8 0.6 0.2 0.1 0.025

0.9 2.5 0.6 0.4 1.7 5.7

the first step is to order the data from least to greatest:

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
0.025	0.1	0.2	0.4	0.6	0.6	0.8	0.9	1.3	1.7	2.5	5.7

For an even number of data points, the quartiles are determined by splitting the ordered data set twice equally (i.e., into fourths). The quartiles are found at the splits and can be adequately estimated by averaging the data points on either side of the split. Using the above data set, Q1 falls between the 3rd and 4th observation and is therefore calculated as:

$$(0.2 + 0.4) / 2 = 0.3$$

Similarly, Q3 falls between the 9th and 10th observation and can be calculated as:

$$(1.3 + 1.7) / 2 = 1.5$$

This can be demonstrated visually as follows:

		Q1			(Q2 or median)			**Q3**			
(1)	(2)	(3) |	(4)	(5)	(6) |	(7)	(8)	(9) |	(10)	(11)	(12)
0.025	0.1	0.2	0.4	0.6	0.6	0.8	0.9	1.3	1.7	2.5	5.7
		|			|			|			
		0.3			(0.7)			**1.5**			

After calculating the quartiles, the next step is to calculate the interquartile range (IQR), or the difference between Q3 and Q1:

$$IQR = Q3 - Q1, \text{ i.e.}$$

$$IQR = 1.5 - 0.3 = 1.2$$

The final step is to calculate the Upper and Lower cutoffs as defined by the Equations 1 and 2 above:

$$\text{Upper cutoff} = 1.5 + 1.5(1.2) = 3.3$$

$$\text{Lower cutoff} = 0.3 - 1.5(1.2) = -1.5$$

(or 0, since a negative Lower cutoff does not make sense when data represent constituent concentrations).

In this case, only one observation is not in the range between 0 and 3.3 (i.e., 5.7, or the twelfth observation). Data points not falling between the upper and lower cutoffs should be reviewed to determine whether evidence exists to suggest that these observations are not representative of the background population. The reviewer should direct the facility (entity responsible for conducting closure) to check such data for sampling and laboratory errors, field evidence of waste materials at the sampling locations, and other plausible causes. Where sufficient evidence indicates that an observation does not truly represent concentrations found in background soil, a substitute observation must be provided. If no specific error can be documented, the observation should be retained in the data set.

Example for <u>odd</u> number of background data:

For odd numbered data sets, the lower quartile (Q1) can be found by multiplying the number of observations (n) by 0.25, and then rounding the result to the next largest integer. The resulting number indicates the observation which corresponds to Q1. Similarly, Q3 can be found by multiplying n by 0.75, and rounding to the next larger integer. This number refers to the observation which corresponds to Q3. For example, with the following data set (where n = 13):

(1)	(2)	(3)	(4)	(5)	(6)	(7)
0.1	0.2	0.4	0.6	0.6	0.8	0.9

(8)	(9)	(10)	(11)	(12)	(13)
1.3	1.7	1.8	2.1	2.5	5.7

For Q1:

$$0.25 \times 13 = 3.25; \text{ rounded up} = 4$$

So, Q1 is the 4th observation or 0.6.

Likewise for Q3:

$$0.75 \times 13 = 9.75; \text{ rounded up} = 10$$

So, Q3 is the 10th observation or 1.8.

Q2 (median) is simply the value in the middle - 7th observation or 0.9.

The rest remains the same as in the previous example for even number of data.

If there are no outliers, statistical analysis may proceed.

If outlier are found, their origin must be investigated (as previously explained) before proceeding with statistical analysis.

3.12.5.1 Outlier Screening Considerations

Availability of some pertinent information on the subject of interest is a prerequisite for conducting statistical analysis. This information is usually contained in a form of a data set generated from a series of observations. Only when these observations are made in accordance with some predetermined rule and followed by a careful data screening process, will the conclusions from statistical analysis be valid. If data do not represent the truth, the results will be more or less irrelevant, no matter how much sophistication was incorporated into the analysis.

One of the reasons why statistical analysis may not render a correct result is the presence of "outliers" in a data set. By some definitions, an outlier is "an observation which appears to be inconsistent with the remainder of the data set" (Barnett and Lewis, 1984), or "an observation which deviates so much from other observations as to arouse suspicions that it was generated by a different mechanism" (Hawkins, 1980). While these definitions provide a good qualitative description of outliers, some formal test is still required to detect their existence within a data set. Due to a relatively long history of this problem, many methods have been developed and are described in statistical literature ("How to Detect and Handle Outliers" by B. Iglewicz and D.C. Hoaglin, 1993, is a good starting reference). One of such methods is the boxplot rule which, in general form, defines the upper and lower fences as:

$$U = Q_3 + k(Q_3 - Q_1) \quad \text{and} \quad L = Q_1 - k(Q_3 - Q_1), \text{ respectively.}$$

Values falling outside the fences (also called the upper and lower cutoff points) are considered to be the potential outliers. In the above equations, Q_1 is the lower quartile, Q_3 is the upper quartile, $(Q_3 - Q_1)$ is the interquartile range, and the multiplicative constant k is one of the two factors determining the probability of labeling an observation as an outlier (the other factor is the number of observations). The common range for k is between 1.5 and 3.0. For the "standard" boxplot (the method recommended by the Ohio EPA) k equals 1.5. It is important to notice the distinction between results of the boxplot method when k takes a value on either side of this range. When k is set to 1.5, the boxplot may show a relatively high number of observations as outstanding, some of which may <u>not</u> be true outliers. On the other hand, when k equals 3.0, <u>all</u> observations that fall outside the cutoff points can be "safely" considered as outliers. A shortcoming, in this case, is that some lesser (but true) outliers may fall inside the fences and remain unflagged. In other words, the "standard" boxplot (k = 1.5) is more likely (approximately nine times - when a normally distributed data set consists of twelve observations) to label an observation as an outlier (albeit possible errors), than a boxplot where k equals 3.0. Hoaglin and Iglewicz (1987) have provided k values with specified probability of identifying at least one outlier in a normally distributed data set, depending on the number of observations. For example, if a data set consists of twelve observations, and k equals 2.2, the probability of labeling at least one observation as an outlier is 5%. The low probability of labeling an observation as an outlier also indicates that the test is "conservative" and that the labeled observation is indeed (very likely) an outlier. In cases where no detailed information exists about the origin of data, the above method can be advantageous by providing certain (predetermined) comfort level in screening out anomalous observations.

When screening observations for the purpose of creating a representative data set for determining background based remediation standards, a considerable amount of information on the data

generating process is usually available. As required, the collection and analysis of soil samples is assumed to be a process controlled by some predetermined sampling methods, analytical procedures and sample handling protocols, where the good understanding of soils, contaminants and relevant site features provides the basis for the choice of sampling locations. Although the intent of all these requirements is to provide reliable information, it is quite possible that some anomalous observations could be made throughout the process. If these observations are judged exclusively by their numerical properties (through the use of a statistical test), there is danger that some of them could be removed from the data set, or retained within, without investigating into the causes for inconsistency. Since an outstanding observation may point to some important issue (like possible site wide contamination, inherent variability of soil, sampling problem, lab error, etc.), it is necessary to utilize all available information when deciding whether the observation will be (justifiably) discarded, or retained in the data set. For that reason, the Ohio EPA recommends a procedure in which the "standard" boxplot method (where k = 1.5) is used for labeling potential outliers in a background data set, followed by a thorough investigation to reveal the reasons for any discovered inconsistency.

The "standard" boxplot method is considered to be accurate when data are normally distributed. In other cases, it should be used with caution. For the heavily skewed distributions, other methods are available and described in statistical literature.

3.12.6 Remarks:

(1) It is frequently found that a BRS has been calculated in the log scale and then exponentiated back to the original scale. This procedure is generally not acceptable because the results of operations conducted on means and standard deviations of transformed data may be biased when directly transformed back into the original scale.

(2) In some cases, a BRS exclusively calculated in the log scale and then exponentiated back to the original scale can be used for the screening purpose - and only if it does not exceed 97.72nd percentile of the untransformed data set. To finally prove that the soil has been successfully remediated, a t-test should be conducted on the log transformed site and background data.

(3) Duplicate observations (resulting from duplicate soil samples) should not be averaged prior to a statistical evaluation. Such averaging could lead to spurious conclusions (for example, an outlier could be masked by a smaller value).

(4) When non-detects are present, the following statistical methods are recommended for data comparison:

Percent non-detects (ND)	Recommended Method
ND <= 15 %	Replace NDs with MDL/2 (half Method Detection Limit) and proceed with the following analysis: - For normally distributed data, use parametric statistics, i.e., *t* test or 95% Upper Confidence Limit test as outlined above. Remark: As an alternative to MDL/2, Cohen's method may be used (when data are normally distributed) to determine sample mean and variance (i.e., standard deviation) in order to proceed with a *t* test, or 95% Upper Confidence Limit test. - If data can not be normalized, use nonparametric statistics such as Wilcoxon Rank-Sum test.
15% < ND<= 50%	- For normally distributed data, use Cohen's method to determine sample mean and variance (i.e., standard deviation) in order to proceed with a *t* test, or 95% Upper Confidence Limit test. - If data can not be normalized, use nonparametric statistics such as Wilcoxon Rank-Sum test, or Test of Proportions.
50% < ND <= 90%	Use nonparametric methods only: - Wilcoxon Rank-Sum Test, or - Test of Proportions
ND> 90%	Use Poison Tolerance Limits, or establish BRS = MDL

(5) Beside the specially designed statistical computer programs, general spreadsheet software (Excel, LOTUS, etc...) can also be very useful in assisting the closure plan reviewers with statistical reviews. Most spreadsheet applications contain many "built-in" functions for calculating statistics like mean, quartiles (or percentiles), variance, standard deviation, etc. However, quartiles (as well as other statistics) calculated by spreadsheet software sometimes may not be the same as if they were determined through the procedures described in this guidance document. The discrepancy is usually caused by the difference in methods.

3.12.7 Statistical Analysis Step-by-Step Guidance

Analyzing the Background Data Set (for the Constituent of Interest)

Step 1: Number of observations

Does the background data set consist of a minimum of 12 (or more) observations derived from 12 (or more) background soil samples (not counting split samples and duplicates)?

NO - Find out the reasons for this deficiency and request additional soil samples in order to obtain a data set with at least 12 observations.

YES - Proceed with Step 2.

Step 2: Number of non-detects (values reported as below the Method Detection Limit - MDL)

Are there any non-detects in the background data set?

NO - Proceed with Step 3.

YES - Check if MDL has been clearly stated and remains the same for all soil samples.

If MDL is not clearly stated (or some other value - like PQL, i.e. Practical Quantification Limit, has been used), contact the facility and request the MDL (and any previously unreported values above the MDL) before proceeding with statistical analysis.

If several different values are reported as MDL, request that additional soil samples be analyzed as necessary to obtain a data set (12 observations minimum) based on the same MDL.

If MDL is clearly stated and remains the same for all soil samples, determine the percentage of non-detects.

If the number of non-detects is less than (or about) 15% of the number of observations in the data set, substitute the non-detects with MDL/2 (one half of the Method Detection Limit) and proceed with Step 3.

If the number of non-detects is more than 15% of the number of observations in the data set, proceed in accordance with recommendations given in Section 3.12.6, remark #4.

Step 3: Normality of the background data set distribution

In order to be used in a meaningful calculation of a background-based Remediation Standard (BRS), the values in a data set have to be normally distributed. To test the normality of a data set, several methods are recommended:

- Shapiro-Wilk (W) test
- Kolmogorov-Smirnov (KS) test with Lilliefors critical values
- Normal Probability plot
- Box and Whiskers plot.

The normality check should at least include the Normal Probability and Box and Whiskers plots, and either W or KS test.

If the values in the data set are normally distributed, proceed with Step 4.

If the values in the data set are not normally distributed, it may not be possible to calculate a meaningful "single number" as a BRS. In that case, determination on whether the soil has been successfully remediated will have to be based on a statistical comparison of the normalized (transformed) background and confirmation data sets.

Step 4: Test for outliers

Use the following equations (see examples in the previous Section "Test for Outliers") to determine whether there is statistical evidence that a background observation appears extreme and therefore does not fit the distribution of the rest of the data:

Upper cutoff = upper quartile + 1.5 (interquartile range) **Equation 1**

Lower cutoff = lower quartile - 1.5 (interquartile range) **Equation 2**

If there are no outliers, proceed with Step 5.

If outlier(s) is (are) found, resolve the outlier issues (as explained in Section 3.12.5.1) and proceed with Step 5.

Remark: If a data set has to be transformed to normality, test for outliers can be conducted prior to transformation (i.e., on the "raw" data), bearing in mind that the heavily skewed distributions require extra caution. Sometimes elimination of outliers (and substitution with other valid observations, as necessary) can, by itself, bring a data set to normality.

Step 5: Calculation BRS from a Normally Distributed Data Set

a) Calculate the mean (μ_b) and standard deviation (S_b) for the background data set.

b) Calculate BRS as:

$$BRS = \mu_b + 2\,S_b$$

If BRS was calculated from a raw (untransformed) background data set, it can be either used for direct comparison with the confirmation concentrations, or in a t test (where the raw confirmation data also has to be normally distributed).

If direct comparison between the BRS and the raw confirmation data shows that no confirmation concentration exceeds the BRS, **STOP HERE** - the soil has been successfully remediated for this constituent.

If direct comparison shows that one or more confirmation concentrations exceed the BRS, a thorough evaluation be conducted to determine if this presents a threat to humans and the environment, whether the elevated concentration(s) should be considered and addressed as "hot spot(s)", whether and how many additional soil samples need to be collected, is it appropriate to perform ("switch" to) a statistical comparison, should these values be included in the data set when conducting a statistical test, etc.

If BRS was calculated from a transformed (normalized) background data set, it can only be used for a statistical comparison (where the confirmation data also has to be normalized with the same transformation.

Proceed with analysis of the confirmation data set.

Analyzing the Confirmation Data Set (for the Constituent of Interest)

Step 1: Number of observations

Does the confirmation data set consist of at least 12 observations derived from an equal number of confirmation soil samples (not counting split samples and duplicates)?

NO - Find out the reasons for this deficiency and request additional soil samples in order to obtain a data set with a minimum of 12 observations. (In some cases, where only direct comparison with BRS is employed, a smaller number of confirmation samples may be sufficient.)

YES - Proceed with Step 2.

Step 2: Number of non-detects (values reported as below the Method Detection Limit - MDL)

Are there any non-detects in the confirmation data set?

NO - Proceed with Step 3.

YES - Check if MDL has been clearly stated and remains the same for all soil samples.

If MDL is not clearly stated (or some other value - like PQL, i.e. Practical Quantification Limit, has been used), contact the facility and request the MDL (and any previously unreported values above the MDL) before proceeding with statistical analysis.

If several different values are reported as MDL, request that additional soil samples be analyzed as necessary to obtain a data set (12 observations minimum) based on the same MDL.

If MDL is clearly stated and remains the same for all soil samples, determine the percentage of non-detects.

If the number of non-detects is less than (or about) 15% of the number of observations in the data set, substitute the non-detects with MDL/2 (one half of the Method Detection Limit) and proceed with Step 3.

If the number of non-detects is more than 15% of the number of observations in the data set, proceed in accordance with recommendations given in the previous Section 3.12.6, Remark #4.

Step 3: Normality of the confirmation data set distribution

In order to be compared with BRS (through a t test), the values in the confirmation data set have to be normally distributed. To test for normality of the confirmation data set, the same methods (previously recommended for the background data set) can be used.

If the values in the confirmation data set are normally distributed, <u>and</u> the values in the background data set are normally distributed, proceed with the t test.

If the values in the confirmation data set are <u>not</u> normally distributed, a logarithmic or some other transformation should be performed <u>on both data sets</u> (confirmation <u>and</u> background) in attempt to normalize them.

If both data sets can be normalized with the same transformation, proceed with the t test.

If the attempt to normalize data fails, nonparametric statistical methods (such as Wilcoxon Rank-Sum test, or Test of Proportions) must be used in order to determine if the soil has been successfully remediated.

<u>t Test</u>

For convenience, t test will be explained through the following example:

Given the background and confirmation data (in mg/kg) for barium,

Ba - Background	Ba - Confirmation
3.43	15.7
43.37	37.5
44.51	43.7
45.04	44.63
48.29	45.88
50.81	49.5
57.74	55.84
62.36	60.71
64.76	70.26
78.27	80.62
79.4	110.3
110.8	115.24

the mean and standard deviation for the background data set are:

$$\mu_b = 57.398 \text{ and } S_b = 25.946$$

and the BRS can be calculated as:

$$BRS = \mu_b + 2\,S_b$$

$$\text{or } BRS = 57.398 + (2 \times 25.946) = 109.29 \text{ mg/kg.}$$

In order for the soil to be declared remediated for barium, a t test must show that the 95% upper confidence limit for the mean of confirmation data is smaller than the BRS, i.e.:

$$\overline{Y} + t_{m-1,\,0.95} \times (S_y/\sqrt{m}) < BRS$$

where:

$\overline{Y}$	-	mean of the confirmation data,
$t_{m-1,\,0.95}$	-	t-distribution critical value for m-1 degrees of freedom (df) and confidence level of 95%,
S_y	-	standard deviation of the confirmation data, and
m	-	number of confirmation data points (observations).

From the confirmation data set:

$m = 12$
$df = m-1 = 11$
$\overline{Y} = 60.823$
$S_Y = 29.236$

From the table below:

$t_{m-1,\,0.95} = 1.796$

t distribution critical values for 95% confidence level

df	4	5	6	7	8	9	10		12
t crt. val.	2.131846	2.015049	1.943181	1.894578	1.859548	1.833114	1.812462		1.782287

df	13	14	15	16	17	18	19	20	21
t crt. val.	1.770932	1.761309	1.753051	1.745884	1.739606	1.734063	1.729131	1.724718	1.720744

df	22	23	24	25	26	27	28	29	30
t crt. val.	1.717144	1.71387	1.710882	1.70814	1.705616	1.703288	1.70113	1.699127	1.69726

Remark: t distribution tables with critical values for other confidence levels and degrees of freedom can be found in various books on statistics.

By entering the values in the t test expression (where the left side represents the upper 95% confidence level for the mean of the confirmation data, and the right side is the BRS),

$$60.823 + 1.796 \; x \; (29.236 \; / \; \sqrt{12}) < 109.29, \quad i.e.:$$

$$75.98 < 109.29$$

it can be shown that the 95% confidence level for the mean of the confirmation data does not exceed the BRS, and the soil can be declared remediated for barium.

Another way to conduct this test is to calculate a t value using confirmation and background data, and then compare it to an appropriate critical value, i.e.:

$$\frac{\overline{Y} - BRS}{S_y / \sqrt{m}} < -t_{m-1,\, 0.95}$$

$$\frac{60.823 - 109.29}{29.236 / \sqrt{12}} < -1.796$$

$$-5.743 < -1.796$$

It is interesting to note that (in this example) the soil can be declared remediated for barium, in spite of the fact that the two confirmation soil samples exhibit concentrations above the BRS.

3.12.8 References

American Society for Testing and Materials, 1997. *Standard Practice for Dealing with Outlying Observations*, ASTM E178-94. American Society for Testing and Materials, West Conshohocken, Pennsylvania.

Bickel, P. J., and K. A. Doksum, 1977. *Mathematical Statistics: Basic Ideas and Selected Topics*, John Wiley & Sons Inc., New York, New York.

Conover, W. J., 1980. *Practical Nonparametric Statistics*, 2nd ed., John Wiley & Sons Inc., New York, New York.

Devore, J., and R. Peck, 1986. *Statistics: The Exploration and Analysis of Data*, West Publishing Company, St. Paul, Minnesota.

Gilbert, R. O., 1987. *Statistical Methods for Environmental Pollution Monitoring*, Van Nostrand Reinhold, New York, New York.

Hoaglin, D. C., F. Mosteller, and J. W. Tukey, 1983. *Understanding Robust and Exploratory Data Analysis*, John Wiley & Sons Inc., New York, New York.

Iglewicz B., and D. C. Hoaglin, 1993. *How to Detect and Handle Outliers*, American Society for Quality Control, Statistics Division, Milwaukee, Wisconsin.

Shapiro S. S., 1990. *How to Test Normality and Other Distributional Assumptions*, American Society for Quality Control, Statistics Division, Milwaukee, Wisconsin.

Snedecor G. W., and W. G. Cochran, 1980. *Statistical Methods*, 7th ed. Iowa State University Press, Ames, Iowa.

U.S. Environmental Protection Agency, 1992. *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance*, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency, 1992. *Statistical Training Course for Ground-Water Monitoring Data Analysis*, EPA/530-R-93-003. Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency, 1997. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846*, 3rd ed., Final Update 3. Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C.