

# Organic Carbon Sampling and Methodology Project: Yakima Railroad Area

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## INTRODUCTION

The magnitude of sorption, distribution of a contaminant between the subsurface solids and groundwater, is a critical parameter in determining site specific clean-up levels which are protective of groundwater. Sorption of many of the most frequently detected groundwater contaminants, such as chlorinated solvents and other hydrophobic organic chemicals (HOC), is directly proportional to the fraction organic carbon ( $f_{oc}$ ) content, also expressed as total organic carbon (TOC), of the sediments (e.g. Schwarzenbach and Westall, 1981). Even in subsurface sediments with very low  $f_{oc}$  a direct correlation between  $f_{oc}$  and the magnitude of HOC sorption,  $K_d$ , has been determined. Accurate measurements of  $f_{oc}$ , in conjunction with standard physicochemical property information for the contaminant of interest (such as solubility, octanol-water partitioning coefficient, or organic carbon partitioning coefficient), can be used to estimate site specific sorption. Thus, accurate measurements of organic carbon are of particular importance to environmental scientists and remediation planners.

Subsurface geologic samples, such as those comprising most aquifers, often have low TOC, and present particular analytical challenges because most analytical techniques for measuring TOC were developed for use on organic rich, carbonate poor, surface soils. Although a number of studies have been conducted to compare various aspects of organic carbon analytical techniques (e.g. Powell et al., 1989; Lee and Macalady, 1989) there are still questions as to which method should be used for different types of sediments. The methods described in this report measure TOC, defined as all organic carbon that is nonvolatile, including dissolved organic carbon.

The four primary goals of this work were: 1) to summarize the strengths and limitations of existing analytical approaches for TOC in geologic materials; 2) to compare the two approaches to TOC analysis which are most appropriate for subsurface materials using a test sample set with different chemical and geological attributes (method comparison); 3) to apply an appropriate technique to a set of Washington samples; and 4) to address TOC sampling and preparation effects. The method comparison included an evaluation of two of the approaches using a test set of six geologic samples with varying proportions of TOC and carbonate (inorganic carbon, IC) contents, and a comparison of acid treatment methods. The samples analyzed in this study consist of four samples supplied by Washington State University and 36 samples from the Yakima Railroad Area (YRRA) supplied by the Washington State Department of Ecology. This report will be useful to Ecology staff: in evaluating TOC analyses, in selecting appropriate sampling and analytical methods for particular samples, and in providing data for a set of Washington samples.

**DESCRIPTIONS OF ESTABLISHED ANALYTIC TOC METHODS**

There are four basic approaches to measuring TOC in soils and sediments, outlined in Table 1. The first approach assumes that the amount of carbonate in the sample is negligible relative to the amount of TOC. TOC can then be measured by one analysis using total carbon methods which do not require extensive sample preparation. The second approach is to measure total carbon and carbonate (inorganic carbon, IC) by two separate analyses to determine the percent of each. The computed difference is the TOC. The third approach requires pre-acidification of the sample to remove carbonate prior to total carbon analysis of the remaining carbon, TOC. The fourth approach measures TOC directly by a titration method, also known as wet oxidation. A known amount of dichromate is added to the sample which should oxidize all organic compounds, assuming all organic carbon has an average valence of zero. TOC is determined by titrating all remaining unreduced dichromate.

**Table 1 - Four Basic Approaches to Total Organic Carbon Measurement**

Approach		Advantages	Disadvantages	Limitations
1	Total Carbon (Assume IC is negligible)	One Analysis		Large errors if IC is present
2	Difference (TC-IC)	Minimize Sample Handling	Two separate analyses	High IC samples show high errors
3	Pre-Acidification (to remove IC)	Minimal Errors	Use of Acid	Acid must be compatible with instrumentation
4	Direct Measure of TOC	Simple titration procedure	Only good for organic rich samples	Does not completely oxidize all organic carbon

IC - inorganic carbon, TC- total carbon, TOC - total organic carbon

On page 4, Table 2 supplies additional information, outlining specific methods for each approach, supplying descriptions of appropriate sample types, and listing references for each method. Although four approaches have been identified from a review of the literature, only two, the difference and pre-acidification approaches, measure TOC consistently and accurately for subsurface geologic materials. Approach 1 is not appropriate unless the IC is negligible relative to the TOC. Approach 4 was developed to quantify larger TOC values in surface soils and sludge material rich in organics. This approach is not appropriate for the analytical accuracy required to determine site specific sorption (Plumb, 1981). Wet oxidation methods do not completely oxidize more refractory organic matter, thus can underestimate the “true” TOC (Powell et al., 1989). Lee and Macalady (1989) found that the standard deviation for wet oxidation replicates were 6 to 20 times greater than for high temperature combustion.

The accuracy of the difference method, Approach 2, depends on the accuracy of the two separate analyses of total carbon and carbonate (Table 2). Although total carbon methods which use high

temperature combustion are reproducible, the inorganic methodology is not as consistent from lab to lab, especially if dolomite is present in the sample (Nelson and Sommers, 1996, Caughey and Barcelona, 1994). This approach yields reasonable results when the absolute error of the carbonate measurement is low compared to the TOC. In other words, samples with high carbonate concentrations relative to TOC have inherent errors that are amplified by combining errors from two separate analyses (Nelson and Sommers, 1996). A discussion of how to compute the analytical error for this method (error propagation) is presented in Appendix B.

Approach 3, pre-acidification, has been shown to yield accurate TOC results for many sample types. Pre-acidification can be achieved with a variety of different kinds of acid. The most important questions to consider are: 1) is the acid compatible with the apparatus and detector in use? 2) will the acid completely evolve the inorganic carbon? 3) how long will it take? and 4) how much acid must be used? Sulfurous acid (used in this study) has been recommended for pre-acidification by Caughey and Barcelona (1994) and Caughey et al. (1995) with the coulometric system. The use of hydrochloric acid is common (e.g. Powell et al., 1989), especially when infrared detection is used. However, chlorine generated when using hydrochloric acid can interfere with coulometer detector reagents. Nitric acid has also been used successfully (e.g. Manchester). The accuracy of TOC by pre-acidification is dependent on total removal of all inorganic carbon prior to the measurement of TOC without causing destruction or removal of organic matter. Powell et al. (1989) found that 5% HCl did not sufficiently remove all carbonate. However, acid that is too concentrated may destroy organic matter in the sample. Caughey et al. (1995) reported 10-80% losses of TOC when concentrated acids such as HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> were used. Multiple applications and treatments are required when weaker acids are used.

Many pre-acidification methods suggest acidification of a sample until all effervescing has stopped (Caughey et al., 1995, Powell et al., 1989, Plumb 1981). This observational, qualitative method for determining an endpoint at which all carbonate has been removed may not be sufficient. In dolomite containing samples with low TOC, the carbonate tends to dissolve slowly, a significant amount of carbonate (IC) may be present compared to the TOC even though effervescing is not obvious. Two quantitative alternatives are to: 1) test an acid treated replicate for the presence of carbonate following acid treatment, or 2) add acid until the pH of the sediment in water has been measured to remain acidic (pH=1) for an extended period of time.

Most of the methods used for Approaches 2 and 3 rely on evolution of carbon as CO<sub>2</sub> with detection by a sensitive and accurate detector. The two most frequently used CO<sub>2</sub> detection methods are IR (infrared) (e.g. Powell et al., 1989, Heron, 1997, and Manchester) and coulometric (Caughey and Barcelona, 1994, Caughey et al., 1995 and as used by WSU).

**Table 2 - Available Methods for each Approach**

Approach	Parameter	Methods	Appropriate for Samples with:	References
1 - Total Carbon (Assume IC is negligible)	TOC	High Temperature Combustion (>900°C)	No Inorganic Carbon	1
	TOC	Ashing, Loss on Ignition (LOI)	IC << TOC	Historic
2 - Difference (TC-IC)	TC	High temperature combustion (>900°C)	Low Inorganic Carbon (Geologic sediments)	1,4,5
	TIC	Acidification to evolve CO <sub>2</sub>	Error on both analyses must be low	1,2,4,5
3- Pre-Acidification (to remove IC)	TOC	High temperature combustion (>900°C)	All Samples (Geologic Sediments)	1-8
	TOC	Methanator (650°C)		3
4 - Direct Measure of TOC	TOC	Wet Oxidation	Organic Rich Samples (Soils)	1,3,4

(1) Nelson and Sommers, 1996, (2) Caughey and Barcelona, 1994, (3) Powell et al., 1989, (4) Lee and Macalady, 1989, (5) Plumb, 1981, (6) Caughey et al., 1995, (7) Caughey et al., 1995, (8) Heron et al., 1997

## MATERIALS AND METHODS

### Sorbents

For this project there are three groups of samples: 1) those supplied by the Washington State University (WSU) geology department for the method comparison; 2) those collected by Department of Ecology staff in the vicinity of Yakima, WA (the eight sites are located within an area known as the Yakima Railroad Area (YRRA)); and 3) “truly representative” field samples from the YRRA. Subsets and combinations of these three sample types are used to address several issues in this text.

The method comparison samples (group 1) were selected because they represent a variety of ranges in the percent of organic and inorganic carbon and were from: Mexico City, MX; Sarnia, Ontario Canada; Borden, Ontario Canada; and Pullman, WA. Two YRRA samples were included in the method comparison for preliminary analyses to determine which method would be used for the remaining YRRA samples; they are Russel Crane 8 (YRRA RC8) and DeMar 6 (YRRA DM6). Table 3 shows the six samples with inorganic carbon and TOC determined by the difference method. The six samples were prepared and analyzed at WSU. Pre-prepared powders of method comparison samples were also sent to the Manchester Environmental Laboratory for TOC analysis as described below. The Manchester lab contracted out the analyses to Sound Analytical, but will be referred to as Manchester for this report.

**Table 3 - Method Comparison Samples: Varying Compositions of Organic and Inorganic Carbon** (Organic carbon determined by difference method, inorganic carbon determined by acidification with 2N H<sub>2</sub>SO<sub>4</sub>)

	TOC (%)	IC(%)	TC/TOC*
Mexico	4.27	0.60	1.14
Sarnia	0.54	4.04	8.46
Borden	0.03	1.71	69.32
Palouse	0.094	0.0006	1.01
YRRA DM6	0.093	0.0035	1.04
YRRA RC8	0.057	0.0020	1.03

\* Ratio indicating the inorganic carbon relative to organic carbon

The Mexico and Sarnia samples are clay rich aquitard materials and are described in Allen-King et al. (1995) and Allen-King et al. (1996). The Mexico sample was deposited in the Holocene in a lacustrine environment. The Sarnia sample was glacially deposited in the Quaternary. The organic material in the Sarnia aquitard is primarily from weathered shales of Devonian age. The Borden aquifer sample was taken from a sandy glaciolacustrine shoreline deposit, and was collected at the same depth as the well characterized sample of Ball et al. (1990). The Pullman

sample (called Palouse here) was collected from the Palouse Formation about 1.5 km east of Pullman, WA at 1.5 meters (4 ft) depth. The sample is loess made up of silt with minor amount of clay (Severson et al., 1992).

The YRRA is primarily a quaternary fluvial deposit of mixed lithology, made up of poorly sorted, coarse cobble material. The samples (group 2) were collected in wide-mouth 4 oz. jars at depths ranging from 0.3 to 3 m (1-10 ft) at each of eight sites for a total of 36 samples. The range of grain sizes collected in each sample was limited by the small jar size. Pebble sizes in the jars, if present, were on the order of 2-3 cm in diameter maximum. Field splits were sent to WSU and the Manchester lab to be prepared and analyzed by the respective lab protocols. Data from the two labs was compared to see the effect of field splitting and sample preparation.

Additional YRRA samples (group 3) and subsets of the YRRA samples were used to evaluate the effect of field sampling and sample preparation procedures. The three aspects of sampling and preparation effects on TOC measurements assessed were: 1) field splitting; 2) exclusion of coarse grain sizes; and 3) inclusion/exclusion of obvious roots.

To assess the effect of exclusion of coarse grain sizes on TOC measurements, two five-gallon bucket samples were collected to provide “truly representative” samples from two sites, Russel Crane (RC) and Noel (N), at 2.4 m (8 ft) depth. The two sites selected are representative of textures commonly found in the YRRA. The samples were dry sieved by hand using sieve sizes -1, -4, -5, and -6 phi (2, 16, 31.5, and 63 mm). A -2 sieve was also included for the Noel sample. Dry sieving which may leave some residue of fines on the surfaces of the larger grain sizes was used instead of wet sieving because this condition is likely more representative of field sampling. The smallest sieve size, 2 mm, was chosen because it is representative of the average grain sizes that were identified in the group 2 typical field samples. Sample preparation is described in the following section. TOC was measured on grains sizes of sieve size -4 phi and finer.

The influence of obvious roots on TOC measurements was determined for three YRRA samples, Mercy 4, Noel 2, and Toys R Us 2. These samples were selected from group 2 because they had obvious visible roots and were sampled at shallow depths, 4, 2 and 2 feet respectively. Representative splits were weighed and the visible roots were picked out and weighed to determine percent weight of the visible roots. The roots alone were then combusted in the same manner as the total carbon analysis as described in the methods section.

### **Sample Preparation**

The WSU sample preparation procedure required splitting the field sample to a working lab quantity while preserving sample representativeness. This entailed sample handling procedures to ensure that all grain sizes present were included in the subsample. Samples which contained grain sizes larger than 2 mm were crushed to reduce all grain sizes to 2 mm, which ensured passage through the rifle splitter. Each of the sieved grain sizes from the two YRRA five gallon bucket samples were crushed before splitting. An approximately 10 gram subsample was divided from the sample using a rifle splitter. All subsamples were pulverized in a shatter box with an alumina bowl (Ball et al., 1990). The bowl was cleaned with pre-fired silica sand between samples to avoid carry over. The silica sand was saved and analyzed to determine carbon



background, if any, due to pulverization. The weight of each sample analyzed was measured to  $\pm 0.00002$  g accuracy.

Two YRRA samples (group 2) were chosen to be method replicates to evaluate in-house consistency of sample preparation procedures. Splits of Lord 6 and Cent 1 were taken before grinding and treated as two separate samples.

Manchester had a similar sample preparation procedure. The entire sample was first crushed in a stainless steel mortar and pestle down to sand-sized particles. Then the entire sample was quartered and a sub-sample was then crushed to a fine powder, size not specified. A 5 - 15 mg sample was analyzed for TOC.

### **Analytical procedures**

#### ***WSU Hydrogeology Lab***

For all samples, high temperature combustion (CM5120, UIC) or acidification (CM5130, UIC) were used to evolve CO<sub>2</sub>, which was titrated using a coulometric system (CM5012, UIC) (Caughey and Barcelona, 1994; Lee and Macalady, 1989). Two or more replicates of each sample were analyzed to evaluate analytical reproducibility and relative error (RE, defined as the standard deviation divided by the mean). Blanks and standards were run with every batch of samples at the rate of 10% of the total number of samples with a minimum of two each per batch. The standard used was CaCO<sub>3</sub>.

#### ***Difference Method***

The total carbon (TC) analysis was achieved by dry combustion at 950°C in the presence of pre-purified oxygen. Combustion releases all inorganic and organic carbon in the form of CO<sub>2</sub> which was titrated coulometrically. Prior to combustion sufficient pulverized sample (0.5 to 1.5 g depending on the sample TOC), targeting a range from 1000 to 3000 mg C (optimum analytical performance), was weighed into a large (5 ml) pre-fired porcelain boat. Temperatures at 900°C or above are recommended for complete oxidation of carbon (Caughey and Barcelona, 1994). For inorganic carbon (IC) determination, pulverized sample ranging from 0.05 to 10 g (depending on sample) was weighed into a pre-cleaned medium porcelain boat (2 ml) and transferred to 10 ml flask. The sample was acidified with 2N H<sub>2</sub>SO<sub>4</sub>, releasing carbonate as CO<sub>2</sub>. Many of the samples had such low carbonate contents that large amounts of sample were needed, up to 10 g. In this case sample was weighed out directly into the 10 ml flask. Accurate IC measurements are dependent on complete mixing of the sample with the acid. Mixing was more difficult when sample sizes were large. For this research, all samples were vortexed while evolving CO<sub>2</sub>. TOC was determined as the difference between the observed TC and IC.

#### ***Pre-acidification: WSU***

Two methods of pre-acidification were used in this study; one method employed sulfurous acid and one used hydrochloric acid. Sulfurous acid is a volatile and relatively weak acid (6% SO<sub>2</sub>). Once treated with H<sub>2</sub>SO<sub>3</sub>, the samples can be completely dried. Because of the lower acid

strength, a greater volume of acid must be used to treat the samples. In order to ensure that complete removal of carbonate was achieved, a replicate was tested by the IC method following acid treatment. Hydrochloric acid is strong, hence complete removal of carbonate was assured. Samples were filtered and rinsed to remove excess chloride prior to drying to minimize interference with the coulometer. The acid strength has been known to destroy some organic matter. Thus, this procedure can result in the destruction and/or removal (by filtration) of some of the organic matter. The acid treatment methods were compared to determine if the filtration and washing procedure resulted in significant removal of TOC.

For both of the methods, the amount of sample to be analyzed was determined by preliminary tests using the difference method. The recommended target for the coulometric system employed is 1000 to 3000 mg C (UIC, 1991), so this was the target range for all samples. Ground sample aliquots ranging from 0.1 to 5 g were weighed in 20 ml beakers for acidification.

*Sulfurous Acid (H<sub>2</sub>SO<sub>3</sub>)* The samples were treated with several applications of H<sub>2</sub>SO<sub>3</sub>, as described in the following paragraph. Following each acid addition, the sample was stirred vigorously with a glass rod to ensure mixing, covered and allowed to mix on an orbital shaker for 3 - 4 hours, and dried in a vacuum oven at low temperature (40°C) (Caughey et al., 1995). Following acidification, the entire sample was transferred to a large pre-combusted porcelain boat, and combusted in the same manner as for the TC analysis, described above. For both pre-acidification techniques described here, care must be taken to transfer the entire sample to the boat. Alternatively, the beaker and sample can be weighed prior to the transfer, to determine the weight gain from the acidification reactions, and then the proportion of sample actually transferred to the boat can be determined. The entire sample is transferred to ensure that the analysis is on a representative sample. Triplicates of all samples were acidified, one of which was used to check for complete removal of inorganic carbon by the IC method described above. If all of the IC had not been removed, additional acid was added and the sample was rechecked.

The amount of H<sub>2</sub>SO<sub>3</sub> needed was estimated from preliminary IC analyses. For this study, the approximate weight of CO<sub>3</sub> in grams was calculated for each sample, then the acid volume was determined at the rate of 60 milliliters H<sub>2</sub>SO<sub>3</sub> per gram CO<sub>3</sub>. An additional 20% of that volume was added to the samples as the final acid application. This quantity of acid was based on qualitative observations from previous work on the method comparison samples. Other methods for determining the appropriate amount of acid can be found in Heron et al. (1997), and Caughey and Barcelona (1994).

The organic carbon content of the acid must be determined (Caughey and Barcelona, 1994; Heron et al., 1997). In this study, TOC concentration in the acid was determined by pipetting a known amount of acid into a large pre-fired porcelain boat, drying, and then combusting. Because of the volatile nature of sulfurous acid, all acid treatments should be conducted in a fume hood.

*Hydrochloric Acid (HCl)* Approximately 10 ml of organic-free water (Millipore) was added to the sample to make a slurry. Concentrated hydrochloric acid (50%) was added to the beaker in 0.5 ml aliquots and the samples were stirred with glass rods to ensure mixing. Acid was added in this manner until no effervescing was observed during stirring. The sample was left overnight

and the pH was checked the following day. If the solution was not acidic (pH=1), then additional acid was added. Once acidification was complete, the sample was vacuum filtered through an organic-free borosilicate filter and washed with organic-free water to remove acid residue (chlorine). Following washing, the filter and sample were transferred to a large, pre-combusted porcelain boat, dried overnight at 40°C, and combusted in the same manner as the total carbon samples described above. Pre-fired silica sand treated with the hydrochloric acid was used to detect background carbon contamination in the acid. Blank filters were also combusted to determine if the filters contained a carbon background. These background carbon checks on the filters and the sand yielded insignificant quantities of carbon contamination. Duplicates of the pre-acidification samples were not analyzed for IC. It is assumed that the end point of sustained acidic pH is sufficient to establish the complete removal of carbonate.

Quartz fiber filters, which do not melt during the combustion analysis, were also tested in this study. The advantage of quartz filters would be pre-combustion before use, however poor sample retention was observed for these filters. Therefore, borosilicate filters which showed good retention of sample were chosen for this study even though they melted.

#### ***Pre-acidification: Manchester Environmental Lab***

The Manchester protocol uses a pre-acidification approach described in Puget Sound Protocols, Conventional Sediment Variables (1986) pages 23-26. This method has been updated and modified as outlined by SOP NO: SAS-0157 supplied by Sound Analytical Services, Inc. for TOC analyses. 5 - 15 mg of sample was weighed into pre-combusted boats, treated with several drops of 1:1 nitric acid until effervescing ceased, dried at 70°F and combusted in the presence of pure oxygen at 900°C (per conversation with Curt Leach, Sound Analytical Services, Inc.). Carbon dioxide was quantified with an IR detector.

#### **Error Analysis**

Errors in TOC analysis come from analytical inconsistencies, differences in sample preparation procedures, and natural variations in field splits. To address analytical error in the WSU lab two or more replicates of all TOC analyses were determined. Because some analyses had more than two replicates, relative errors (RE=standard deviation/mean) were determined instead of relative differences (RPD= difference/mean). For the difference method, error propagation methods (Meyer, 1975 Appendix B) were needed to combine error for the two separate analyses, TC and IC, used to compute TOC. For the pre-acidification methods, two replicates were used for each sample, and RE was used to quantify error to be consistent with the difference method.

The YRRA TOC data determined by the WSU and Manchester labs was compared to quantify the amount of error between labs. The error between labs is presented in Appendix A as RPD.

## RESULTS AND DISCUSSION

### Method Comparison

#### *Difference and pre-acidification methods*

Table 4 lists TOC measured by three different methods in the WSU lab, including standard deviation and relative error calculated using analytical replicates. The TOC results obtained by all three treatment methods are comparable. Overall, relative errors were lowest for the samples which were pre-acidified with sulfurous acid. The largest relative errors are associated with the difference method, for example 27.4% RE for the Borden sample. This large error is due to the combination of error from two separate analyses and the large amount of inorganic carbon relative to organic carbon. This is an example of how samples with high carbonate content are better analyzed by a pre-acidification method. The difference method TOC values may also be affected if the amount of inorganic carbon has been underestimated due to incomplete evolution of CO<sub>2</sub> when dolomite is present. Dolomite destruction requires longer reaction times and stronger acids (Caughey and Barcelona, 1994; Heron et al., 1997). This may be the case for samples like Sarnia and Borden, which are carbonate rich and may contain dolomite.

**Table 4 - TOC (%) measured by three different methods at WSU**

	TOC - Difference Method (3 replicates)			TOC - Pre-acidification - $\text{H}_2\text{SO}_3$ (2 replicates)			TOC - Pre-acidification - HCl (2 replicates)		
	Mean (%)	SD (%)	Relative Error (%)	Mean (%)	SD (%)	Relative Error (%)	Mean (%)	SD (%)	Relative Error (%)
Mexico	4.27	0.007	0.17	4.65	0.11	2.4	3.91	0.13	3.2
Sarnia	0.54	0.02	3.8	0.52	0.007	1.4	0.51	0.005	1.1
Borden	0.025	0.007	27.4	0.022	0.0002	0.94	0.019	0.0002	1.0
Palouse	0.094	0.0015	1.6	0.096	0.0018	1.9	0.089	0.0034	3.8
YRRA DM6	0.093	0.0004	0.4	0.094	0.00014	0.15	0.089	0.0037	4.1
YRRA RC8	0.057	0.0006	1.0	0.057	0.00007	0.12	0.055	0.0013	2.4

SD = Standard Deviation;

Relative Error (%) = (Standard Deviation / Mean ) \* 100

The TOC values determined by the two different pre-acidification methods were compared using analysis of variance for each individual method comparison sample. Analysis of variance for each sample revealed that only Mexico and Borden were significantly different, at the 95% confidence level, even though the means appear lower for most of the HCl treated samples. There are several reasons why the HCl filtration method can yield lower TOC than the H<sub>2</sub>SO<sub>3</sub> method: 1) the HCl rinsing procedure may extract and wash away significant amounts of

organic carbon, and 2) the concentrated hydrochloric acid may destroy organic carbon (Caughey et al., 1995, Heron et al, 1997).

The high Mexico mean for the H<sub>2</sub>SO<sub>3</sub> pre-acidification treatment could be due to incomplete evolution of CO<sub>2</sub> by pre-acidification. The H<sub>2</sub>SO<sub>3</sub> TOC value, an average of two replicates, is approximately 9% higher than the difference method TOC value. A replicate of the pre-acidified Mexico sample was tested for the presence of carbonate prior to the two TOC analyses. However, the replicate tested for the presence of carbonate was lower in weight than the other two replicates by 3 and 16%. The replicates with more mass may have required additional acid that was not apparent by checking the replicate with the lowest weight.

### ***Method Choice: YRRA***

Two samples from the set of YRRA samples were evaluated in the method comparison to gain preliminary data to help choose an appropriate method for the remaining YRRA samples. The two YRRA samples, YRRA DM 6 and YRRA RC 8, had low amounts of inorganic carbon. Comparable results of the two samples prepared at WSU were determined by the difference and pre-acidification methods as shown on Table 5. Because no significant interference was apparent from the inorganic fraction of the samples the difference method, which required the least effort, was used for the remaining YRRA samples. The data for the remaining YRRA samples is presented in Appendix A.

## **Sample Preparation and Field Sampling Effects**

### ***Interlaboratory comparison***

The interlaboratory comparison portion of this study had two aspects: the six method comparison samples were prepared (split and pulverized) at WSU according to the WSU methods and analyzed by both labs; and all of the YRRA samples were split in the field and field splits were analyzed by both labs. The purpose of the first aspect is to compare the analytical procedures for samples with widely varying properties which were uniformly prepared. The second aspect allows comparison of the effects of field splitting and sample preparation techniques.

***Sample Preparation Effects*** The results of TOC analyses of the six method comparison samples, conducted by both the WSU and Manchester lab using pre-acidification methods are shown in Table 5. RE (%) was calculated for only one sample (Palouse) at Sound Analytical using three analytical replicates. TOC values measured for four of the samples, including the YRRA samples, prepared at one lab and analyzed at both labs had RPDs less than 10%. The organic carbon content in the Borden sample is very low, thus 12% RPD does not represent a larger amount of carbon. The RE calculated for the Palouse sample at Sound Analytical does not account for the difference between labs (RPD). Overall RPD between labs, 0 - 24%, is small for the method comparison samples prepared at one lab, compared to the RPD calculated on the field splits of the YRRA samples (group 2) presented in the next section. Close agreement between the analyses generated for the same sample powders indicate that with consistent

sample preparation, the pre-acidification method shows reproducible results between labs regardless of choice of acid or detector.

**Table 5 - Interlaboratory Comparison of samples prepared at WSU**

	WSU (Hydrogeology Lab)		Department of Ecology (Sound Analytical)		Interlaboratory Comparison
	TOC - Mean*	RE(%)	TOC - Mean**	RE (%)	%RPD
YRRA DM 6	0.094	0.15	0.094		0
YRRA RC 8	0.057	0.12	0.057		0
Mexico	4.65	2.4	4.200		10
Sarnia	0.52	1.4	0.470		8
Borden	0.022	0.94	0.026		12
Palouse	0.096	1.9	0.075	5.7	24

\* Pre-acidification with H<sub>2</sub>SO<sub>3</sub>, two replicates

\*\* Pre-acidification with H<sub>2</sub>NO<sub>3</sub>, three analytical replicates for Palouse sample only

**Field Sampling Effects** The relative percent difference (%RPD=(difference/mean)\*100) for the field splits of YRRA samples (group 2) analyzed by the two labs ranges from -29.3% to 86.1%. Positive values indicate that the Manchester lab analyses yielded larger values for TOC. Prior to sample preparation, grain size was classified as either coarse or fine, depending on whether or not grain sizes larger than 2 mm were observed. When the data was sorted by coarse or fine, the average RPDs were 29.2% and 4.6% for the coarse and fine classes, respectively, which is significant at the 90% confidence level. The approximately 30% higher mean TOC reported for coarse textured samples is likely a result of difficulties encountered in subsampling coarsely textured materials in the lab. TOC for fine grained samples were more reproducible between labs. These results highlight the importance of representative subsampling and preparation procedures.

Overall the two TOC data sets compiled by WSU and Manchester were log normally distributed determined by Lilliefors probability analysis, using SYSTAT. Analysis of variance of the two data sets showed that they were not significantly different at the 95% confidence level.

**Grain Size and Roots**

**Grain size distribution and TOC** The grain size analysis done on the two "truly representative" YRRA samples, Russel Crane (RC) and Noel (N), is presented in Table 6. These two sites are very different in their distribution of grain sizes and represent material typical of the YRRA site samples, shown graphically in Figure 1. The grain size analysis done by Ecology for "truly representative" samples shows that the Airport and DeMar sites are similar to the Noel Site, and the Lord and Mercy sites are similar to the Russel Crane site. The YRRA samples (group 2) submitted to WSU and Manchester were limited in the distribution of grain size by the small size of the sample jars, maximum grain size was approximately 3 cm on average. The extreme

poorly sorted nature of the Yakima gravels increases the difficulty of collecting representative field samples which can be easily handled by analytical laboratories.

The distribution of TOC for the different grain sizes is also presented in Table 6. Figure 2 shows how TOC decreases with increasing grain size. In the YRRA, TOC is concentrated in the smaller grain sizes; 48%<sup>c</sup> (85%)<sup>d</sup> and 60%<sup>c</sup> (70%)<sup>d</sup> of the measured TOC is in the < 2 mm grain size for RC and N respectively, Figure 3.

**Table 6 - Grain Size distribution and TOC for representative samples**

Sample	Grain Size	Weight (kg)	% by Weight	TOC (%)
YRRA RC8	field split			0.057 <sup>a</sup> (0.083) <sup>b</sup>
Bulk YRRA RC	< 2 mm	1.62	5.5	0.200
Bulk YRRA RC	2 - 16 mm	1.11	3.7	0.025
Bulk YRRA RC	16 - 31.5 mm	1.91	6.4	0.012
Bulk YRRA RC	31.5 - 63 mm	6.65	22.4	-
Bulk YRRA RC	> 63 mm	18.42	62	-
Weight average TOC				0.023 <sup>c</sup> (0.013) <sup>d</sup>
YRRA N8	field split			0.062 <sup>a</sup> (0.057) <sup>b</sup>
Bulk YRRA N	< 2 mm	10.46	26.9	0.067
Bulk YRRA N	2 - 4 mm	1.74	4.49	0.045
Bulk YRRA N	4 - 16 mm	5.64	14.5	0.022
Bulk YRRA N	16 - 31.5 mm	8.82	22.7	0.013
Bulk YRRA N	31.5 - 63 mm	5.98	15.4	-
Bulk YRRA N	> 63 mm	6.18	15.9	-
Weight average TOC				0.030 <sup>c</sup> (0.026) <sup>d</sup>

a WSU field split, 4 oz jar: analysis by difference method

b Manchester field split, 4 oz. jar: analysis by pre-acidification

c TOC calculated by weighted average, larger grain sizes assume TOC to be same as 16 - 31.5 mm grain size

d TOC calculated by weighted average, larger grain sizes assume TOC is zero

Sample representativeness is an important issue for determining appropriate TOC concentrations used for sorption computations which consider the entire bulk sample. The “true” TOCs estimated as the weighted average TOC from the grain size analysis, are 0.023% (0.013%) and 0.030% (0.026%) for YRRA RC and YRRA N, respectively (Table 6). The YRRA samples (group 2) field splits collected in 4 oz. jars at the same depth, have TOC 100-400% greater than the “true” values. These results demonstrate the effect that biased field sampling can have on very coarse grained, poorly sorted aquifer material.

**Roots** The amount of organic carbon in the visible roots was negligible compared to the TOC measured for the subsamples of Mercy 4, Noel 2, and Toys R US 2 determined by the difference method.

## **Error Analysis**

Figure 4 shows RE for analytical error on the replicates of the method comparison samples analyzed by the difference method. The difference method errors were calculated by error propagation of the two separate analyses of TC and IC. An explanation of how this was done is in Appendix B. The %RE for the difference method increases with increasing carbonate content consistent with observations of Powell, et al. (1989).

Two method replicates, YRRA Lord 6 and YRRA Cent 1, were prepared and analyzed at WSU to show the variations in analysis within the WSU lab for subsample splits. The method replicates show that consistent sample preparation methods yield RPD of 18 - 28% for the YRRA samples. The Manchester lab did not supply any information about method replicates done in their lab.



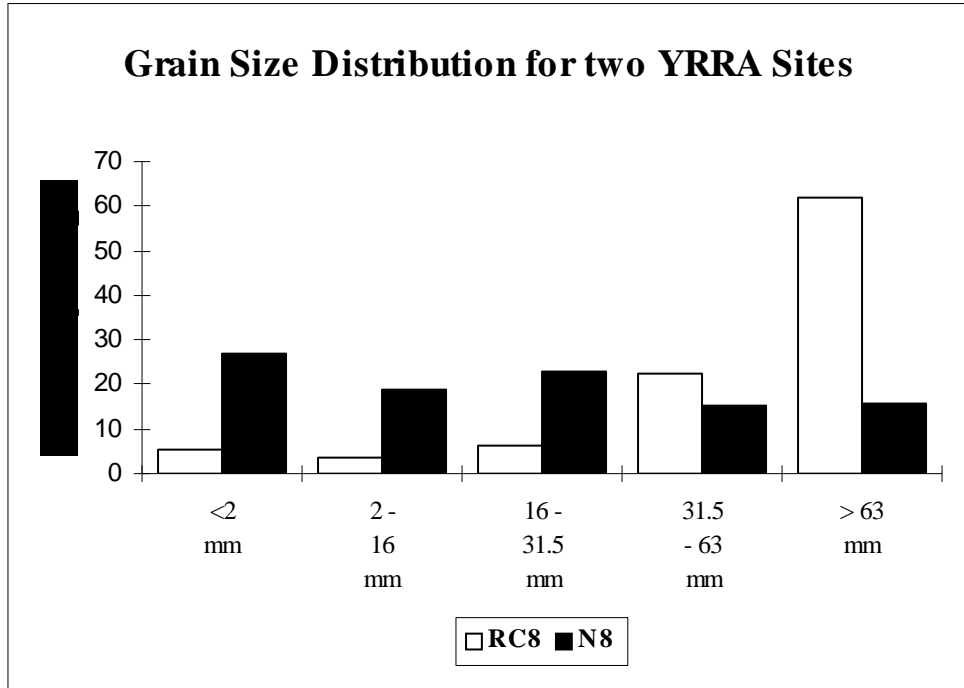


Figure 1 - Grain size distribution for RC8 and N8 determined by dry sieving and weighing each size fraction.

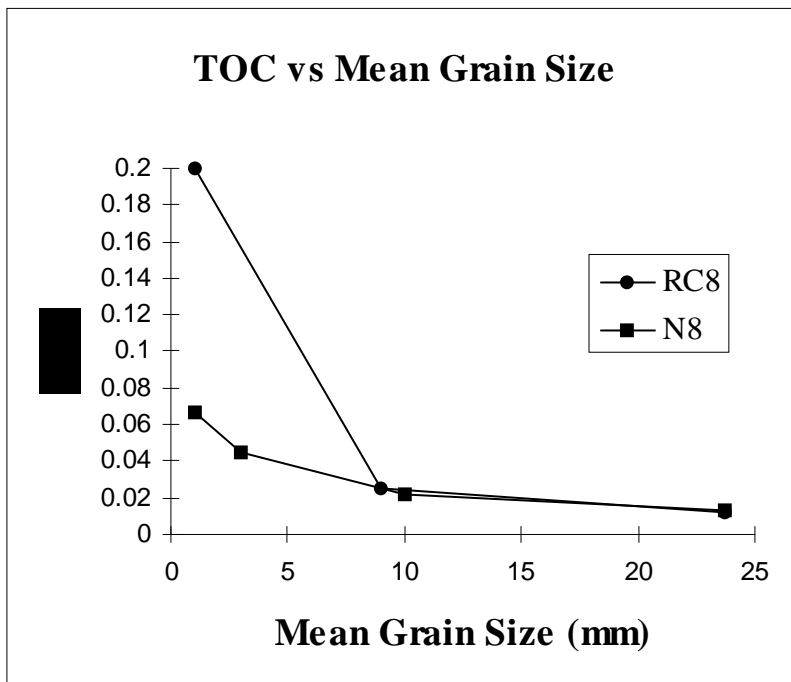


Figure 2 - TOC decreases with increasing grains size. RC8 and N8 are “truly” representative field samples taken at 8 feet depth.

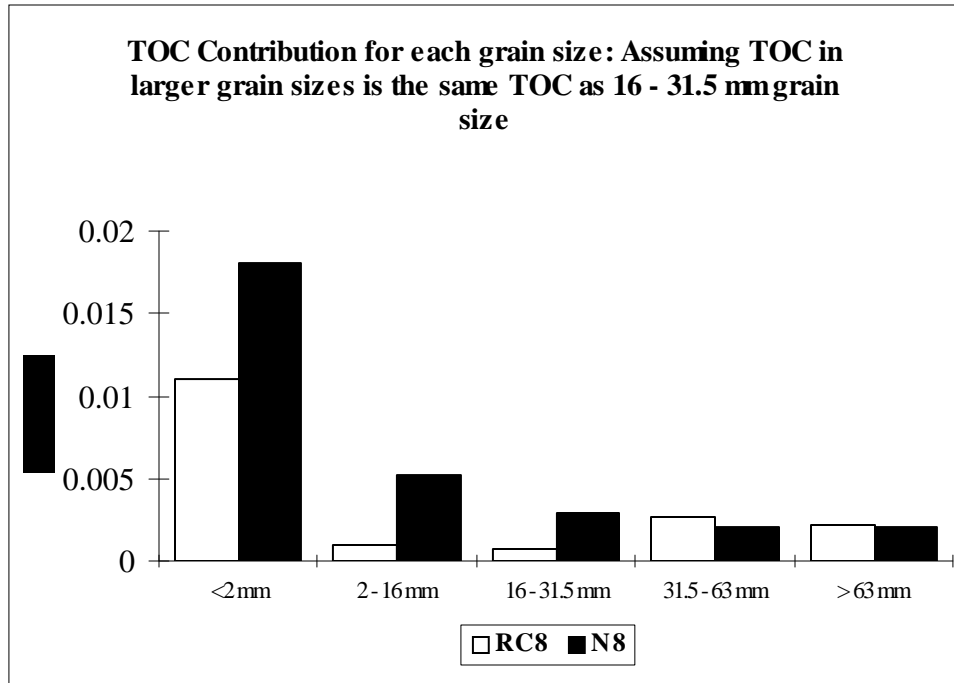


Figure 3 - TOC contribution for each grain size: assuming TOC in larger grain size is the same TOC as 16 - 31.5 mm grain size. TOC is concentrated in the smallest grain size.

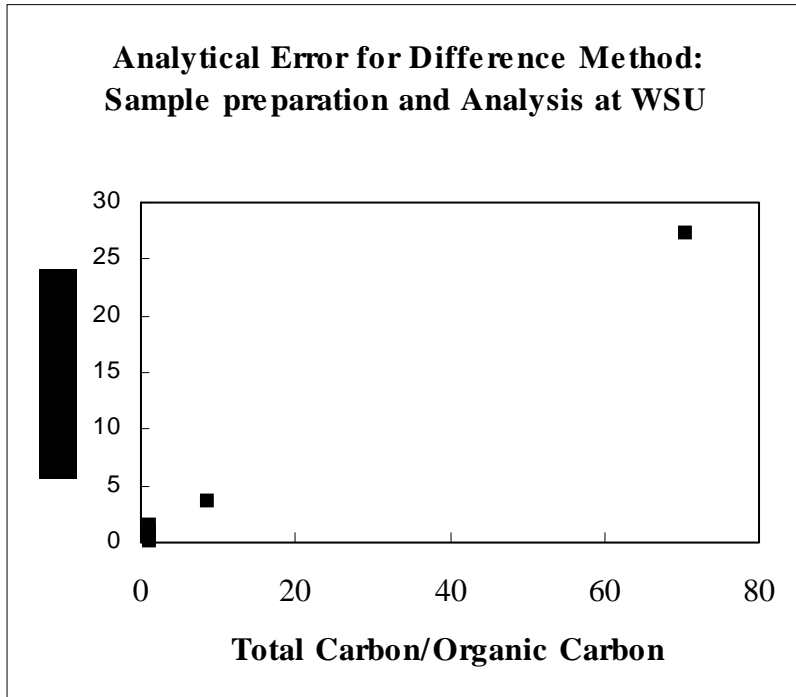


Figure 4 - Error propagation for the difference method show that % RE increases as the amount of inorganic carbon increases.

## **SUMMARY**

### **Descriptions of Established Analytic Methods**

- LOI and wet oxidation are not appropriate methods for geologic samples with low TOC.
- Difference and pre-acidification methods are most appropriate for geologic samples with low TOC.

### **Method Comparison**

- The difference method yielded reasonable TOC values for all samples except when  $IC \gg TOC$ .
- The pre-acidification method using sulfurous acid showed the lowest errors overall.
- Hydrochloric acid evolves inorganic carbon successfully, although the washing procedure and concentrated acid may affect the measurement of TOC overall.

### **Field Sampling and Sample Preparation Effects**

- TOC was analytically reproducible between labs when sample preparation was consistent.
- Exclusion of coarse grain-sizes during field sampling over-estimates TOC.
- Grain size may have significant effect on TOC (due to sample preparation methods?).
- Grain size distribution analysis is very important if only a fraction is submitted to the lab. (Sample representativeness must be preserved)

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APPENDIX A  
Yakima Railroad Area TOC Data

Manchester Lab (Sound Analytical)				Washington State University			Observations		Interlaboratory Comparison of Organic Carbon Data		
Common Name	Client ID (WSU #)	Analysis Done on 8/23/96		Percent Total Carbon	Percent Inorganic Carbon	%OC	Fine/Coarse	Depth (ft)	Mean	Difference	%RPD (Diff/Mean)
		Total Organic Carbon (mg/kg)	%OC								
Toys R US	308281	2400	0.240	0.2060	0.00219	0.2038	Coarse	2	0.222	0.036	16.3
Toys R US	308282	4700	0.470	0.2713	0.00765	0.2637	Coarse	4	0.367	0.206	56.2
Toys R US	308283	1600	0.160	0.1029	0.00234	0.1006	Coarse	8	0.130	0.059	45.6
Russel 2	308284	610	0.061	0.0385	0.00252	0.0360	Coarse	2	0.048	0.025	51.7
Russel 6	308285	820	0.082	0.0379	0.00174	0.0362	Coarse	6	0.059	0.046	77.6
Russel 4	308286	570	0.057	0.0519	0.00252	0.0494	Coarse	4	0.053	0.008	14.4
Russel 8	308287	830	0.083	0.0593	0.00196	0.0573	Coarse	8	0.070	0.026	36.6
Mercy 2	308288	17000	1.700	1.9054	0.06867	1.8367	Coarse	2	1.768	-0.137	-7.7
Mercy 4	308289	6200	0.620	0.8235	0.00437	0.8191	Coarse	4	0.720	-0.199	-27.7
Mercy 6	308290	2200	0.220	0.1941	0.00381	0.1903	Coarse	6	0.205	0.030	14.5
Mercy 8	308291	1000	0.100	NR			NR				
Lord 2	308292	1100	0.110	0.0657	0.00193	0.0638	Coarse	2	0.087	0.046	53.2
Lord 4	308293	820	0.082	0.0356	0.00218	0.0335	Coarse	4	0.058	0.049	84.1
Lord 6	308294	740	0.074	0.0360	0.00301	0.0330	Coarse	6	0.053	0.041	76.7
Lord 6 MR				0.4200	0.00229	0.0390					
Lord 8	308295	620	0.062	0.0329	0.00511	0.0278	Coarse	8	0.045	0.034	76.2
Lord 10	308296	560	0.056	0.0483	0.00493	0.0434	Coarse	10	0.050	0.013	25.5
Noel 2	308297	5900	0.590	0.6405	0.07127	0.5693	Fine	2	0.580	0.021	3.6
Noel 4	308298	4000	0.400	0.6099	0.21162	0.3983	Fine	4	0.399	0.002	0.4
Noel 6	308299	2100	0.210	0.2845	0.00243	0.2821	Fine	6	0.246	-0.072	-29.3
Noel 8	308300	570	0.057	0.0648	0.00312	0.0617	Coarse	8	0.059	-0.005	-8.0
DeMar 2	308301	6900	0.690	0.7159	0.39797	0.3179	Fine	2	0.504	0.372	73.8
DeMar 4	308302	3100	0.310	0.3359	0.00470	0.3312	Fine	4	0.321	-0.021	-6.6
DeMar 6	308303	1400	0.140	0.0960	0.00348	0.0925	Fine	6	0.116	0.047	40.8
DeMar 8	308304	NR	NR	NR			NR				
Air 2	308305	3500	0.350	0.4039	0.00510	0.3988	Fine	2	0.374	-0.049	-13.0
Air 4	308306	2600	0.260	0.7176	0.44487	0.2727	Coarse	4	0.266	-0.013	-4.8
Air 6	308307	1600	0.160	0.1865	0.00629	0.1802	Fine	6	0.170	-0.020	-11.9
Air 8	308308	2000	0.200	0.2883	0.05539	0.2329	Fine	8	0.216	-0.033	-15.2
Air 10	308309	1900	0.190	0.2224	0.03910	0.1833	Fine	10	0.187	0.007	3.6
Cent 1	308310	130	0.013	0.0130	0.00221	0.0108	Coarse	1	0.012	0.002	18.5
Cent 1 MR				0.0170	0.00240	0.0140					
Cent 2	308311	270	0.027	0.0138	0.00307	0.0108	Coarse	2	0.019	0.016	86.1
Cent 3	308312	590	0.059	0.0580	0.00189	0.0561	Coarse	3	0.058	0.003	5.0
Cent 4	308313	200	0.020	0.0221	0.00173	0.0204	Coarse	4	0.020	0.000	-1.9
Cent 5	308314	300	0.030	0.0290	0.00227	0.0268	Coarse	5	0.028	0.003	11.4
Cent 6	308315	340	0.034	0.0315	0.00185	0.0297	Coarse	6	0.032	0.004	13.6
Cent 7	308316	1000	0.100	0.1143	0.00211	0.1122	Coarse	7	0.106	-0.012	-11.5

MR - Method Replicates are subsamples, and treated as two separate samples which are prepared and analyzed separately

NR - not received at the WSU laboratory

Analytical Replicates are listed on the next page

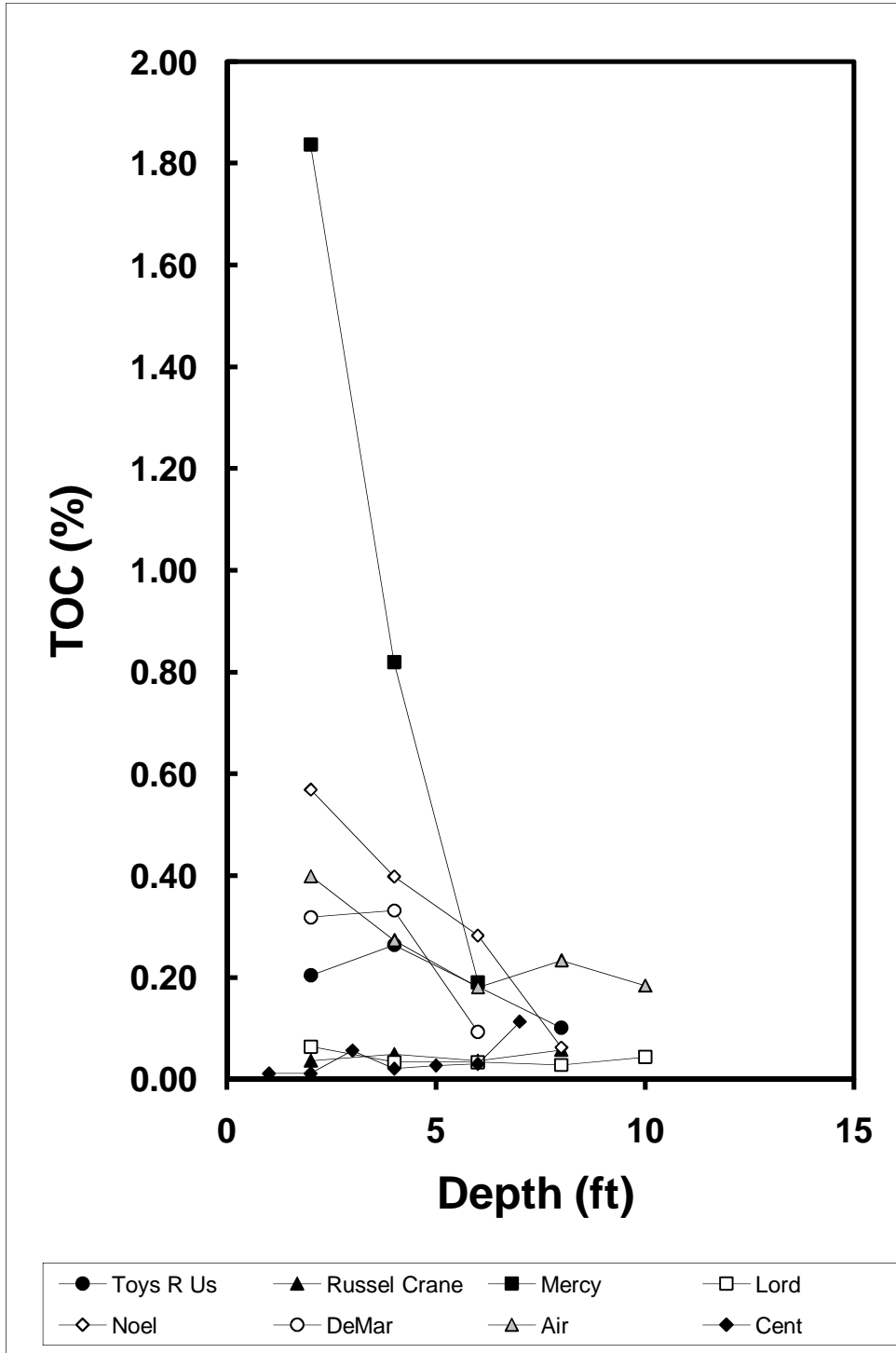
### Analytical Replicates of YRRA Samples

<b>Total Carbon</b>					
Sample	ID #	Sample Weight (g)	% TC	RPD (%)	Comments
Air4	308306	1.3016	0.7175		
Air4 -R	308306R	1.0235	0.7186	-0.141	
Toys R US	308282	1.1520	0.2713		
Toys R US F	308282R	1.1041	0.2297	16.639	
Noel 6	308299	1.8981	0.2845		
Noel 6 R	308299R	1.1761	0.2825	0.691	
Cent 1	308310	2.1942	0.0130		
Cent 1 R	308310R	2.1707	0.0126	3.045	
Noel 2-4 mm			0.0489		
Noel 2-4 mm R			0.0477	2.363	
<b>Inorganic Carbon</b>					
Sample	ID #	Sample Weight (g)	% IC	RPD (%)	Comments
Mercy 6	308290	3.0739	0.0038		
Mercy 6 R	308290R	4.3937	0.0012	104.984	**
Air 8	308308	3.6883	0.0554		
Air 8 R	308308R	4.5579	0.0548	1.119	
Russel 2	308284	5.3983	0.0025		
Russel 2 R	308284R	5.1101	0.0025	-1.195	
Noel 4	308298	5.0583	0.2116		
Noel 4 R	308298R	1.4737	0.2093	1.084	
Noel 4 -16 mm			0.0063		
Noel 4 -16 mm R			0.0064	-0.953	

"R" denotes an analytical replicate

\*\* The RE for TOC of Mercy 6 was determined to be 18% by error propagation combining the errors of TC and IC even with the large error on the IC measurement

**TOC vs. Depth, Yakima Railroad Area Samples,  
TOC determined by difference method**





## APPENDIX B

### **Error Propagation for the Difference Method**

The accuracy of the difference method relies on the accuracy of two separate analyses each with its own error. Before combining errors, the error on each parameter must be determined. For this exercise only analytical errors will be incorporated. Each parameter should be measured by two or more replicates. A mean and standard deviation should be determined for each parameter. The parameters needed are:

Mean total carbon (TC)	2 or more replicates
Standard Deviation (TC)	2 or more replicates
Mean inorganic carbon (IC)	2 or more replicates
Standard Deviation (IC)	2 or more replicates

Difference Method Equation:

$$\text{TOC} = \text{TC} - \text{IC}$$

Error Propagation Equation (Meyer, 1975):

$$S^2_{\text{TOC}} = S^2_{\text{TC}} + S^2_{\text{IC}}$$

S = standard deviation

$S^2$  = variance

Once the variance is determined for TOC, take the square root to find the standard deviation  
Relative Error (RE) = Standard Deviation / Mean. The mean TOC = mean TC - mean IC.

APPENDIX C

**Quality Assurance Project Plan (QAPP)**  
*Organic Carbon Sampling and Methodology Project*  
*Yakima Railroad Area*

*Prepared by: Rick Roeder, Department of Ecology, Christene Albanese, WSU*

*July 1996*

**Department of Ecology**  
**Toxics Cleanup Program**

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# I. PROJECT DESCRIPTION

## A. Historical Information

As work within the Yakima Railroad Area (YRRA) continues towards cleanup, the issue of appropriate cleanup levels protective of groundwater has arisen. The EPA Soil Screening Guidance and the Ecology Soil to Groundwater Pathway project both identify Fraction of Organic Carbon (foc) as a key factor in the development of soil cleanup levels protective of groundwater. The EPA Soil Screening Guidance was signed on April 26, 1996. For various reasons, including the EPA guidance, the determination of site-specific cleanup levels is becoming more common at cleanup sites throughout Washington. As a result, there is a need for a uniform lab method by which foc values will be developed at cleanup sites in Washington. For the YRRA there is an immediate necessity for foc values representative of natural or background levels found throughout the area. Additionally, there is a need to begin a process of gathering organic carbon information across the state.

### 1. Project Objectives

This study has three primary objectives: 1) the development of a default or background foc for the YRRA; 2) the development of a formal laboratory procedure for fraction of organic carbon that will be used in the Ecology Soil to Groundwater Pathway guidance; and 3) creation of the basis from which statewide organic carbon information can be developed.

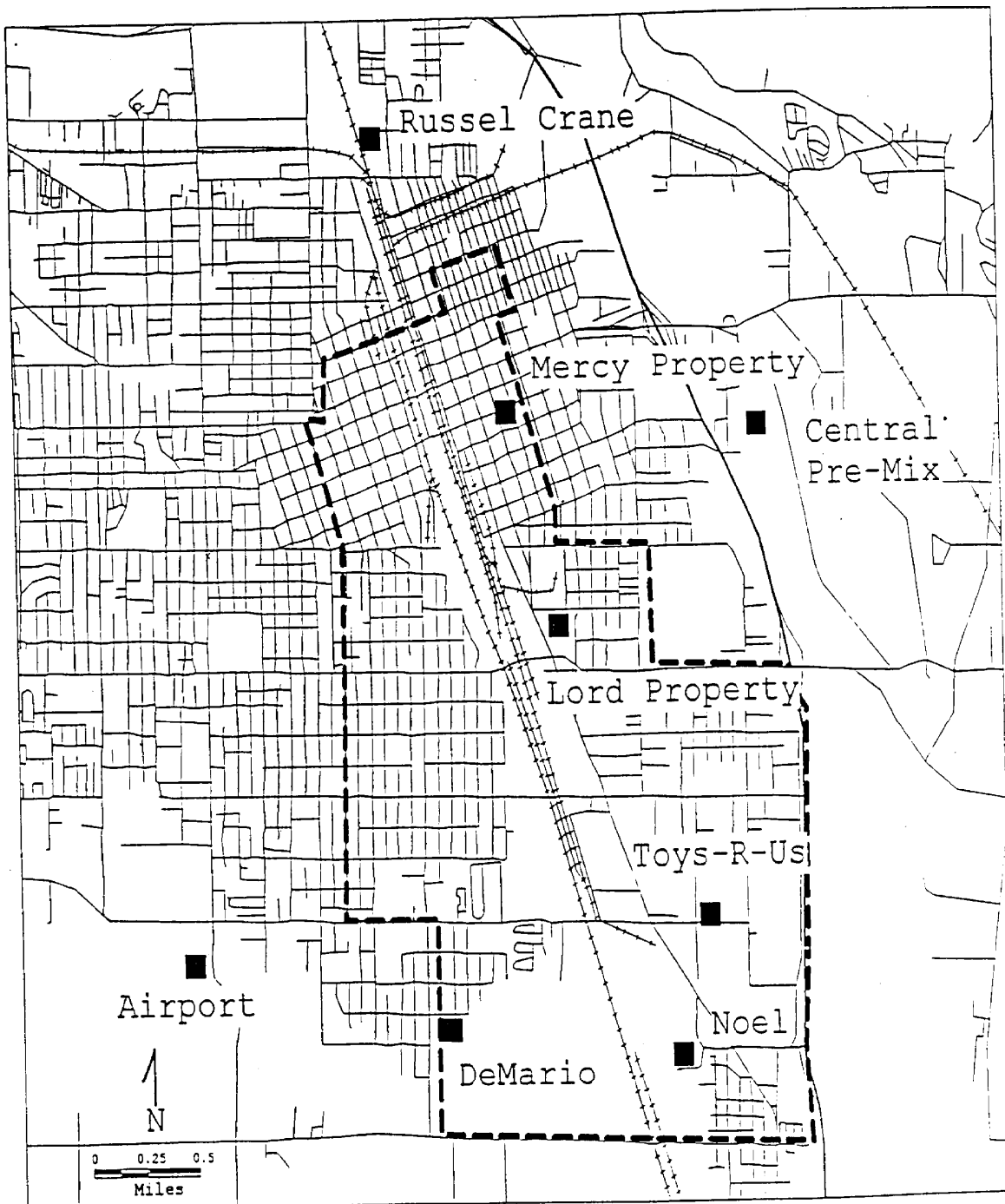
### 2. Sites

Eight locations within the Yakima Railroad Area will be sampled in this study. Sites shall be selected based on the following characteristics: a) shallow groundwater depth (i.e. 20 ft. or less); b) site history which indicates a low potential for contamination; c) location within the YRRA with regards to known contamination; and d) site access from owner/operators. A summary of each site to be investigated in this study is given in Table 1. A site location map is also given in Figure 1.

**Table 1: Site Descriptions**

<b>Site Name</b>	<b>Description</b>
Russell Crane	Vacant Lot
Mercy Property	City lot which had home on it for 50+ years
Lord Property	Vacant lot: former City jail about 60 years ago
Toys R Us	Former pasture. Store recently constructed.
Noel Property	Field/pasture
Deario Property	Field/pasture
Airport	Vacant field off west end of airport
Central Pre-Mix	Large gravel quarry east of Downtown

**Yakima Railroad Area  
Organic Carbon Sampling Locations  
Figure 1**



## B. Design

A series of test pits will be excavated at the locations identified in Figure 1, except for Central Pre-Mix to accommodate the collection of soil samples in what appears to be undisturbed or natural conditions. All samples will be taken from above the saturated zone. Additionally, samples will be taken at what is known as the Central Pre-Mix Gravel quarry. This quarry, nearly 150 feet deep, provides a unique opportunity to visually log the formations and sample materials at various depths within the saturated zone. Additional information on sampling is given in Section IV.

Duplicates will be taken at all sample locations. One batch of samples will be shipped to Manchester Laboratory for sample analysis, the other batch will be shipped to Washington State University (WSU) for analysis.

At WSU a comparison of organic carbon methods will be conducted using a variety of samples. Once the different methods are evaluated for effectiveness and limitations, a method will be chosen to determine the organic carbon for YRRA samples.

## II. PROJECT ORGANIZATION

This study is being sponsored by the Washington State Department of Ecology, Toxics Cleanup Program. Ecology personnel will conduct the actual field sampling. The laboratory work, including method research, sample analysis, and method development, will occur at Washington State University. Key personnel, at both Ecology and WSU, for this project are listed in Table 2.

**Table 2: Key Project Personnel**

<b>Name</b>	<b>Title</b>	<b>Phone Number</b>
<b>Richelle Allen-King</b>	Professor	509-335-1180
<b>Rick Roeder</b>	Site Manager	509-454-7837
<b>Tom Mackie</b>	Hydrogeologist	509-457-7109
<b>Christene Albanese</b>	Graduate Student	509-335-4812

## III. DATA QUALITY OBJECTIVES

### A. Overview

The two primary goals at WSU will be an organic carbon method comparison and the evaluation of the samples taken from the Yakima Railroad Area (YRRA). The parameters measured will be total carbon (TC), inorganic carbon (IC), and organic carbon (OC). The samples chosen for the method comparison will be selected to represent a variety of different types of samples, each containing different amounts of OC and IC.

The first measurement of OC will simply be computed as the difference between TC and IC. Second, pre-acidification techniques will be used to remove all IC prior to the measurement of OC. The data from each analysis will be evaluated for relative error to determine which method yields values with the least amount of error and how each method performs with the different types of samples.

**B. Analytical Precision and Bias**

All analyses will be done using a Carbon Dioxide Coulometer, UIC Inc. Model 5012. The coulometer does not require operator calibration, however the WSU lab always uses CaCO<sub>3</sub> as the standard to check coulometer performance before running samples. Blanks are also run daily. The following table show the frequency of standards and blanks:

Standards	10% of total number of samples	minimum, 2
Blanks	10% of total number of samples	minimum, 2

**C. Data Representativeness**

Duplicates will be run for the organic carbon method comparison to evaluate reproducibility and relative percent error. Once a method is chosen for the YRRA samples, 10% of all samples will be in duplicate for quality control.

**D. Sample Preparation**

All samples are ground in an aluminum bowl. The bowl will be rinsed with pre-fired silica sand between samples to avoid carry-over sample contamination. The silica sand will be saved and analyzed to determine background carbon contamination, if any exists.

The two pre-acidification techniques will use H<sub>2</sub>SO<sub>3</sub> and HCl to remove IC. The acid will also be checked for carbon contamination and background levels by running samples with only acid.

The weight of each sample analyzed is measured to +/- 0.00002 grams.

**IV. SAMPLING PROCEDURES**

**A. Soil**

Soil samples will be collected from the test pits and the walls of the Central Pre-Mix quarry. At each test pit location, samples will be taken at 2, 4, 6, 8, 10 and 12 feet or in each formation encountered. At the quarry, samples will be taken from at least 2 feet back within the pit walls at each formation. Duplicates will be taken of all samples. One complete batch of samples will go to WSU for analysis and one batch will go to Manchester for TOC analysis.

**B. Sampling Schedule**



It is anticipated that all of the field work for this study will be completed by July 26, 1996. Method research and development and sample analysis will be completed by approximately January 1, 1997.

**C. Sample Containers, Identification, and Custody**

Pre-cleaned sampling containers will be provided by Manchester Laboratory. All samples will be labeled using standard Manchester Laboratory labels. Upon field collection, samples will be transported to WSU for analysis. Duplicate samples will be transported to Manchester Laboratory for analysis. Chain of custody forms will be completed for all samples.

**V. ANALYTICAL PROCEDURES**

A summary of all laboratory analytical procedures is given in Table 3.

**Table 3: Laboratory Analytical Procedures**

<i>PARAMETER</i>	<i>MATRIX</i>	<i>METHOD</i>
<b>WSU Samples:</b>		
Total Carbon	Soil	UIC, Combustion at 950 C
Inorganic Carbon	Soil	UIC, Acidification w/2N H <sub>2</sub> SO <sub>4</sub>
Organic Carbon: Pre-acidified with H <sub>2</sub> SO <sub>3</sub>	Soil	UIC Combustion at 950 C
Organic Carbon: Pre-acidified with HCl	Soil	UIC, Combustion at 950 C
<b>Manchester Samples:</b>		
f <sub>oc</sub>	Soil	EPA 415.1

**VI. DATA REDUCTION, REVIEW AND REPORTING**

All of the data in this study will be initially compiled, reviewed, and checked for errors and omissions by Christene Albanese, WSU, and Rick Roeder, Site Manager, Toxics Cleanup Program.

**VII. QUALITY CONTROL PROCEDURES**

**A. Field QC**

For data QA/QC purposes, standard sampling methods and analytical protocols will be used in this study.

## **B. Laboratory QC**

Samples for QC purposes will be designated by the project manager for laboratory analysis. All samples are being duplicated and run through Manchester Lab. Routine QC procedures will be followed by both WSU and Manchester Laboratory.

## **VIII. PERFORMANCE AND SYSTEMS AUDITS**

Since this is not a large, long-term project, it is not anticipated that an audit of the procedures used in this study will be needed. However, this study is being conducted for research purposes and close records will be maintained as to the success of the procedures used.

## **IX. PREVENTATIVE MAINTENANCE**

Standard operating procedures for soil and ground water sampling will be followed in this study. In order to minimize any delays or other problems, extra equipment will be taken to the field (i.e. tools, buckets, extra sampling bottles, etc.). Each site will also undergo a field inspection ahead of time to check for any potential sampling problems (i.e. underground or overhead utilities, surface pavement, etc.).

## **X. DATA ASSESSMENT PROCEDURES**

Routine data assessment (i.e. comparative analysis) procedures will be used to evaluate the data from this study. Strict criteria has not been derived for assessing the data quality objectives since it is anticipated that there will be a high degree of variance in the leaching test data. However, as stated in the data quality objectives, the data from each laboratory leaching test will be evaluated on a method by method basis.

### **A. Precision**

The relative percent difference between field replicate or duplicate samples will be analyzed using the following formula:

$$*RPD = (A-B)/((A+B)/2)*100 = \%$$

A = original sample, B = replicate or duplicate sample

### **B. Bias**

Field blanks will not be used in this study.

### **C. Qualified Data**

If statistical procedures are used to assess the data, one-half the detection limit value will be used for samples reported at less than laboratory detection limits.

## **XI. QUALITY ASSURANCE REPORTS**

A report on the overall accuracy and completeness of the data generated in this study will be prepared as part of the final project report. This report will also include a brief summary of any problems encountered and other pertinent information.

## **XII. SOP-1: TEST PIT SAMPLING AND DOCUMENTATION**

### **OVERVIEW**

This SOP gives details on the procedures that will typically be used to collect and document samples from field test pits.

### **EQUIPMENT**

- Backhoe with standard sized bucket (24" or 36")
- Stainless steel hand trowels or scoops
- Shovels
- Stakes
- Measuring tape
- Sample containers
- Field notebook, pencil, and straight edge
- Camera

### **TYPICAL PROCEDURES**

Stake the location of the test pit. All test pits will selected based on historical site information (i.e. previous sampling data, etc.).

Identify overhead obstructions and underground utilities which may interfere with the backhoe operation. Using a backhoe, excavate the test pit to the desired depth. Sample depth and frequency will vary for each test pit location.

All soil samples will be collected by one of two methods: a) from the backhoe bucket after excavation, b) by use of a rod-mounted stainless steel core barrel or similar coring device. Sampling or site personnel will not enter the test pit for sample collection.

The physical and lithologic conditions of the test pit will be logged in a field notebook. This documentation shall include: A field sketch of the test pit documenting lithologic conditions

(type of soil encountered); depth of pit at the center and both ends; depth to groundwater (if encountered); visible evidence of contaminants (i.e. sheens, odor, staining, etc.); types and depths of debris encountered (if any); orientation of the test pit (strike and dip or compass bearing from true north); approximate distance to visible structures; location and depth of sample collected in the test pit; organic vapor monitoring results; and a photographic log of the test pit. Photographs will be taken of the inside of the test pit and the general vicinity. The date and time of each photograph will be documented in the field notebook.

Upon completion of the test pit excavation, the test pit will be backfilled with excavated material and compacted to preexisting or relative in-situ conditions.

### **XIII. Final Report**

The results of the data analysis from both WSU and Manchester will be compiled by WSU into a final project report. This method comparison will show which methods work best for different types of soils. Clear descriptions of methodology and examples showing effectiveness and limitations will be presented for each method evaluated. This information should then be usable at the discretion of the site manager to evaluate which method is most applicable to the soils at their site.