Analysis of Organic Carbon (foc) in Fractured Bedrock

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Abstract

The retardation of transport of organic contaminants in groundwater through fractured bedrock is controlled by the fraction of organic carbon (foc) on the surface of the fractures. However, there is only limited data as to the foc values in fractured bedrock. One such data gap is the foc of metasedimentary bedrock of phyllite grade in northern New England. Therefore, the foc was analyzed in 19 samples of this type of bedrock collected from fractures at various depths in two different cored borings from a site in northern Maine. The samples used for analyses of foc (goc/g) were from bedrock core collected immediately adjacent to fractures. These bedrock core samples included the fracture surfaces themselves and the bedrock core extending back to less than one cm from the fracture.

The Walkley-Black method was used to quantify the foc (grams organic carbon per gram bedrock core or goc/g) in the bedrock cores. The Walkley-Black method consists of chemically oxidizing the organic carbon to CO_2 and subsequently quantifying the oxidant used for this chemical reaction. The results showed that the average, the mean and the geometric mean of the foc values for these 19 samples was 0.0019 goc/g, 0.0019 goc/g and 0.0019 goc/g, respectively, with a standard deviation of 0.0003 goc/g and a 17.4% relative standard deviation. Therefore, the 95% confidence interval for the foc of this fractured bedrock material was 0.0012 to 0.0025 goc/g. These statistical analyses show the following: one, the foc from the site bedrock cores are statistically greater than the MDL (0.0001 goc/g) of the Walkley-Black analytical method; and, two, the average, median and geometric mean foc values of the site bedrock cores from varying depths are nearly identical, indicating that there is little variability in the foc values of the bedrock at the site. Given that these bedrock core samples were collected from two different wells and from depths varying from 11 to 90 feet, it is unlikely that they were contaminated with natural organic carbon from above ground.

Introduction

The retardation of transport of organic contaminants in groundwater through fractured bedrock is controlled by the fraction of organic carbon (foc) on the surface of the fractures. However, there is only limited data as to the foc values in fractured bedrock. One such data gap is the foc of metasedimentary bedrock of phyllite grade in northern New England. Hence, the foc was analyzed from bedrock core samples collected from fractures at various depths in two different cored borings in the aforementioned geological setting in Maine.

The samples used for analyses of foc (grams of organic carbon per gram of bedrock core or goc/g) were from bedrock core collected immediately adjacent to fractures in the cores. These samples included the fracture surfaces themselves and the bedrock core extending back to less than one cm from the fracture.

Site Description

The geological setting of the site from where the bedrock cores were collected was characterized during a remedial investigation at the site. The overburden consisted of surficial materials consisting of various compacted sands, silt, and gravel deposited during the advancement and retreat of glacial ice sheets. The bedrock geology at the site was characterized by review of regional geology reports (Osberg et al., 1985) and mapping the subsurface during the remedial investigation conducted at the site. The consolidated bedrock beneath the site consisted of alternating layers of metasedimentary bedrock of phyllite grade.

Data collected during drilling at the site to a depth of 182 feet below ground surface (bgs) indicated that the frequency of fractures in the bedrock decreased with depth. The depth at which the frequency of the fractures decreased varied from between 50 to 85 feet bgs. The fractures ranged in size from less than one millimeter to approximately one centimeter.

Sample Collection

Bedrock core samples were collected from two separate wells, referenced as MW-203 and PW-207, drilled to depths of 98 and 134 feet bgs, respectively. Thirty-four fractures were noted in the bedrock core collected during drilling of the MW-203 well. Thirty-three fractures were observed in the bedrock core collected from the PW-207 well. These fractures ranged in structure from likely, possibly or less likely to be transmissive. A total of 19 bedrock core samples were collected from these two wells at depths varying from 11 to 90 feet. Ten samples were collected from MW-203 and 9 samples were collected from PW-207. The samples used for analyses of foc (goc/g) were from bedrock core collected immediately adjacent to the fractures. These bedrock core samples included the fracture surfaces and the bedrock core extending to one cm or less from the surface of the fracture.

The bedrock core samples were then submitted to a contract analytical laboratory (PTS Laboratories, Santa Fe Springs, CA) for analysis of the fraction of organic carbon (foc). The foc in the bedrock cores was analyzed using the Walkley-Black method (1934) as described in Methods of Soil Analysis (1982).

Analytical Methods

There are two general methods used to measure the foc in bedrock cores:

1. Measurement of weight loss by ignition of organic matter.

2. Chemical oxidization of the organic carbon to carbon dioxide (CO_2) and either subsequent quantification of the oxidant used for the reaction or direct quantification of the CO_2 produced during this oxidation process.

Analysis of foc by weight loss is subject to errors caused by volatilization of substances other than organic materials, such as water, hydroxides, mineral carbonates, and mineral sulfides. Quantification of foc by the weight loss method is particularly sensitive to the presence of carbonates and sulfides in bedrock cores. There are, however, weight loss methods that are designed to differentiate between organic carbon and the aforementioned interfering materials, but they require considerable care and are less accurate at low foc values, such as those expected at this site. Hence, the weight loss method was not well suited for measuring the foc of the bedrock core at this site.

The chemical oxidation of organic carbon is better suited for analysis of foc in bedrock cores. This method uses a strong chemical oxidant, such as chromic acid, to oxidize organic carbon to CO_2, as shown in chemical reaction 1. Then one can either quantify the chemical oxidant used to oxidize the organic carbon or measure the quantity of CO_2 formed during this reaction. In addition, this general approach is not subject to interference by volatilization of other constituents in the bedrock cores, such as carbonates and sulfides.

Chemical reaction 1:

$$4C^{\circ} + 2Cr_2O_7^{2-} + 16H^{+} \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$

There are at least two such chemical oxidation methods. The method of Baccini, which was described by Schwarzenbach & Westall (1981), first acidifies the sample to eliminate interference by carbonates. Then a strong oxidant is used to chemically oxidize the organic carbon to CO_2. The resulting CO_2 is subsequently reduced to methane and quantified using a flame ionization detector. Unfortunately, this method has not been described in detail in a referred journal. Therefore, it would not have been appropriate to use to characterize the foc in this bedrock core. A more commonly used method to quantify foc in bedrock core is the Walkley-Black method (1934) as described in Methods of Soil Analysis (1982). This method is preferred for RBCA and DOD/DOE projects (PTS Laboratories).

The Walkley-Black method uses an excess of chromic acid to oxidize (digest) organic matter to CO_2. The remaining chromic acid that is not consumed during the oxidation of the organic carbon is then quantified by titration with ferrous sulfate, which is summarized in chemical reaction 2. The difference in chromic acid prior to and after the oxidation of the organic carbon represents the total chromic acid used to oxidize the organic carbon in the sample. The latter can be calculated using the chemical stoichiometry of the reaction.

Chemical reaction 2:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

However, prior to oxidizing the organic carbon in the bedrock core, it is absolutely necessary to eliminate any anthropogenic sources of carbon, such as non-aqueous phase liquids (NAPL), from the bedrock core samples. This was done using the Dean-Stark solvent extraction method (API RP40) to remove all anthropogenic hydrocarbons (NAPLs) from the sample (PTS Laboratories). This extraction method did not interfere with the subsequent analysis of the natural organic carbon associated with the bedrock core.

Subsequently, the samples were dried at 150°C to a constant weight (normally 16 hours). This latter step oxidizes all inorganic minerals, including ferrous bearing minerals to ferric oxides, and precludes their interference during the oxidation of the samples with chromic acid. This procedure completely eliminates any positive bias in the reported foc data that might have occurred due to the presence of ferrous ions and other reduced minerals.

The Walkley-Black method is very accurate for samples that contain less than 2% organic carbon matter (Methods of Soil Analysis, 1982). The minimum detection limit (MDL) for the foc using the Walkley-Black method was 0.0001 goc/g (PTS Laboratory analytical report).

Results

Tables 1 and 3 show the foc values of the bedrock core collected from the fractures located at various depths in the wells MW-203 and PW-207. Tables 2 and 4 summarize the statistical analysis of the foc values of the bedrock cores from each or these wells.

Table 1: Fraction organic carbon of bedrock collected at fractures in MW-203.

Sample Source	Depth (ft bsg)	foc (goc/g)
MW-203	13	0.00170
MW-203	23	0.00185
MW-203	27	0.00185
MW-203	38	0.00170
MW-203	42	0.00240
MW-203	47	0.00190
MW-203	52	0.00230
MW-203	58	0.00180
MW-203	69	0.00170
MW-203	82	0.00115

Table 2: Statistical summary of foc data from MW-203 bedrock core.

Statistical Parameter	Calculated Value
Number of samples analyzed (n)	10
Average foc (goc/g)	0.0018
Median foc (goc/g)	0.0018
Geometric mean foc (goc/g)	0.0018
Standard deviation of foc (goc/g)	0.0003
%Relative standard deviation	18.8
-/+ 95% Confidence intervals	0.0012 to 0.0025

Table 3: Fraction organic carbon of bedrock collected at fractures in PW-207.

Sample Source	Depth (ft bsg)	foc (goc/g)
MW-207	11	0.00195
MW-207	19	0.00220
MW-207	24	0.00220
MW-207	29	0.00235
MW-207	35	0.00135
MW-207	45	0.00190
MW-207	55	0.00205
MW-207	87	0.00175
MW-207	90	0.00160

Table 4: Statistical summary of foc data from PW-207 bedrock cores.

Statistical Parameter	Calculated Value
Number of samples analyzed (n)	9
Average foc (goc/g)	0.0019
Median foc (goc/g)	0.0020
Geometric mean foc (goc/g)	0.0019
Standard deviation of foc (goc/g)	0.0003
%Relative standard deviation	16.6
-/+ 95% Confidence intervals	0.0013 to 0.0026

Table 5: Statistical summary of foc data from MW-203 and PW-207 bedrock cores.

Statistical Parameter	Calculated Value
Number of samples analyzed (n)	19
Average foc (goc/g)	0.0019
Median foc (goc/g)	0.0019
Geometric mean (goc/g)	0.0019
Standard deviation of foc (goc/g)	0.0003
%Relative standard deviation	17.4
-/+ 95% Confidence intervals	0.0012 to 0.0025

The summaries of the foc data in Tables 2 and 4 show several important facts:

1. The foc values from the bedrock cores samples are statistically greater than the MDL (0.0001 goc/g) of the Walkley-Black analytical method.

2. The average, median and geometric mean values for the foc of the bedrock cores samples from varying depths are nearly identical, indicating that there is little variability in the foc values in the bedrock cores at this site.

3. The standard deviations of the foc measurements in the bedrock cores from these two wells is 0.0003 goc/g (MW-203) and 0.0003 goc/g (PW-207), which is 18.8% and 16.6% of the average foc for the bedrock core from each well.

4. The 95% confidence intervals of the foc of the bedrock core from these two wells are 0.0012 to 0.0025 goc/g (MW-203) and 0.0013 to 0.0026 goc/g (PW-207).

Table 5 summarizes the statistical analysis of the foc values of the bedrock cores from both wells together. The similarity of this data to that statistical analysis of the foc values from each individual well indicates that there is very little variation in the foc values of the bedrock from different locations at the site.

The foc was also analyzed from three separate samples taken from the same bedrock core at a depth of 55 feet in the PW-207 well. (Only one of these samples was included in the data summarized in Table 3.) Table 6 shows the statistical repeatability of this type of analysis.

Table 6: Repeatability of analysis of the foc from one bedrock core sample.

Statistical Parameter	Calculated Value
Number of samples analyzed (n)	3
Average foc (goc/g)	0.0016
Median foc (goc/g)	0.0015
Geometric mean (goc/g)	0.0016
Standard deviation of foc (goc/g)	0.0004
%Relative standard deviation	24.0
-/+ 95% Confidence intervals	0.0008 to 0.0024

The data in Table 6 shows that the percent relative standard deviation of these three analyses of the foc from the same bedrock core is 24%. This data also shows that the 95% confidence interval of the foc values measured in this particular bedrock core sample is 0.0008 goc/g to 0.0024 goc/g. These results show that there is good repeatability in using the Walkley-Black method for analysis of the foc in the bedrock core collected from the MW-203 and PW-207 wells.

Discussion

The samples of bedrock core collected for analysis of the foc originated from 19 different locations in two different wells varying in depth from 11 to 90 feet. Therefore, it is very unlikely that the bedrock core samples were contaminated with natural organic carbon from above ground. In addition, any extraneous anthropogenic carbon, such as NAPL, was extracted prior to analysis of the foc.

The analyses of the foc in the fractured bedrock from the MW-203 and PW-207 wells are accurate and significant quantitative values. Schumacher's review of "Methods for the determination of total organic carbon (TOC) in soils and sediments" (NCEA-C-1282, EMASC-001, April 2002) identifies the Walkley-Black method, which was used to analyze the reported foc values, as the "reference" method for comparison to other methods for analyzing total organic carbon. Schumacher also points out that if anything, the Walkley-Black method may underestimate the total organic carbon in a sample, due to possible incomplete oxidation of organic carbon. Usually, the incomplete oxidation of total organic carbon in environmental samples is corrected for by multiplying the measured foc by 1.30 (Walkley & Black, 1934; Schulte, 1995). This correction was made for all of the reported data. Schumacher's (2002) review of this method also identified several potential problems that could occur. These potential problems are summarized below.

1. Excess chloride (Cl^-) in percent weight quantities, as found in saline soils, may interfere with the quantitative titration of reduced chromium (Walkley, 1947). However, given that the primary mineral at the site is metasedimentary bedrock of phyllite grade (consisting of various types of aluminosilicate minerals), it is highly unlikely that there was sufficient chloride in the bedrock core samples for this to occur.

2. Manganese oxides may interfere with the analysis of foc through competing with the dichromate ion for any oxidizable carbon (Walkley, 1947). However, in such cases the reported foc would be an underestimate of the foc present in the bedrock core. In addition, Walkley (1947) reported that in the case where "the ratio of MnO_2 to carbon is 8.5 to 1, the error in the carbon determinations would only be 0 to 6 percent."

The lab's Method of Detection Limit (MDL) for the foc measured using the Walkley-Black method is 0.0001 goc/g. Therefore, the averages and the means of the foc values of the bedrock cores collected from each well are statistically significantly greater than the MDL of the Walkley-Black method.

In addition to the aforementioned statistical analysis of the foc data, triplicate samples (n = 3) from the same bedrock core (including one sample from the 19 bedrock core samples) were analyzed for their foc to determine the repeatability of the Walkley-Black method. The average, the mean and the geometric mean of the foc values of these replicate samples was 0.0016 goc/g, 0.0015 goc/g and 0.0016 goc/gm, respectively. The standard deviation of these measurements was 0.0004 goc/g.

Conclusions

Nineteen bedrock core samples were collected from fractures of two cored borings for analysis of the foc. The foc in these samples were quantified using a method based on sound analytical chemistry and widely used for similar types of analyses. Although this method was originally developed for media different from that present at the site, there were few if any interfering materials in the site bedrock core that would contribute to an overestimation of the foc. Therefore, the foc of the bedrock and can be used to provide a reasonable estimate of the potential for sorption of organic contaminants to the organic carbon in the bedrock and the subsequent fate and transport of the same contaminants.

In addition, the samples of bedrock core collected for analysis of foc originated from 19 depths varying in depth from 11 to 90 feet from two locations. Therefore, it is very unlikely that the bedrock core samples were contaminated with natural organic carbon from above ground. Based on the careful selection of sample locations and the number of samples collected, the measured foc values are considered to be representative of the foc at points of contact for any organic contaminants within the fractured bedrock at this site.

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