Bull. Environ. Contam. Toxicol. (1997) 58:893-900
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Bulletin of Environmental Contamination and Toxicology

Screening of Volatile Organic Compounds in River Sediment

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Received: 18 December 1996/Accepted: 5 February 1997

Volatile organic compounds (VOCs), such as trichloroethene, toluene and xylenes have been reported to be detected from river water (Environment Agency Japan 1996, Tanabe et al. 1996) and sediment (Ferrario et al. 1985, Kawata and Ozaki 1992), because a part of VOCs charged into river can be distributed to river sediment. Fifty-three common VOCs in water have been simultaneously determined with good accuracy and precision by gas chromatography - mass spectrometry (GUMS) with headspace method (Tanabe et al. 1996) as well as purge-and-trap method (Lin et al. 1993). However, simultaneous determination methods for the VOCs in sediment have not been established. Several GC or GUMS methods have been reported to determine some VOCs in sediment; purge-and-trap (Bianchi et al. 1991, Charles and Simmons 1987, Ferrario et al. 1985, Hiatt 198l), distillation (Kawata et al. 1986), headspace (Kawata et al. 1988) and solvent extraction (Yoshikawa et al. 1987). Among them headspace GCNS method appears to be the most appropriate method for screening the VOCs in sediments, because of its simplicity in analytical procedure. Hewitt et al. (1992) have reported that headspace method gave no statistically different results from purge-and-trap method for GUMS determination of four VOCs in soil. Voice and Kolb (1993) have reported that headspace GC method gave better results to determine nine VOCs in soil than purge-and-trap method or solvent extraction method followed by headspace.

However, headspace analysis of some VOCs in sediments could give insufficient recoveries. This is because VOCs adsorb to sediment (Charles and Simmons 1987). To improve their low recoveries from sediment, we have previously used a stable isotope-labeled compound as an internal standard to determine eight chlorinated VOCs (Kawata et al. 1988). However, this method is not proper for determining simultaneously as many as 53 VOCs with various physical properties. Therefore, we investigate headspace GUMS method with standard addition method for simultaneous screening of them in sediment. In this paper, we describe effects of a few headspace conditions on the VOC recoveries from sediment, and present screening results of the VOCs in sediments from mouths of rivers and a port in Niigata, Japan.

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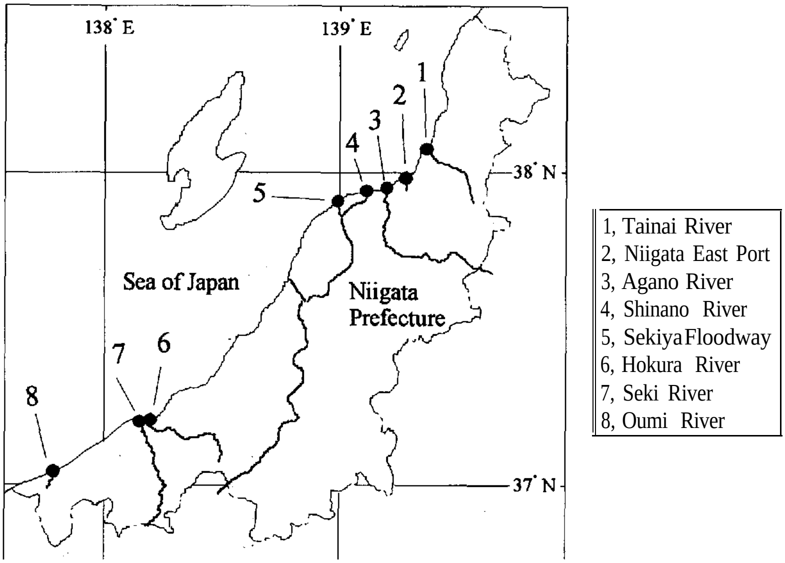

Figure 1. Sampling sites.

MATERIALS AND METHODS

An ultrasonic apparatus UT204 (Sharp, Osaka, Japan) and an automated headspace analyzer HP-7694 (Hewlett-Packard) was used. A mass spectrometer Automass 50 (JEOL, Tokyo, Japan) was used for quantitative analysis. Twenty-mL crimp-cap vials, Teflon-faced silicone septa and aluminum crimp-caps were purchased from Hewlett-Packard. Standard mixtures in methanol were purchased from Supelco. Other reagents were purchased from Wake (Osaka, Japan). Sodium chloride and cupric sulfate were heated overnight at 110°C. Distilled water boiled by irradiation of microwave was used for preparation of an aqueous solution of 5 M sodium chloride and 0.2 M cupric sulfate. A methanol solution containing 15 µg/ml of fluorobenzene and 4-bromofluorobenzene was prepared as an internal standard solution.

Sediments were collected from mouths of seven rivers and a port in Niigata Prefecture (Figure 1) on September 1995. The sediment samples were stored in 100 ml glass bottles with Teflon coated screw caps at -20°C without headspace. One g of each sediment was weighted into a crimp-cap vial. Seven samples were prepared for each sediment. To each sample was added 11.5 ml of the sodium chloride and cupric sulfate solution and 4 µl of the internal standard solution. Five samples out of the seven were spiked to levels of 0.1, 0.3, 1, 3 and 10 ng/g of VOCs for standard addition quantification, respectively. These samples were sealed with the septa and the aluminum crimp caps. The vials were shaken vigorously for 1 min and stood for 24 hr at 5°C . Then, they were transferred to the headspace analyzer for GC/MS determination in the selected ion monitoring (SIM) mode. Operating conditions of the headspace analyzer were as follows: vial equilibration temperature, 70°C ; vial equilibration time, 20 min; loop temperature, 140°C ; transfer line temperature, 180°C; pressurizing time, 0.1 min; injection pressure, 10 psi; injection time, 0.05 min; loop fill time, 0.01 min; loop equilibration time, 0.05 min. GUMS conditions were as follows: column, a fused-silica column Supelcowax VOCOL (3.0 µm film thickness, 60 m long, 0.32 mm i.d.), column temperature programmed from 35°C (held for 3 min) to 230°C (held for 7 min) at a rate of 10°C/min; ionization temperature, 230°C; carrier gas pressure programmed from 7.5 psi to 30 psi (held for 0.5 min) at a rate of 99 psi/mm, then back to 7.5 psi at the same rate; ion source temperature, 230°C ; ionization current, 350 µA; electron energy, 70 eV. The selected ions for SIM quantification of the VOCs are listed in Table 1 together with the temperature-programmed retention indices (PTRIs) calculated by following equation:

$$PTRI_A = 100N + 100(t_A - t_N) / (t_{N+1} - t_N)$$

where $PTRI_A$ is the PTRI of compound A t_A is retention time of compound A, and t_N and t_{N+1} are the retention times of the normal alkanes bracketing the compound A with carbon number N and N+l. Every VOC was separated under the conditions except for *o*- and *p*-chlorotoluene, and *m*- and *p*-xylene.

Crimp-cap vials with 1 g of sediments, containing 13 % organic matter, spiked with 10 ng each of the 53 VOCs were used for investigation of effects on a few

Table 1. PTRIs and selected ions for SIM determination of VOCs investigated

#.	Compound	PTRI	*m/z*	#	Compound	PTRI	*m/z*
1	Benzene	723	78, 77	29	*trans*-1,3-Dichloropropene	810	75, 77
2	Bromobenzene	1052	156, 77	30	Ethylbenzene	938	91 106
3	Bromochloromethane	685	128, 49	31	Hexachlorobutadiene	1346	225, 260
4	Bromodichloromethane	782	83, 85	32	Isopropylbenzene	1001	105, 120
5	*n*-Butylbenzene	1143	91, 134	33	*p*-Isopropyltoluene	1105	119, 134
6	*sec*-Butylbenzene	1095	105, 134	34	*n*-Propylbenzene	1035	91, 120
7	*tert*-Butylbenzene	1078	119, 91	35	Styrene	980	104, 78
8	Chlorobenzene	940	112, 114	36	1,1,1,2-Tetrachloroethane	940	131, 133
9	*o*- Chlorotoluene and	1059	91, 126	37	1,1,2,2-Tetrachloroethane	1018	83, 131
10	*p*-Chlorotoluene			38	Tetrachloroethene	879	166, 164
11	Dibromochloromethane	897	129, 127	39	Tetrachloromethane	712	117, 119
12	1,2-Dibromo-3-chloropropane	1251	157, 155	40	Toluene	834	92, 91
13	1,2-Dibromoethane	912	107, 109	41	Tribromomethane	1019	173, 171
14	Dibromomethane	788	93, 95	42	1,2,3-Trichlorobenzene	1400	180, 182
15	1,2-Dichlorobenzene	1175	146, 148	43	1,2,4-Trichlorobenzene	1339	180, 182
16	1,3-Dichlorobenzene	1127	146, 148	44	1,1,1-Trichloroethane	696	97, 99
17	1,4-Dichlorobenzene	1137	146, 148	45	1,1,2-Trichloroethane	855	97, 99
18	1,1-Dichloroethane	630	63, 65	46	Trichloroethene	755	130, 95
19	1,2-Dichloroethane	720	62, 64	47	Trichloromethane	674	83, 85
20	1,1-Dichloroethene	555	61, 96	48	1,2,3-Trichloropropane	1032	110, 61
21	*cis*-1,2-Dichloroethene	665	61, 96	49	1,2,4-Trimethylbenzene	1082	105, 120
22	*trans*-1,2-Dichloroethene	604	61, 96	50	1,3,5-Trimethylbenzene	1045	105, 120
23	Dichloromethane	587	84, 86	51	*m*- Xylene and	942	91, 106
24	1,2-Dichloropropane	766	63, 62	52	*p*-Xylene		
25	1,3-Dichloropropane	871	76, 78	53	*o*-Xylene	978	91, 106
26	2,2-Dichloropropane	662	77, 97		Fluorobenzene *	732	96
27	1,1-Dichloropropene	703	75, 110		4-Bromofluorobenzene *	1028	174
28	*cis*-1,3-Dichloropropene	840	75, 110				

* Internal standard

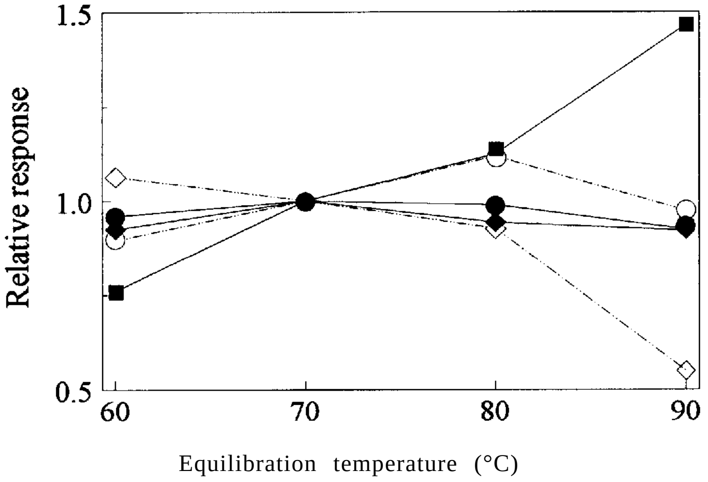

Figure 2. Effect of vial equilibration temperature. Relative responses: relative ratio of C_G at a temperature to that at 70°C. ●, Mean for the 53 VOCs; ■, 1,2-dibromo-3-chloropropane; ◆, 1,2-dichloropropane; ○, *trans*-1,3-dichloropropene; ◇, 1,2,3-trichlorobenzene. Vial equilibration time was 20 min.

items: vial equilibration temperature, vial equilibration time and sonication. The spiked sediment and another one (containing 10 % organic matter) spiked with 1 ng each of the VOCs were used to evaluate recoveries. Vials containing 12 ml of the sodium chloride and cupric sulfate solution and 4 µl of the internal standard solution were spiked to levels of 0.1, 0.3, 1, 3 and 10 ng of the VOCs for calibration curves.

RESULTS AND DISCUSSION

Sensitivity of the head-space analysis is increased by increasing VOC concentrations in headspace gas, C_G In our previous work, C_G increased with vial equilibration temperature from 20 to 45°C for eight VOCs, l,l-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, *cis*- and *trans*-1,2-dichloroethenes, 1, 1 ,l-trichloroethane, tetrachloroethene and trichloroethene (Kawata et al. 1988). Moreover, Voice and Kolb (1993) have reported that headspace analysis of soil samples containing 0 to 3.41 % organic matter with equilibration for one hr at 95°C provided recoveries of 55.73 to 94.07 % for benzene, dichloromethane, ethylbenzene, tetrachloroethene, toluene, 1, 1, 1 -trichloroethane, trichloroethene, *p*-xylene and *o*-xylene. Since higher temperatures were expected to provide higher C_G, we examined effect of temperature on C_G from 60°C to 90°C The results show that there were four patterns between vial equilibration temperature and C_G. The typical four patterns on ratios of C_G's at a temperature to those at 70°C, relative responses, vs vial equilibration temperature are shown in Figure 2. The equilibration temperatures giving maximal C_G, T_M, of each VOC are listed in Table

2. Mean of the relative responses were 0.96 at 6O°C, 0.99 at 80°C and 0.92 at 90°C. The numbers of VOCs given the maximal C_G at 60, 70, 80 and 90°C were, 18, 18, 10 and 7, respectively. In spite of the results by Voice and Kolb (1993) the 29 compounds, including benzene, ethylbenzene, tetrachloroethene, toluene, 1, 1, 1-trichloroethane, *p*-xylene and *o*-xylene, gave lower recoveries at 90°C than those at 6O°C, 70°C or 80°C (Table 2). This appears to be caused by the differences in the properties of the soils and the sediment, in particular the higher organic matter in the sediment than those in the soils. Therefore, we chose 70°C as the best vial equilibration temperature for the simultaneous analysis of the 53 VOCs, because the temperature provided both the maximal relative response and the maximum in number of VOCs given the maximal C_G as described above.

Table 2. Evaluation results of headspace conditions together with recoveries and minimum detectable concentrations

#	T_M	R_T	R_S	R^a	rsd ^{a}	R^b	rsd ^{b}	MDC
1	70*	0.96	1.03	70.1	0.66	97.6	2.77	0.1
2	70*	0.97	1.01	28.6	9.55	27.3	6.10	0.2
3	70	0.87	1.03	71.8	2.59	69.1	4.34	0.6
4	70	0.98	1.01	66.7	2.60	70.5	2.06	0.2
5	60*	1.09	0.78	11.5	9.80	15.4	11.0	0.1
6	60	1.04	0.85	21.8	12.1	22.8	5.24	0.06
7	60*	1.02	0.89	22.6	9.37	25.3	3.56	0.07
8	70*	1.03	1.11	43.2	6.33	38.7	3.42	0.08
9	60	1.03	0.91	51.7	10.0	49.4	0.42	0.06
+10								
11	80	0.92	1.25	57.8	3.09	55.4	4.21	0.2
12	90	0.98	1.13	50.7	4.32	54.9	14.5	2
13	80	0.84	1.22	67.2	4.37	64.4	5.83	0.3
14	80	0.93	1.01	78.7	4.67	77.0	3.46	0.5
15	60	0.98	0.79	17.6	15.6	18.0	5.77	0.3
16	60	0.96	0.78	17.5	13.0	17.6	3.12	0.3
17	60*	0.95	0.80	15.9	20.2	21.7	5.76	0.3
18	70*	0.98	1.05	81.9	0.66	82.4	4.02	0.2
19	80	1.01	1.02	71.5	4.36	83.3	2.76	0.3
20	70*	0.98	1.06	76.5	1.74	83.0	1.52	0.2
21	80*	0.90	1.03	78.7	1.41	76.5	3.79	0.2
22	80*	0.96	1.05	69.1	0.68	69.9	5.97	0.2
23	90	0.89	1.02	49.3	1.56	83.3	3.73	0.4
24	70*	0.93	1.02	78.8	0.80	75.2	0.53	0.2
25	90	0.90	1.23	72.9	2.80	66.2	2.14	0.2
26	60*	0.59	1.05	79.5	3.82	92.8	3.00	0.2
27	70*	0.95	1.03	74.8	2.02	73.9	3.90	0.1
28	80*	0.57	0.99	41.7	8.23	48.6	18.9	0.2
29	80	0.69	1.02	43.3	9.91	51.1	17.7	0.2
30	80*	0.97	1.08	47.5	6.58	43.8	1.34	0.03
31	60	0.98	0.43	6.5	13.0	9.9	0.58	3
32	60*	1.04	1.00	35.5	7.07	35.4	5.21	0.05
33	60	1.01	0.76	16.0	16.1	18.2	8.64	0.1
34	60	0.99	0.94	29.1	10.0	28.3	3.54	0.04
35	60*	1.10	1.01	24.8	11.6	23.6	7.66	1
36	70*	0.99	1.19	50.7	4.85	46.3	2.16	0.3
37	70*	0.57	1.18	57.8	2.41	55.5	4.23	0.6
38	70*	0.97	1.15	53.5	4.90	50.4	4.57	0.2
39	80*	1.04	1.07	68.6	0.79	70.3	6.13	0.1
40	70*	1.03	0.94	20.7	4.52	59.7	1.49	0.1
41	90	0.93	1.21	59.7	4.47	53.3	4.89	1
42	60*	1.29	0.72	7.1	8.64	11.1	19.2	3
43	60*	1.17	0.66	7.1	9.20	11.2	20.6	2
44	70*	1.04	1.05	75.9	2.23	81.4	2.60	0.1
45	90	0.95	1.01	69.2	3.47	68.4	2.59	0.3
46	90	1.18	1.00	63.4	3.41	61.1	8.61	0.09
47	70*	0.99	1.03	70.5	0.34	79.7	2.80	0.1
48	90	0.97	1.19	51.5	4.59	58.9	8.92	1
49	60	1.09	0.84	19.5	13.1	24.4	1.08	0.09
50	60	1.07	0.85	23.3	9.98	24.1	10.1	0.08
51	70*	1.09	1.05	81.4	5.54	81.1	2.52	0.02
+52								
53	70*	1.09	1.06	41.6	6.31	40.9	5.64	0.05

T_M: equilibration temperatures giving maximal C_G.

R_T: relative ratios of C_G for 60-min incubation to that for 20-min incubation.

R_S: relative ratios of C_G with sonication to that without sonication.

[a] Mean recovery, R (%), and relative standard deviation, rsd (%), of a VOC of 10 ng from sediment containing 13 % of organic matter (n=3).

[b] Mean recovery and relative standard deviation of a VOC of 1 ng from sediment containing 10 % of organic matter (n=3).

* shows VOCs giving the minimum C_G at 90°C.

MDC: minimum detectable concentration (ng/g).

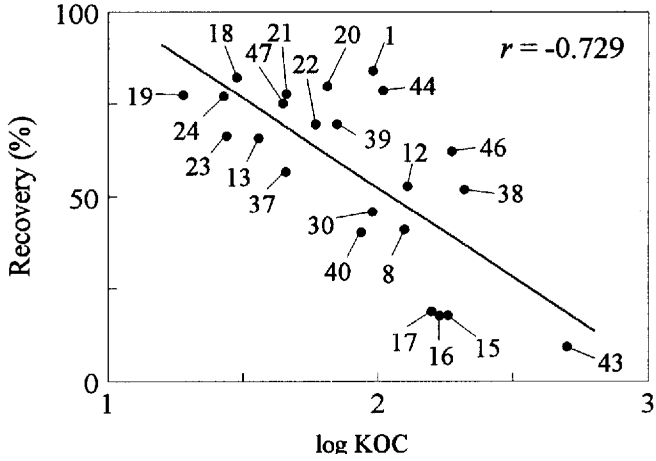

Figure 3. Relation between mean recoveries of VOCs and their K_{OC}. Linear line shows regression calculated by the least-squares method.

Vial incubation time for equilibration of the VOCs was examined at the proposed temperature. In our previous work, the equilibration was given by 20 min incubation. In contrast, Voice and Kolb (1993) have reported that vial incubation of 60 min at 95°C gave good results for the nine VOCs in soil. Relative ratios of C_G for 60-min incubation to that for 20-min incubation, R_T, for the 53 VOCs are given in Table 2. Mean R_T value of the 53 VOCs was 0.93. Although R_T's of trichlorobenzenes and trichloroethene were more than 1.1, those of 2,2-dichloropropane, 1,3-dichloropropenes, and 1,1,2,2-tetrachloroethane, which were not evaluated by Voice and Kolb (1993), were less than 0.7. This could be caused by their decomposition under the investigated conditions. We therefore incubated the vials for 20 min at 70°C.

Effects of ultrasonicaton on C_G's of VOCs were examined, because C_G's were expected to be increased by sonication (Kawata et al 1988, Voice and Kolb 1993). The prepared vials containing the sediments spiked with the VOCs were sonicated for 15 min at 70°C prior to the headspace analyses, The C_G ratios of the resulting responses to those without sonication, R_S are given in Table 2. The R_S values were widely ranged from 0.43 for hexachlorobutadiene to 1.25 for dibromochloromethane. The R_S's were >l.O for 34 VOCs and >l.l for 10 VOCs (Table 2). Hence, sonication was effective for these VOCs in increasing their recoveries on headspace analysis. In contrast, the R_S values of 12 compounds were <0.9. In particular, those of 1,2,4-trichlorobenzene and hexachlorobutadiene were decreased to <0.7, suggesting that these compounds decomposed by sonication under the conditions investigated (Bhatnagar and Cheung 1994). Consequently, we rejected sonication for the simultaneous determination of the 53 VOCs.

Recoveries of the spiked VOCs from the two sediments were determined under the recommended condition described above (Table 2). The recoveries, however, were ranged widely from 6.5% (hexachlorobutadiene) to 97.6% (benzene). Mean recoveries from the sediments were >70 % for 14 VOCs, 50 - 70 % for 16 VOCs and <50 % for 23 VOCs. Thereby, higher temperature, which increased GC/MS response for some VOCs, did not provide satisfactory recoveries of the other VOCs from the sediments. The relation between the recoveries and the soil sorption coefficient, Koc, for 23 compounds (Chiou et al. 1988, Rogers and McFarlane 1981, Sabljic 1984) is given in Figure 3. Since the recoveries were significantly correlated with Koc values, they can depend on properties of VOC (such as Koc) as well as those of sediments (such as organic matter content).

Consequently, the headspace method was not suitable for the simultaneous determination without another improvement, such as isotopic dilution method using a number of stable isotope-labeled isomers or standard addition method. The former method is not proper for the simultaneous determination of the VOCs with the diverse recoveries from sediments. We, therefore, selected the standard addition method (MaNeal and Hollifield 1990) to determine the 53 VOCs by headspace GC/MS. Although the 53 VOCs could not be determined simultaneously by the ordinary headspace method, the proposed conditions described above are useful for their sensitive and accurate determination on the standard addition method. The minimum detectable concentrations were ranged from 0.01 rig/g for *m*- and *p*-xylene to 3 ng/g for hexachlorobutadiene and 1,2,3-trichlorobenzene (Table 2). Calibration curves were linear (r>0.995) over the minimum detectable concentration to 120 ng/g for the VOCs.

This method was applied to screening of the VOCs in sediments from seven river mouths and a port in Niigata Prefecture. Among the 53 VOCs, 1,2- and 1,4-dichlorobenzenes, ethylbenzene, *p*-isopropyltoluene, toluene, 1,2,4- and 1,3,5-trimethylbenzenes, and *m*-, *p*- and *o*-xylenes, were detected at the investigated sites Their concentrations are given in Table 3 together with water content and organic matter content of the sediments. Typical SIM chromatograms of standards and samples without standard addition are shown in Figure 4. Every VOC was determinable well without interferences.

Table 3. Concentrations of VOCs identified in sediments

Site	VOCs detected (ng/g)									W_C	OM
	#15	#17	#30	#33	#40	#49	#50	#51+52	#53	(%)	(%)
1	0.4	0.5	0.07	0.8	0.5	0.65	0.89	0.14	0.09	32	9.5
2	<0.3	<0.3	0.40	0.7	0.1	0.77	<0.08	0.78	0.45	36	7.4
3	<0.3	<0.3	0.04	<0.1	<0.1	0.08	<0.08	0.08	0.07	19	0.61
4	<0.3	0.1	0.50	<0.1	<0.1	0.42	0.28	0.91	0.58	37	7.0
5	1.4	0.8	1.0	1.1	0.2	1.3	0.97	3.1	1.2	46	5.8
6	0.6	0.7	1.4	1.9	0.8	4.0	4.3	5.2	3.2	38	1.6
7	0.9	0.8	0.75	1.6	1.2	1.2	0.81	1.2	0.63	34	12
8	0.5	0.4	0.10	0.1	1.0	0.13	0.08	0.12	co.05	30	2.0

W_C: water content.
OM: organic matter content.

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