Pergamon

Geochimica et Cosmochimica Acta, Vol. 68, No. 6, pp. 1281–1292, 2004

0016-7037/04 $30.00 + .00

doi:10.1016/j.gca.2003.09.004

Reactivity of organic matter in aquifer sediments: Geological and geochemical controls

N. Hartog,[1,*] P. F. van Bergen,[1] J. W. de Leeuw,[1] and J. Griffioen[2]

[1]Department of Geochemistry, Faculty of Earth Sciences, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands
[2]Netherlands Institute of Applied Geosciences TNO, P.O. Box 6012, 2600 Delft, The Netherlands

(*Received August* 3, 2002; *accepted in revised form September* 3, 2003)

Abstract—Reduction rates in aquifers are commonly carbon limited, but little is known about the molecular composition and degradability of sedimentary organic matter (SOM) in aquifer sediments. The composition, source and degradation status of SOM in aquifer sediments of fluvio-glacial (Pleistocene) and shallow marine (Pliocene) origin, were determined using flash pyrolysis-gas chromatography/mass spectrometry. Incubation experiments (106 d) were used to assess the reactivity of SOM towards molecular oxygen. A dominance of lignin-derived components and long chain odd-over-even predominant alkanes indicate that terrestrial higher land plants were the main source of SOM even in the shallow marine sediments, while bacterial lipid-derived hopanoids and *iso*- and *anteiso*-C_{15} and C_{17} fatty acids indicate a minor contribution of microbial biomass. No compositional difference was observed between SOM present in the fine (<63 μm) and coarse fraction (63–2000 μm). A significant part of SOM was not present as low-molecular-weight compounds but was macromolecularly bound. For the fluvio-glacial sediments, a relatively higher abundance of resistant macromolecular compounds was in agreement with stronger signs of aerobic lignin, alkane and hopanoid oxidation. The more degraded status of SOM in the fluvio-glacial sediments was consistent with their significantly lower SOM mineralization (2–6%) during incubation, as compared with the shallow marine sediments (9–14%). The reactivity towards oxygen of SOM was controlled by the extent of past aerobic oxidation. Not the age of SOM, but the extent of oxygen exposure during syn- and postdepositional conditions seems most important in affecting the degradation status of SOM in aquifer sediments and thus their ability to reduce oxidants. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

The natural reduction capacity of aquifer sediments is of general importance to the redox processes within groundwater, but has only received increased attention over recent years. This is mainly related to the natural attenuation of nitrate in groundwater percolating from agricultural fields (Bradley et al., 1992; Moncaster et al., 2000; Pauwels et al., 2000; Pauwels et al., 1998; Postma et al., 1991; Robertson et al., 1996; Smith and Duff, 1988) and to the background consumption of oxidants injected during organic contaminant remediation (Barcelona and Holm, 1991; Schreiber and Bahr, 1999).

The reactivity of sedimentary organic matter (SOM) towards oxidants plays a prominent role in controlling the redox status of groundwater systems, since its oxidation can drive the formation of secondary solid reductants such as pyrite (FeS_2) or siderite ($FeCO_3$). These minerals are formed during sediment diagenesis and are often found in close association with organic matter (Anderson et al., 1997; Grimes et al., 2001).

Several factors are known to affect the reactivity of SOM towards oxidants, including environmental conditions, such as pH, temperature and oxidant concentrations (Tyson, 1995; van Bergen et al., 1998), physical protection mechanisms as sorption to mineral surfaces (Collins et al., 1995; Keil et al., 1994; Mayer, 1994) and the chemical composition (i.e., quality) of SOM (Canuel, 1996; Henrichs, 1993; Kristensen and Holmer, 2001).

Over the last decades, research has focused on the degradability of SOM in surface soils and marine sediments (Hedges and Oades, 1997) and references therein). In aquifers, SOM is ubiquitously present but generally in low contents (0.01–0.2 wt%). Field studies have shown that SOM oxidation rates in aquifers are generally carbon limited (Bradley et al., 1992; Hansen et al., 2001; Postma et al., 1991; Starr et al., 1996). These findings suggest that the composition of SOM is a rate-controlling factor. To date, however, little is known about the molecular composition and reactivity of SOM in aquifer sediments. Hence, the aims of this study were 1) to assess the controls on the molecular composition of SOM present in two distinct aquifer-forming geological formations and 2) to verify the relationship between the molecular composition of SOM in these sediments and its reactivity towards molecular oxygen.

2. GEOLOGICAL SETTING

The study site is located in the eastern part of The Netherlands, near groundwater pumping location ′t Klooster (Fig. 1A). Here, thick sedimentary deposits of near-shore marine and fluvial origin (van den Berg et al., 2000) form interconnected aquifers (van Beek and Vogelaar, 1998). Regional groundwater levels are shallow (2–6 *m*-bs). The hydrogeological base at over 120 m below surface (*m*-bs) is formed by unconsolidated Miocene marine deposits of silty clay, loam and very fine sand of the Breda Formation (Fig. 1B). These are overlain by Pliocene deposits composed of calcareous silty and medium fine sands. At the location of core 34C-104 these deposits have been eroded. The erosion valley is filled with Upper Pliocene fluvial coarse sands and covered with Middle Pleistocene fluvio-glacial calcareous very fine sand and clay deposited during the Saalian. The upper 30 m of the deposits consist of Upper

* Author to whom correspondence should be addressed, at Department of Earth Sciences, University of Waterloo, Waterloo, ON N2L 3G1, Canada. (nhartog@uwaterloo.ca).

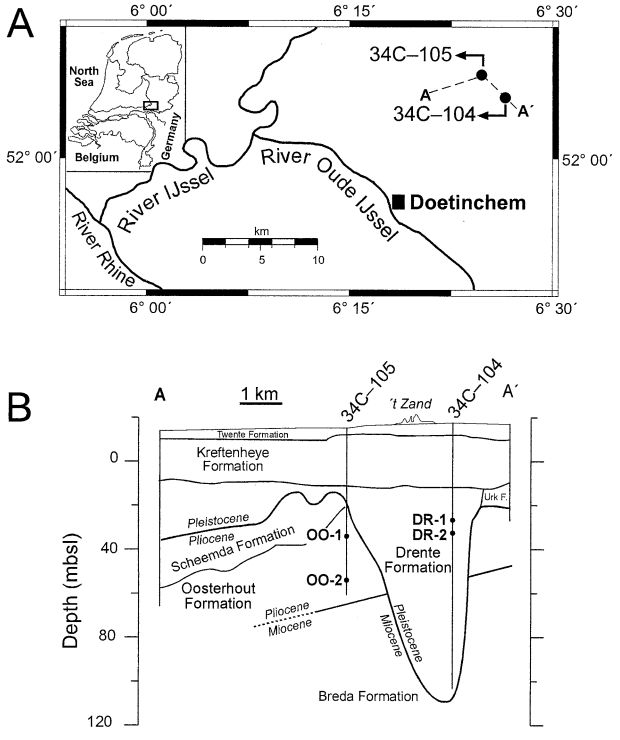

Fig. 1. (A) Location of the study area near Doetinchem, The Netherlands, showing the location of the geological cross section along A-A′ and the cores used. (B) Geological cross section along A-A and location of the selected samples. Adapted from Van Beek and Vogelaar (1998) and Van den Berg et al. (2000).

Pleistocene fluvial and fluvio-glacial sediments, including a 5 m thick top layer of Weichselian noncalcareous sands and loam, which are of fluvial and aeolian origin. Holocene aeolian deposits of the Holocene Kootwijk Formation (e.g., *'t Zand*) form the local topography (van den Berg et al., 2000).

The largest part of the sedimentary sequence is presently under anoxic conditions. Groundwater chemical analysis roughly reveals the following redox zonation. Oxygen is consumed within the first 10 m below surface. The NO_3/Fe redoxcline lies between 6 and 12 m below surface, while sulfate disappears in the depth interval between 30 and 55 m below surface (Griffioen, 2001; van Beek and Vogelaar, 1998).

3. MATERIALS AND METHODS

3.1. Sediment Selection

Sediment cores were obtained in 40-cm-long stainless steel tubing with a 90 mm inner diameter, using a hollow stem auger with a Nordmeyer drilling rig. Pristine sediment samples were taken at two stratigraphic depths from the Pleistocene fluvioglacial Drente Formation (DR-1 and DR-2—core 34C-104) and from the Pliocene shallow marine Oosterhout Formation (OO-1 and OO-2—core 34C-105). At these depths, iron-reducing conditions currently prevail (van Beek and Vogelaar, 1998). These sediment samples (Table 1, Fig. 1B) were selected because their geological formations form important aquifer units in the local hydrogeology, have a similar provenance (river Rhine), and were deposited in contrasting environments (van den Berg et al., 2000).

3.2. Sample Processing

Sediment samples collected were stored in glass bottles at 8°C until they were wet sieved into four particle size fractions: 0–63 μm (fine), 63–2000 μm (coarse fraction), a separate 0–2000 μm (total) fraction. The >2000 μm fraction (<5 wt%) was discarded. Fractions were freeze-dried (−40°C) and stored in glass jars under N_2 at 8°C in the dark until subsamples were taken for bulk sediment chemical analysis, organic matter isolation and batch incubation experiments.

3.3. Bulk Sediment Chemistry

Total Al, Si, Fe and S contents of the total fraction samples were determined by X-ray fluorescence spectroscopy, using a XARL8410 spectrometer. Total inorganic carbonate (TIC) contents were determined by weight loss after acid digestion with 2.6 mol/L HCl. Subsequently, total organic carbon (TOC) contents were measured in duplicate on decarbonated freeze-dried sediment fractions by combustion in an elemental analyzer (NA1500 NCS, Carlo Erba) with an analytical precision (1σ) better than 5%.

3.4. Organic Matter Isolation

Samples were treated with excess 10% HCl to remove carbonates and settled overnight, after which the samples were centrifuged at 2200 rpm for 7 min and the supernatant was decanted. Samples were then treated with excess 38% HF to dissolve the silicate mineral matrix, shaken at 250 rpm for 2 h, after which the samples were centrifuged at 2200 rpm for 7 min and the supernatant was decanted. Subsequently, the samples were washed three times with distilled water by centrifugation and decantation as described above. Then, the HCl/HF procedure as described above was repeated. Finally, samples were treated with 30% HCl to remove any potential fluoride gels and were washed as described above until the samples were diluted to an aqueous pH of 7. Samples were freeze-dried and weighed.

Table 1. Bulk characteristics of the sediment samples studied.

Core	Sample	Depth (m-bs)	TOC (wt %)	TIC (wt %)	SiO_2 (wt %)	Al_2O_3 (wt %)	Fe (wt %)	S (wt %)	TOC (wt %)	TIC (wt %)
					0–2000 μm				0–63 μm	
34C-104	DR-1	26.7	0.10	1.14	86.3	7.8	1.55	0.53	0.33	0.76
34C-104	DR-2	32.7	0.11	1.32	85.4	8.2	1.41	0.47	0.42	0.6
34C-105	OO-1	34.0	0.14	1.59	84.5	7.1	4.15	0.68	1.08	0.69
34C-105	OO-2	54.0	0.12	1.73	83.9	6.0	4.14	0.69	0.89	0.27

Table 2. Medium composition of the unamended and glucose-amended incubations.

Component	Unamended	Glucose amended
pH Buffer (g/L)		
KH_2PO_4	4	4
K_2HPO_4	4	4
Basic media (mg/L)		
$CaCl_2 \cdot {}_2H_2O$	13.25	6.63
NaCl	10	5
NH_4Cl	1.7	0.85
Amendment (g/L)		
Glucose	—	0.4
Trace metals (μg/L)		
$FeCl_3$	120	60
H_3BO_3	50	25
$CuSO_4 \cdot 5\ H_2O$	10	5
KI	10	5
$MnSO_4 \cdot H_2O$	45	22.5
Na_2MoO_4	20	10
$ZnSO_4 \cdot 7\ H_2O$	75	37.5
$CoCl_2 \cdot 6\ H_2O$	50	25
$Alk(SO_4) \cdot 12\ H_2O$	20	10
Vitamins (μg/L)		
Nicotinic acid	100	50
Ca-panthothenate	200	100
Cyanocobalumin	25	12.5
Inositol	100	50
P-aminobenzoate	20	10
Thiamine · HCl	50	25
Pyridoxine · HCl	25	12.5
Biotine	10	5
Riboflavine	10	5
Folic acid	10	5
Thiotic acid	10	5

The dried isolates were stored in glass at 8°C in the dark until analysis by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

3.5. Curie-Point Pyrolysis–Gas Chromatography/Mass Spectrometry

The organic matter isolates were pressed onto a ferromagnetic wire with a Curie temperature of 610°C. Py-GC/MS analyses were carried out on a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a FOM-3LX unit for pyrolysis. The GC was interfaced to a VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range of *m/z* 50−800 and a cycle time of 1.7 s (resolution 1000). The gas chromatograph, equipped with a cryogenic unit, was programmed from 0°C (5 min) to 300°C (10 min) at a rate of 3°C/min. Separation was achieved using a fused silica capillary column (25 m × 0.32 mm) coated with CP Sil-5CB (film thickness 0.4 μm). Helium was used as a carrier gas.

3.6. Sediment Fraction Incubations

A few grams of fine or 20 g of total fractions were added to individual reactions chambers (100 mL bottle, Duran). Fifty milliliters of solution containing vitamins, trace elements and K_2HPO_4/KH_2PO_4 were added (Table 2). The phosphate buffer serves as an additional pH buffer to the carbonate buffer present in the sediment and impedes potential pyrite oxidation (Elstinow et al., 2001). One additional set of total fraction samples received glucose amendments and half the amounts of vitamins and trace elements (Table 2) to check for substrate limitations. The reaction chambers were connected to the closed circuit of a 30-channel computerized respirometer (Columbus Instruments Micro-Oxymax). The respirometer was used to measure simultaneously O_2 uptake and CO_2 production every 4 h as an indication for the respiration activities of the microorganisms in the sediment samples. Carbon dioxide ($p_{CO2} = 10^{-3.35\pm0.34}$ atm) and oxygen ($p_{O2} = 10^{-0.68\pm0.001}$ atm) levels in the headspaces of the reaction chambers were kept constant throughout the experiments, of which the repeatability was shown during a previous study (Hartog et al., 1998). The evaporation of water in the reaction chambers enlarges the headspace volumes causing reduced oxygen concentrations. Therefore, a reaction chamber with 50 mL of the added solution was simultaneously run as a blank. Reported oxygen consumptions were corrected for this background 'consumption'. The effect of evaporation on the CO_2 production was negligible, because of the low atmospheric concentrations of CO_2 in the headspace atmosphere. The sediment slurries were incubated for 106 d in the dark at 25°C (±1°C), while shaken gently at 100 rpm to ensure sufficient mixing of the solid and water phase and to enhance exchange with the gas phase in the reaction chambers.

4. RESULTS

4.1. Physical and Bulk Geochemical Characteristics

The bulk mineral composition of the total fraction samples consists of quartz as indicated by the dominance (>80 wt%) of SiO_2 (Table 1). The particles in both the Drente and Oosterhout total fraction samples are predominantly (>90 wt%) larger than 63 μm. Total organic carbon contents are low in all total fractions (0.1–0.14 wt%). Highest TOC contents are observed in the fine fractions (0.3–1.0 wt%). Total sulfur contents and especially total iron contents are higher in the Oosterhout total fraction samples relative to those of the Drente samples.

4.2. Pyrolysis–Gas Chromatography/Mass Spectrometry

Curie point pyrolysis-GC/MS was used as a qualitative method to characterize the chemical composition of SOM in the selected aquifer sediments. The flash heating results in an evaporate/pyrolysate mixture due to the evaporation of "free" low-molecular-weight (LMW) compounds and the pyrolysis of macromolecular compounds (Faure and Landais, 2001). Due to the presence of an unresolved complex mixture (UCM) in all evaporate/pyrolysate mixtures (Fig. 2), the organic composition of the isolates does not fully represent the chemical composition of SOM present in the incubated sediment samples. Also acid hydrolysis of organic compounds during HF/HCl isolation inevitably results in the loss of some compounds, studies have indicated that HF/HCl treatment (Table 3) does not significantly affect the bulk composition of the organic matter isolated (Sanchez-Monedero et al., 2002; Schmidt et al., 1997).

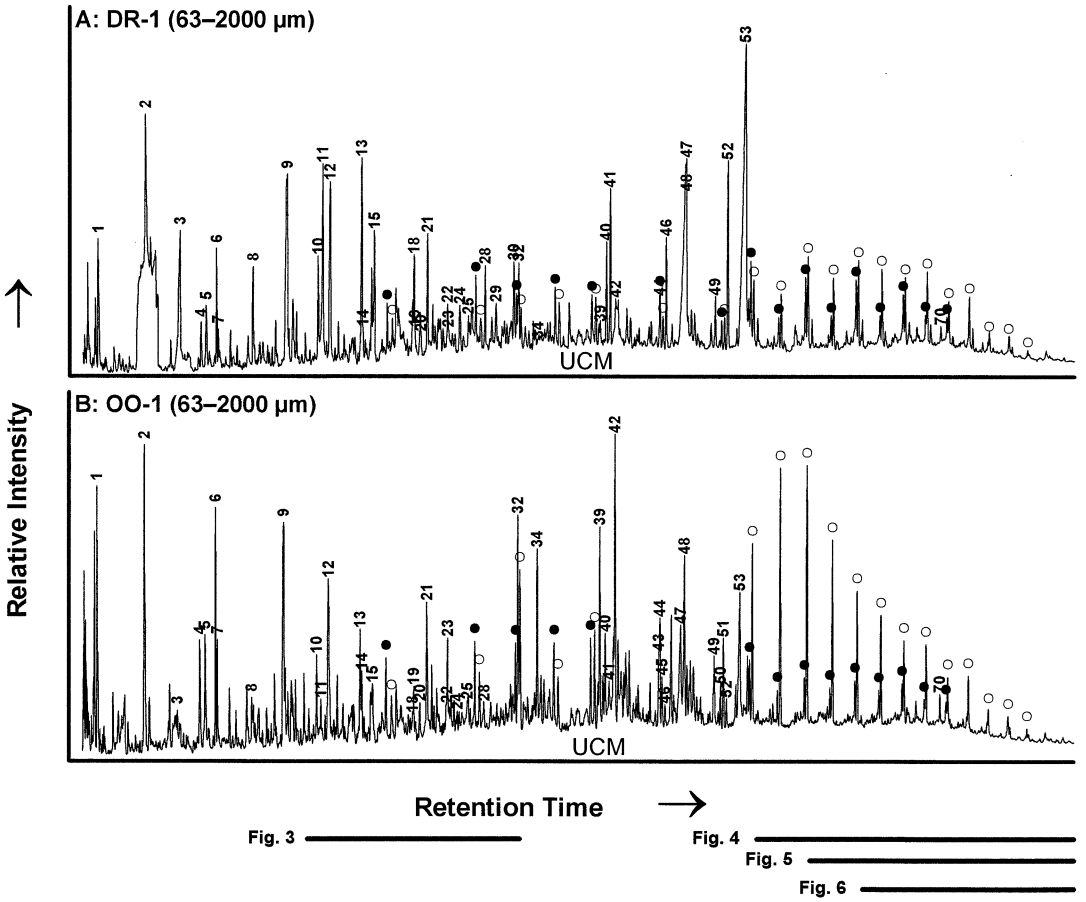

Fig. 2. Representative gas chromatograms of the evaporate/pyrolysate mixtures of (A) the Drente samples and (B) the Oosterhout samples. Peak numbers refer to the compounds listed in Table 4. Solid circles = alkene; open circles = alkane. Gray bars indicate the trace position in Figures 3-6.

4.2.1. Bulk Chemical Composition of SOM

Overall, the obtained organic matter compositions of the samples are remarkably similar for the fractions analyzed. The evaporate/pyrolysate mixtures are dominated by aromatic compounds and homologous series of alk-1-enes and alkanes, with contributions from alkylthiophenes, fatty acids and branched hydrocarbons. However, the gas chromatogram of the fine fraction of the DR-1 sample was dominated by C_{16} and C_{18} nitrils and fatty acids, and showed a homologous series of alkenes. Because of the paucity of other identifiable compounds, this fraction will not be discussed further. The amount of isolate obtained from the coarse fraction of the OO-2 sample was insufficient to be analyzed. The total ion current traces of the Drente and Oosterhout evaporates/pyrolysates show a significant contribution of unidentified compounds present as UCM. The main compounds identified (Table 4) can be grouped into four classes of compounds and are discussed accordingly: lignin-derived compounds (LG), long-chain aliphatics (ALK), fatty acids (FA), and hopanoids (HOP).

The types of compounds detected in the evaporate/pyrolysate mixtures are similar for the Drente and Oosterhout fractions. However, lignin-derived markers dominate the Drente samples, whereas the Oosterhout samples show an equal contribution from aliphatics and lignin-derived compounds (Fig. 2, Table 4).

4.2.2. Lignin-Derived Pyrolysis Products

Lignin-derived 2-methoxyphenol (guaiacol) pyrolysis products are relatively abundant in all samples. A small amount of 2,6-dimethoxyphenol (syringol) was detected only in the evaporate/pyrolysate mixture of the OO-2 fine fraction.

As indicated by the summed mass chromatograms *m/z* 124 + 138 + 150 + 152 + 164 + 166 (Fig. 3), 2-methoxyphenol (**I**;

Table 3. Organic geochemical results.

Sample	Fraction	Initial sample (g)	Removal[a] (%)	Alkane/ alkene[b]	CPI[c] alkanones
DR-1	Fine	0.13	95.7	n.d[d]	n.d.
DR-1	Coarse	14.47	98.8	2.19	4.04
DR-2	Fine	0.87	98.8	1.22	3.24
DR-2	Coarse	14.39	98.2	1.75	3.78
OO-1	Fine	1.42	94.0	3.28	2.55
OO-1	Coarse	16.29	99.3	5.93	2.31
OO-2	Fine	13.44	92.9	2.49	2.79

[a] Matrix removal efficiency of the HF/HCl treatment.
[b] Calculated average for C_{23}-C_{31}.
[c] Calculated as $CPI = [2C_{29}(C_{28}+C_{30})]$.
[d] Not determined.

Table 4. Compounds identified in the evaporate/pyrolysate mixtures.

Peak[a]	Compound name	Characteristic Fragments (*m/z*)	M+ (*m/z*)	Compound class[b]
1	benzene	78	78	
2	toluene	91, 92	92	
3	2-furaldehyde	95, 96	96	
4	C_2-alkylbenzene	91, 106	106	
5	C_2-alkylbenzene	91, 106	106	
6	styrene	104	104	
7	C_2-alkylbenzene	91, 106	106	
8	5-methyl-2-furaldehyde	53, 109, 110	110	
9	phenol	94	94	
10	2-methylphenol	107, 108	108	
11	2-methoxyphenol (guaiacol)	81, 109, 124	124	LG
12	3-methyl- and 4-methylphenol	107, 108	108	
13	C_4-alkylbenzene	133, 134	134	
14	naphthalene	128	128	
15	4-methyl-2-methoxyphenol	123 + 138	138	LG
16	dodecene	55 + 69	168	ALK
17	dodecane	57, 71	170	ALK
18	ethyl-2-methoxyphenol	137, 152	152	LG
19	C_1-naphthalene	127, 162	162	
20	C_1-naphthalene	127, 162	162	
21	4-vinyl-2-methoxyphenol	135, 150	150	LG
22	4-(2-propenyl)-2-methoxyphenol	164	164	LG
23	1-chloronaphthalene	127, 162	162	
24	4-formyl-2-methoxyphenol	151, 152	152	LG
25	*cis*-4-(1-propenyl)-2-methoxyphenol	164	164	LG
26	butadecene ($C_{14:1}$)	55, 69	196	ALK
27	butadecane (C_{14})	57, 71	198	ALK
28	*trans*-4-(1-propenyl)-2-methoxyphenol	164	164	LG
29	4-acetyl-2-methoxyphenol	151	166	LG
30	4-(propane-2-one)-2-methoxyphenol	137, 180	180	LG
31	pentadecene ($C_{15:1}$)	55, 69	210	ALK
32	3,5-di-(tert-butyl)-phenol	191, 206	206	CONT
33	pentadecane (C_{15})	57, 71	212	ALK
34	C_{18}-alkane (branched)	57, 71	254	ALK
35	hexadecene ($C_{16:1}$)	55, 69	224	ALK
36	hexadecane (C_{16})	57, 71	226	ALK
37	heptadecene ($C_{17:1}$)	55, 69	238	ALK
38	heptadecane (C_{17})	57, 71	240	ALK
39	C_{18}-alkane (branched)	57, 71	254	ALK
40	prist-1-ene ($C_{19:1}$)	69, 126, 266	266	ALK
41	prist-2-ene ($C_{19:1}$)	69, 126, 266	266	ALK
42	C_{20}-alkane (branched)	57, 71	282	ALK
43	nonadecene ($C_{19:1}$)	55, 69	266	ALK
44	octasulfur (S_8)	64, 256	256	
45	nonadecane (C_{19})	57, 71	268	ALK
46	methylhexadecanoate	74, 270	270	
47	hexadecanoic acid (C_{16})	73, 256	256	FA
48	C_{24}-alkane (branched)	57, 71	338	ALK
49	octadecanenitrile (C_{18})	57, 97	265	
50	henicosene ($C_{21:1}$)	55, 69	294	ALK
51	henicosane (C_{21})	57, 71	296	ALK
52	methyloctadecanoate (C_{18})	74, 298	298	
53	octadecanoic acid (C_{18})	73, 284	284	FA
54	docosene ($C_{22:1}$)	55, 69	308	ALK
55	docosane (C_{22})	57, 71	310	ALK
56	tricosene ($C_{23:1}$)	55, 69	322	ALK
57	tricosane (C_{23})	57, 71	324	ALK
58	tetracosene ($C_{24:1}$)	55, 69	336	ALK
59	tetracosane (C_{24})	57, 71	338	ALK
60	pentacosene ($C_{25:1}$)	55, 69	350	ALK
61	pentacosane (C_{25})	57, 71	352	ALK
62	hexacosene ($C_{26:1}$)	55, 69	364	ALK
63	hexacosane (C_{26})	57, 71	366	ALK
64	hepatcosene ($C_{27:1}$)	55, 69	378	ALK
65	heptacosane (C_{27})	57, 71	380	ALK
66	octacosene ($C_{28:1}$)	55, 69	392	ALK
67	octacosane (C_{28})	57, 71	394	ALK
68	nonacosene ($C_{29:1}$)	55, 69	406	ALK
69	nonacosane (C_{29})	57, 71	408	ALK
70	nor-17(21)-hopene	191, 231, 367	396	HOP
71	triacontene ($C_{30:1}$)	55, 69	420	ALK
72	triacontane (C_{30})	57, 71	422	ALK
73	hentriacontane (C_{31})	57, 71	434	ALK
74	dotriacontane (C_{32})	57, 71	448	ALK
75	tritriacontane (C_{33})	57, 71	462	ALK
76	pentatriacontane (C_{34})	57, 71	476	ALK

[a] Peak numbers refer to Figure 2.
[b] Lignin-derived compounds (LG), long-chain aliphatics (ALK), fatty acids (FA), and hopanoids (HOP), contaminants (CONT).

see Fig. 3 for structures), 4-methyl-2-methoxyphenol (**II**) and 4-ethyl-2-methoxyphenol (**III**) are the dominant guaiacyl-lignin derivatives in the Drente samples. In the Oosterhout samples, 4-vinyl-2-methoxyphenol (**IV**) is the most important guaiacyl-lignin derivative. In addition, 2-methoxy-4-(2-propenyl)-phenol (**V**) and the 2-methoxy-4-(1-propenyl)-phenol isomers (**VII** and **VIII**) are as important as 2-methoxyphenol (**I**) and 4-methyl-2-methoxyphenol (**II**). The oxidized lignin derivatives 4-formyl-2-methoxy-phenol (**VI**), 4-acetyl-2-methoxyphenol (**IX**) and 4-(propan-2-one)-2-methoxyphenol (not shown) were most pronounced in the Drente samples.

4.2.3. Alkanes, Alkenes

In both the Oosterhout and Drente samples, the alkane distribution was dominated by long chain (C_{23}-C_{31}) alkanes with

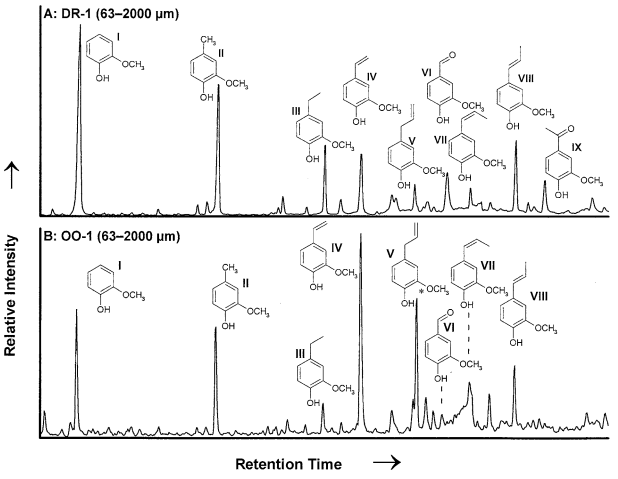

Fig. 3. Representative partial mass chromatograms for guaiacyl derivatives (*m/z* 124 + 138 + 150 + 152 + 164 + 166) of the evaporate/pyrolysate mixtures of (A) the Drente samples (B) the Oosterhout samples. *Coelution of 1-chloronaphthalene ($M^+ = 164$) with 2-methoxy-4-(2-propenyl)-phenol (V). Roman numbers in bold refer to compounds.

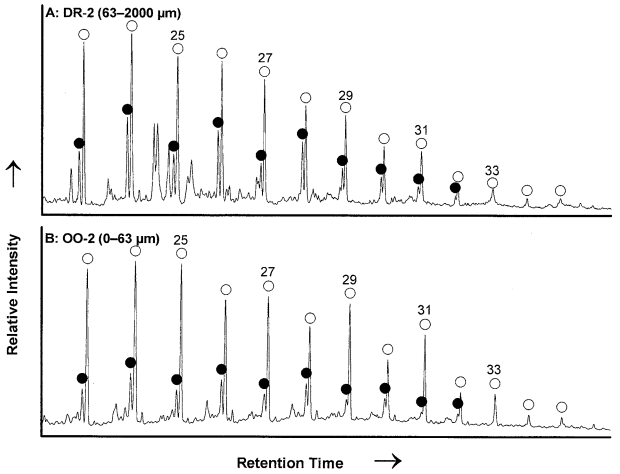

Fig. 4. 32 Representative partial mass chromatograms for alkenes and alkanes (*m/z* 55 + 57) of the evaporate/pyrolysate mixtures of (A) the Drente samples and (B) the Oosterhout samples. Solid circles = alkene; open circles = alkane. Numbers above peaks indicate number of carbon atoms.

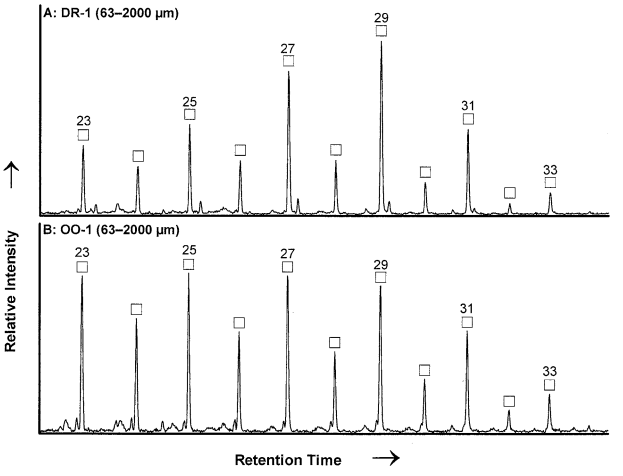

Fig. 5. Representative partial mass chromatograms for 2-alkanones (*m/z* 59) of the evaporate/pyrolysate mixtures of (A) the Drente samples and (B) the Oosterhout samples. Numbers above peaks indicate number of carbon atoms.

a maximum in the C_{23}–C_{25}-range, as illustrated by the mass chromatograms *m/z* 55 + 57 in Figure 4. The relative amounts decrease from the C_{24}-alkane towards the longer alkanes. In the distributions of C_{27}-C_{31} alkanes, the odd-carbon-numbered alkanes were relatively more pronounced in the Oosterhout samples, whereas alkene counterparts accompanied the alkanes less prominently as compared with the Drente samples (Table 3).

In the Oosterhout samples, several branched alkanes (C_{18}, C_{20} and C_{24}) were clearly present (Table 4, Fig. 2). Whereas the overall hydrocarbon content of the Drente samples was lower than that of the Oosterhout samples, the relative amounts of prist-1-ene (2,6,10,14-tetramethyl-1-pentadecene) and prist-2-ene (2,6,10,14-tetramethyl-2-pentadecene) were more pronounced in the Drente samples (Table 4, Fig. 2).

4.2.4. 2-Alkanones

The 2-alkanone distributions, as indicated by the mass chromatograms *m/z* 59 (Fig. 5) were dominated by the C_{23} to C_{31}2-alkanones with a maximum at C_{29} for the Drente samples, while in the Oosterhout samples the 2-alkones were more evenly distributed. In the C_{25}- to C_{31}-2-alkanone distributions, the 2-alkanones with an odd carbon number were relatively most pronounced in the Drente samples as compared with the Oosterhout samples. The odd-over-even predominance can be expressed using a carbon preference index (CPI). The following equation was used for the CPI calculation:

$$CPI = \frac{2C_{29}}{(C_{28} + C_{30})}$$

Calculated CPIs for the 2-alkanones in the Drente samples (3.2–4.0) were higher as compared with the Oosterhout samples (2.3–2.8).

4.2.5. Fatty Acids

The fatty acid distribution displayed a strong even-over-odd predominance and ranged from C_{12} to C_{26}, as indicated by the mass chromatograms *m/z* 60 + 73 (not shown). The C_{16} and C_{18} fatty acids dominated the mixtures. In all Drente samples, the C_{16} fatty acid was relatively less important than the C_{18} fatty acid, whereas they were equally important in the samples from the Oosterhout Formation. Small relative amounts of *iso*- and *anteiso*-C_{15} and C_{17} fatty acids were detected in the Oosterhout samples. Only minor amounts of *iso*- and *anteiso*-C_{15} were observed in the Drente samples.

4.2.6. Hopanoids

A number of triterpenoidal hydrocarbons of hopanoid origin were identified in all samples. Hopanoid distributions ranged from C_{27} to C_{33} (Fig. 6). Maxima in the hopanoid distributions were at C_{27} in the Drente samples and at C_{29} in the Oosterhout samples. The hopanes were present in both the 17α(H),21β(H) (i.e., $\alpha\beta$) as well as the less stable natural $\beta\beta$ configuration.

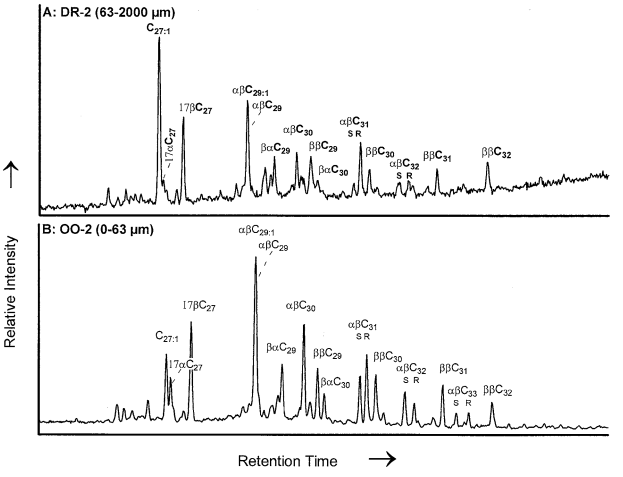

Fig. 6. Representative partial mass chromatograms for hopanoids (*m/z* 191) of the evaporate/pyrolysate mixtures of (A) the Drente samples and (B) the Oosterhout samples.

Table 5. Cumulative results for the incubations of the unamended fine and total fractions, and the glucose-amended total fractions.

Fraction	Sample code	Total O_2 consumption (μmol/g · sed)	CO_2/O_2 (molar)	TOC (wt %)	TOC-oxidized[a] (% initial)
<63 μm	DR-1	6.1	0.96	0.33	2
	DR-2	6.4	0.71	0.42	2
	OO-1	83.4	0.59	1.08	9[b]
	OO-2	47.3	0.76	0.89	6
0–2000 μm	DR-1	5.3	0.99	0.10	6
	DR-2	1.9	1.19	0.11	2
	OO-1	16.9	0.64	0.14	14[b]
	OO-2	11.1	1.17	0.12	11
0–2000 μm + glucose	DR-1	25.9	1.11	0.04[c]	62[c]
	DR-2	25.5	1.15	0.04[c]	71[c]
	OO-1	34.3	0.86	0.04[c]	52[c]
	OO-2	31.1	1.09	0.04[c]	60[c]

[a] The initial TOC contents and total oxygen consumptions (RQ = 1) were used to calculate the amount of organic carbon oxidized.
[b] Maximum estimate due to the possible contribution of pyrite oxidation.
[c] Represents the glucose-C added as a calculated sediment weight percentage.

The relative amounts of the more stable 22S and the natural 22R isomers were variable for the C_{31}- to C_{33}-hopanes. Trisnor-17(21)-hopene (C_{27}) and nor-17(21)-hopene (C_{27}) prominently accompanied C_{27}- and C_{29}-hopane counterparts.

4.3. Incubation Experiments

4.3.1. Oxygen Consumption of the Unamended Sediment Fractions

Sediment fractions were incubated for 106 d under constant atmospheric conditions to assess their reactivity towards oxygen. Oxygen consumption rates decreased continuously during all unamended incubations. However, two major differences in reactivity were observed. Firstly, the fine and total fractions of the Oosterhout samples consumed up to 14 times more O_2/gthan the corresponding fractions of the Drente samples. Secondly, the weight-based oxygen uptake of the fine fractions was 1.2 to 4.9 times higher than that of the corresponding total fractions (Table 5).

4.3.2. Oxygen Consumption of the Glucose-Amended Sediment Fractions

In the glucose-amended incubations, oxygen consumption rates were elevated during the first 20 d as compared with the unamended incubations (Fig. 7). This resulted in a 17–24 μmol O_2/g higher total oxygen consumption, indicating the mineralization of 52–71% of the glucose added (Table 5). Oxygen consumption rates of the amended samples equaled those of the unamended incubations towards the end of the incubations (Fig. 7) and the absolute differences in total O_2/g uptake between the glucose-amended incubations were similar to the differences between the corresponding unamended total fractions (Table 5).

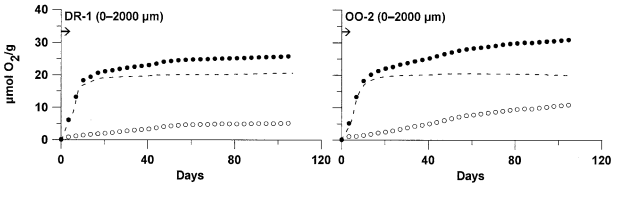

Fig. 7. Cumulative oxidation consumption during the incubation of the glucose-amended (solid circles) and unamended (open circles) total fraction of the DR-1 and OO-2 sediment samples. Dashed lines represent the glucose-attributed difference between the amended and unamended fractions. The arrows on the y-axes indicate the amount of glucose added to the amended fractions.

4.3.3. Respiration Quotients of the Incubations

Molar respiratory quotients (RQ) of CO_2 production and O_2 consumption of the unamended incubations were near unity, ranging between 0.59 and 1.19 (Table 5). The lowest RQs were observed for the incubations of the OO-1 sediment samples. The RQs of the glucose-amended total fraction incubations were closer to unity than the unamended samples.

5. DISCUSSION

In this study we characterized SOM in aquifer sediments from two distinct geological formations, assessed its origin and degradation status, and measured its reactivity towards molecular oxygen.

5.1. "Free" and Macromolecular SOM

During flash heating of SOM, "free" LMW compounds evaporate, whereas compounds bound within a macromolecular structure are revealed as degraded products upon pyrolysis (Faure and Landais, 2001). The significant presence of alkenes relative to their alkane counterparts (Fig. 4, Table 3) indicates that a substantial part of the straight chain hydrocarbons are pyrolysis products released from macromolecular structures (Derenne et al., 1991; Lichtfouse et al., 1998a). Moreover, the importance of hopenes relative to their hopane counterparts (Fig. 6) and unsaturated isoprenoids (Table 4) indicates that, during early diagenesis, a significant fraction of SOM has been incorporated within macromolecular structures in both the Drente and Oosterhout samples (Ambles et al., 1996; Lichtfouse et al., 1998b; Qu et al., 1996; Reiss et al., 1997).

Since unsaturated counterparts did not accompany the fatty acids and 2-alkanones, these compounds occur as such in both

the Oosterhout and Drente samples and therefore simply evaporate. Summarizing, SOM is thus present as macromolecules and "free" LMW compounds in both the Drente and Oosterhout samples. However, the higher ratio of alkane to alkene counterparts (Table 3) as well as the dominance of hopane over hopene counterparts (Fig. 6) indicates "free" LMW compounds are relatively more important in the SOM of the Oosterhout samples than in the SOM of the Drente samples.

5.2. Origin of Sedimentary Organic Matter

The bulk inorganic composition of the Oosterhout sediments is in line with a shallow marine depositional environment as opposed to the sediments from the Drente formation. The elevated total sulfur and total iron contents in the Oosterhout sediments (Table 2) is attributed to the presence of iron sulfides, formed under sulfate-reducing conditions. Glauconite (a Fe(II), Fe(III)-silicate mineral) can be an additional source of iron. Glauconite is indicative of diagenesis in shallow marine environments (Berner, 1971) and is frequently observed in the Oosterhout Formation (Griffioen, 2001; van den Berg et al., 2000). Thus, the inorganic geochemical composition of the Oosterhout samples is consistent with the near coastal origin of the formation. Therefore, an input of marine-derived organic matter to SOM would be expected during the deposition of the Oosterhout sediments.

Despite the coastal depositional environment of the Oosterhout Formation, no compounds of an unequivocal marine origin were observed in the Oosterhout samples. Instead, the abundance of long chain (C_{23}–C_{33}) alkanes (Fig. 4) and 2-alkanones (Fig. 5) with an odd-over-even predominance of the C_{27} to C_{33}-alkanes (Fig. 4) is characteristic for aliphatics derived from the cuticular waxes of higher plants (Eglinton and Hamilton, 1967). Finally, the importance of guaiacyl lignin-derived markers in the total ion current traces (Fig. 2) reflects the input of angiosperm wood components (Saiz-Jimenez and De Leeuw, 1986). Thus, the SOM in both the Drente and Oosterhout sediments is dominantly of a terrestrial, higher plant origin.

Besides a higher plant-derived origin, a small input of bacterial biomass to SOM is observed. This is indicated by the presence of C_{27}–C_{33}-hopanoids (Fig. 6), which are derived from C_{35}-bacterial hopanoids and related bacterial lipids (Dorsselaer et al., 1974; Kannenberg and Poralla, 1999; Otto and Simoneit, 2001; Rullkötter, 1983), as well as by small amounts of *iso*- and *anteiso*-C_{15} and C_{17} fatty acids in the Oosterhout samples (Leo and Parker, 1966; Schmitter et al., 1978). Although living biomass is undoubtedly present, hopanoids with functional groups attached to their hopanoid skeleton were not observed. Therefore, dead bacterial biomass is probably the main source of the microbial-derived SOM with an insignificant contribution of active bacterial biomass.

5.3. Diagenetic Effect on the Composition of Sedimentary Organic Matter

Signs of diagenetic SOM oxidation are found in both the Drente and Oosterhout samples, but results indicate that SOM degradation in the Drente samples has been more intense. Firstly, side chains of the lignin derivatives are shorter in the Drente samples and lignin derivatives with an oxidized propyl side chain (**VI** and **IX**, Fig. 3) are more abundant in the Drente samples (Fig. 3), as compared with the Oosterhout samples. These features are typical for aerobic lignin degradation (Dittmar and Lara, 2001), and thus indicate a more extensive aerobic oxidation of the propyl side chain on guaiacyl-lignin derivatives (Dijkstra et al., 1998; Kuder and Kruge, 1998) in the Drente samples. Secondly, a higher degree of side-chain oxidation of the hopanoids is indicated for the Drente samples, where C_{27}-hopanoids are dominant, while the longer hopanoids ($>C_{29}$) are more prominent in the Oosterhout samples (Fig. 6). The oxidation of linear side chains is thus more pronounced in the Drente samples than in the Oosterhout samples.

The higher degree of side-chain oxidation is in line with the aforementioned relative importance of macromolecular SOM in the Drente samples. The presence of 2-alkanones with a high odd-over-even predominance (Fig. 4, Table 3) indicates the partial oxidation of corresponding plant wax-derived alkanes (Ambles et al., 1993). Since odd-over-even predominance is typical for plant wax-derived alkanes, the more pronounced odd-over-even predominance of these 2-alkanones (Fig. 4) as compared with the long-chain alkanes (Fig. 3) indicates that these alkanes are preferentially oxidized over macromolecular alkyl moieties. Therefore, the higher CPIs for the 2-alkanones in the Drente samples (Table 3) as compared with the Oosterhout samples imply that the plant wax derived lipid fraction in the Drente samples is more degraded than in the Oosterhout samples. Since macromolecular SOM is in general more resistant to oxidation than "free" LMW compounds (e.g., Jenisch-Anton et al., 2000), the greater importance of macromolecular SOM in the Drente samples can be explained by a more extensive oxidation of SOM as compared with the Oosterhout samples.

5.4. Geochemical Controls on the Reactivity of SOM

The less degraded status of SOM in the Oosterhout samples is in agreement with their high affinities towards molecular oxygen during incubation, as compared with the Drente samples. However, verification that mineralization of SOM was the most important oxidation reaction during the incubations is needed, because of the potential oxidation of other reduced components such as pyrite or glauconite-Fe(II). The observed RQs are near unity in the unamended and amended (as expected for glucose oxidation) incubations and thus point to the respiration of organic matter as dominant oxygen consuming process during the sediment incubations (Table 5). The lowest RQs (0.6) are observed for the unamended OO-1 incubations hint towards the oxidation of pyrite as an additional oxygen consuming process (Hartog et al., 2002) and would suggest that the phosphate present could not fully impede pyrite oxidation. However, RQs lower than unity can also reflect the oxidation of substrates as aliphatic compounds or fatty acids (e.g., Dilly, 2001).

Calculations for the unamended incubations indicate that total SOM oxidation after 106 d ranged from 2% in the Drente to at most 14% in the Oosterhout total fraction samples (Table 5), corresponding to first-order degradation constants of $1.91 \cdot 10^{-4}$/d and $1.42 \cdot 10^{-4}$/d, respectively. In contrast, initial oxygen consumption was much faster during the amended

incubations. However, rates became similar to the corresponding unamended samples after 20 d (Fig. 7). An estimated 52 to 71% of the added glucose was respired after 20 d, which is similar to the mineralization observed during glucose-amended soil experiments (Sollins et al., 1996; Tsai et al., 1997; Witter and Dahlin, 1995). The high initial oxidation rates during the glucose-amended incubations indicate that microbial activity could be stimulated, despite the reduced nutrient concentrations (Table 2). Because a fraction of the unrespired glucose was likely transferred into biomass (Tsai et al., 1997), the similar final respiration rates of the amended and unamended incubations indicate that a more active microbial population did not stimulate the respiration of SOM. Therefore, we conclude that the oxidation of SOM towards molecular oxygen was not controlled by nutritional, oxidant or microbial limitations, but was instead limited by its reactivity (i.e., substrate limited) during the incubations.

The aerobic degradation rates of SOM observed in the Drente and Oosterhout samples are substantially slower than that of fresh organic matter in soils and marine sediments (Hedges and Oades, 1997; Henrichs, 1993; Sollins et al., 1996). For example, 37 to 47% of the organic matter of fresh plant residues was lost during 85 d of incubation (Franchini et al., 2002). This indicates that the organic matter present in aquifer sediments studied is already substantially degraded, as was confirmed by the absence of readily degradable compounds as sugars or cellulose in the aquifer sediments studied here. Moreover, the significantly lower oxygen consumptions during the incubations of the Drente samples and the more degraded status of their SOM point to the chemical composition of SOM being a main control on its reactivity, as was previously shown for soil humic material (Almendros and Dorado, 1999).

Besides the chemical composition as a control on the degradability of SOM, results suggest a small particle-size effect. The similar chemical composition of the SOM present in the fine and coarse fractions, the significantly higher amounts of SOM in the fine fractions (Table 1) and the smaller average extent of SOM degradation (Table 5) in the fine fractions (4.8%) compared with that in the corresponding total fractions (8.3%) suggests that the degradation of SOM is hampered in the fine fraction samples (Anderson et al., 1981; Christensen and Sørensen, 1985). However, this particle size effect is less apparent than that of chemical composition.

5.5. Geological Controls on the Degradation Status of SOM

A general decrease in SOM reactivity with increasing sediment age might be expected, since reactive organic compounds are degraded preferentially. In contrast, our results show that absolute age is not controlling the degradation status of SOM since the reactivity of SOM is significantly higher in the samples from the Oosterhout Formation than in those from the Drente Formation, despite the age difference of over 3 My. Although a generally lower reactivity in older aquifer sediments is expected (Jakobsen and Postma, 1994), differences in conditions during or after burial must have overridden the effect of age with respect to SOM reactivity in the sediments studied.

As indicated by the oxidized lignin-derivatives (Fig. 3.) and 2-ketones (Fig. 5), a more severe aerobic degradation of SOM is responsible for the less preserved status of SOM in the Drente samples, as compared with the Oosterhout samples. The importance of oxygen availability in microbial SOM degradation is related to the enzymatic ability of most aerobic microorganisms to perform a total mineralization of complex organic substrates like lignin (Benner et al., 1984; Miki et al., 1987; Odier and Monties, 1983) and recent studies have pointed to the oxygen exposure time (OET) of sediments as the dominant control on the degradation status of SOM (Gélinas et al., 2001; Hartnett et al., 1998; Hulthe et al., 1998). A significantly higher OET of the Drente sediments can therefore explain its more degraded and less reactive SOM, as compared with the Oosterhout sediments. This would suggest that the OET of the Oosterhout sediments during and after deposition was sufficiently shorter to preserve reactive organic matter. The different depositional environments for the Drente and Oosterhout Formation are a likely cause for different OETs. Higher sediment deposition rates and less reworking of the sediments in the shallow marine Oosterhout Formation as compared with the fluvio-glacial Drente sediments can have resulted in shorter sediment OETs (Betts and Holland, 1991; Gélinas et al., 2001; Hartnett et al., 1998). In line with this interpretation, Routh et al. (1999) observed more intensive degradation of SOM in terrestrially deposited regressive sediments as compared with offshore-deposited transgressive sediments (Routh et al., 1999).

Moreover, marine-derived organic matter is more prone to oxidation, since recalcitrant biomacromolecules (as lignin) are less abundant in organic matter derived from marine microorganisms (Aller, 1998; Colombo et al., 1996). Therefore, the input of marine-derived organic matter may have enhanced relative preservation of terrestrial SOM, additional to the effect of shorter exposure of oxygen to the shallow marine Oosterhout sediments.

In addition to aerobic oxidation during deposition or early diagenesis, reexposure to oxygen following a period of anoxia will affect the degradation status of SOM (Hulthe et al., 1998). Various changes in hydrogeological conditions, from intensified drainage to tectonic uplift, can cause a return to oxic conditions. Specific examples for the area studied are the development of push-moraines (van den Berg et al., 2000) during the Saalian glaciation, which strongly affected regional groundwater pressures and velocities (van Weert et al., 1997), and the fluvio-glacial incisions (Fig. 1B) that may have increased oxygen exposure of adjoining sediments.

After primary deposition and diagenesis, SOM can be eroded and redeposited. Fluvio-glacial deposits, such as the Drente Formation, frequently include sediments that are reworked by glacial erosion. The reworking of sediments increases OET (Binger et al., 1999), and thus affects the reactivity of SOM. Reworked organic matter has been found to be the dominant form of SOM in several fluvio-glacial sediments (Allen-King et al., 1997; Binger et al., 1999; Buckau et al., 2000a; Keller and Bacon, 1998; Postma et al., 1991). For example, SOM in Pleistocene aquifer sediments contained organic components that were reworked from Miocene deposits within a braided river system (Postma et al., 1991). Also in the Drente sediments, the presence of reworked organic matter is likely, since reworked fluvial sediments from the Pleistocene Urk Formation (Fig. 1B) contributed to the Pleistocene Drente sediments (van

Beek and Vogelaar, 1998; van den Berg et al., 2000). Thus, sediment reexposure to oxic conditions during sediment reworking likely resulted in further degradation of SOM in the Drente sediments as compared with the Pliocene Oosterhout sediments.

The sediments studied were taken from stratigraphic depths that are under iron reducing conditions (van Beek and Vogelaar, 1998). These sediments are presumably under anoxic conditions for the greatest part of their burial history as the groundwater system studied is largely anoxic (Griffioen, 2001; van Beek and Vogelaar, 1998). However, if anaerobic degradation would have a predominant effect on the preservation status of SOM, age would be expected to relate negatively with SOM reactivity. In contrast, since aerobic SOM degradation is orders of magnitude faster than anaerobic degradation of SOM (Canfield, 1994; Kristensen and Holmer, 2001), the exposure of SOM in aquifer sediments to oxic groundwater significantly diminishes its reactivity during anaerobic degradation by, for instance, nitrate, iron (III) or sulfate reducers.

5.6. Sedimentary Organic Matter as a Reactive Component in Aquifers

Few other studies have characterized organic matter present in groundwater systems on a molecular level. In a study on depositional environments, Routh et al. (2001) characterized the composition of solvent-extractable organic compounds in sediments from an aquitard/aquifer system. As in the current study, they revealed the preservation of hopanoid compounds and long-chain alkanes with odd-over-even predominances. Other studies on SOM in aquifer sediments have focused on its role as the principal sorbent of organic contaminants (Murphy and Zachara, 1995; Pignatello, 1998) and have shown that its bulk chemical composition controls its sorption capacity (Karapanagioti and Sabatini, 2000; Kleineidam et al., 1999; Weber et al., 1998). Salloum et al. (2002) showed that the sorption of phenanthrene was particularly dependent on the aliphatic content of SOM. In studies on the molecular composition of dissolved organic matter (DOM), several compounds resembling those present in SOM have been identified, such as hopanoic acids and C_{16} to C_{18} fatty acids (Sukhija et al., 1996) and lignin derived phenols (Simmleit and Schulten, 1989; Standley and Kaplan, 1998). In addition, (Leenheer et al., 2003) recently suggested terpenoids (such as hopanpolyols) as major precursors of DOM. While natural DOM is a mobile, refractory constituent of most groundwater (Pettersson et al., 1994; Thurman, 1985), several studies used the composition of DOM to identify its source (Grøn et al., 1996; Sukhija et al., 1996; Wassenaar et al., 1990). While DOM in shallow groundwater is predominantly derived from the soil zone (Wassenaar et al., 1990), the in-situ microbial degradation of SOM can also be an important source of DOM in deep aquifers (Aravena et al., 1995; Artinger et al., 2000; Buckau et al., 2000a; Buckau et al., 2000b; Wassenaar et al., 1990).

Our results bring forward that the composition of SOM in aquifer sediments is variable, due to both its origin and OET. In addition to the sorption capacity of SOM, its reactivity towards oxidants is controlled by the molecular composition of SOM as shown in this study. To date, the reactivity of SOM in aquifer sediments is generally considered 'low' (Christensen et al., 2000). However, SOM degradation rates range over several orders of magnitude (Jakobsen and Postma, 1994; Korom, 1992). Overall, the chemical composition is an important property of aquifer sediments and more research is needed to better define the control of SOM composition on its reactivity.

6. CONCLUSIONS

Organic compounds with a terrestrial, higher plant origin dominate the composition of SOM in the aquifer sediments from the fluvio-glacial Drente and near coastal Oosterhout Formation. No indications for an input of marine-derived organic matter in SOM were found. While SOM is present both as high- and low-molecular-weight components, the macromolecular fraction of SOM is more important in the Drente samples. The dominance of resistant macromolecular compounds is in line with the more degraded status of the SOM in the Drente samples as indicated by its more degraded hopanoid and lignin side chains and the more extensive oxidation of its long chain alkanes. These oxidation features point to the effect of aerobic degradation on the diagenetic status of SOM in aquifers.

In the Pliocene Oosterhout sediments SOM is up to an order of magnitude more reactive towards oxygen than in the Pleistocene Drente formation, despite the age difference of over 3 My. Hence, syn- and postdepositional conditions are more important than absolute age in controlling the degradation status of SOM. Especially the oxygen exposure time during and after sediment deposition is considered a controlling factor.

Acknowledgments—The authors are indebted to H. J. J. van Buijsen (TNO Environment, Energy and Process Innovation) for his support during the sediment incubations. We wish to thank C. H. van der Weijden for his comments and useful discussions that helped to improve this manuscript. We acknowledge the constructive comments of three anonymous reviewers.

Associate editor: P. A. Maurice

REFERENCES

Allen-King R. M., McKay L. D., and Trudell M. R. (1997) Organic carbon dominated trichloroethene sorption in a clay-rich glacial deposit. *Ground Water* **35,** 124–130.

Aller R. C. (1998) Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. *Mar. Chem.* **61,** 143–155.

Almendros G. and Dorado J. (1999) Molecular characteristics related to the biodegradability of humic acid preparations. *Eur. J. Soil Sci.* **50,** 227–236.

Ambles A., Jambu P., Jacquesy J. C., Parlanti E., and Secouet B. (1993) Changes in the Ketone Portion of Lipidic Components During the Decomposition of Plant Debris in a Hydromorphic Forest-Podzol. *Soil Sci.* **156,** 49–56.

Ambles A., Grasset L., Dupas G., and Jacquesy J. C. (1996) Ester- and ether bond cleavage in immature kerogens. *Org. Geochem.* **24,** 681–690.

Anderson D. W., Saggar S., Bettany J. R., and Stewart J. W. B. (1981) Particle size fractions and their use in studies of soil organic matter: I. The nature and distribution of forms of carbon, nitrogen, and sulfur. *Soil Sci. Soc. Am. J.* **45,** 767–772.

Anderson L. I., Dunlop J. A., Horrocks C. A., Winkelmann H. M., and Eagar R. M. C. (1997) Exceptionally preserved fossils from Bickershaw, Lancashire UK (Upper Carboniferous, Westphalian A (Langsettian)). *Geol. J.* **32,** 197–210.

Aravena R., Wassenaar L. I., and Barker J. F. (1995) Distribution and Isotopic Characterization of Methane in a Confined Aquifer in Southern Ontario, Canada. *J. Hydrol.* **173,** 51–70.

Artinger R., Buckau G., Geyer S., Fritz P., Wolf M., and Kim J. I. (2000) Characterization of groundwater humic substances: Influence of sedimentary organic carbon. *Appl. Geochem.* **15,** 97–116.

Barcelona M. J. and Holm R. T. (1991) Oxidation-reduction capacities of aquifer solids. *Environ. Sci. Technol.* **25,** 1565–1572.

Benner R., Maccubbin A. E., and Hodson R. E. (1984) Anaerobic biodegradation of the lignin and polysaccharide components of lignocellulose and synthetic lignin by sediment microflora. *Appl. Environ. Microbiol.* **47,** 998–1004.

Berner R. A. (1971) *Principles of Chemical Sedimentology*. McGraw-Hill.

Betts J. N. and Holland H. D. (1991) The oxygen content of ocean bottom waters, the burial efficiency of organic carbon, and the regulation of atmospheric oxygen. *Global Planet. Change* **97,** 5–18.

Binger C. A., Martin J. P., Allen-King R. M., and Fowler M. (1999) Variability of chlorinated-solvent sorption associated with oxidative weathering of kerogen. *J. Contam. Hydrol.* **40,** 137–138.

Bradley P. M., Fernandez M. Jr., and Chapelle F. H. (1992) Carbon limitation of denitrification rates in an anaerobic groundwater system. *Environ. Sci. Technol.* **28,** 2377–2381.

Buckau G., Artinger R., Fritz P., Geyer S., Kim J. I., and Wolf M. (2000a) Origin and mobility of humic colloids in the Gorleben aquifer system. *Appl. Geochem.* **15,** 171–179.

Buckau G., Artinger R., Geyer S., Wolf M., Fritz P., and Kim J. I. (2000b) Groundwater in-situ generation of aquatic humic and fulvic acids and the mineralization of sedimentary organic carbon. *Appl. Geochem.* **15,** 819–832.

Canfield D. E. (1994) Factors influencing organic carbon preservation in marine sediments. *Chem. Geol.* **114,** 315–329.

Canuel E. A. (1996) Reactivity of recently deposited organic matter: Degradation of lipid compounds near the sediment-water interface. *Geochim. Cosmochim. Acta* **60,** 1793–1806.

Christensen B. T. and Sørensen L. H. (1985) The distribution of native and labelled carbon between soil particle size fractions isolated from long-term incubation experiments. *J. Soil Sci.* **36,** 219–229.

Christensen T. H., Bjerg P. L., Banwart S. A., Jakobsen R., Heron G., and Albrechtsen H.-J. (2000) Characterization of redox conditions in groundwater contaminant plumes. *J. Contam. Hydrol.* **45,** 165–241.

Collins M. J., Bishop A. N., and Farrimond P. (1995) Sorption by mineral surfaces: Rebirth of the classical condensation pathway for kerogen formation? *Geochim. Cosmochim. Acta* **59,** 2387–2391.

Colombo J. C., Silverberg N., and Gearing J. N. (1996) Biogeochemistry of organic matter in the Laurentian Trough, II. Bulk composition of the sediments and relative reactivity of major components during early diagenesis. *Mar. Chem.* **51,** 295–314.

Derenne S., Largeau C., Casadevall E., Berkaloff C., and Rousseau B. (1991) Chemical Evidence of Kerogen Formation in Source Rocks and Oil Shales Via Selective Preservation of Thin Resistant Outer Walls of Microalgae—Origin of Ultralaminae. *Geochim. Cosmochim. Acta* **55,** 1041–1050.

Dijkstra E. F., Boon J. J., and van Mourik J. M. (1998) Analytical pyrolysis of a soil profile under Scots pine. *Eur. J. Soil Sci.* **49,** 295–304.

Dilly O. (2001) Microbial respiratory quotient during basal metabolism and after glucose amendment in soils and litter. *Soil Biol. Biochem.* **33,** 117–127.

Dittmar T. and Lara R. J. (2001) Molecular evidence for lignin degradation in sulfate-reducing mangrove sediments (Amazônia, Brazil). *Geochim. Cosmochim. Acta* **65,** 1417–1428.

Dorsselaer A. V., Ensminger A., Spyckerelle C., Dastillung M., Sieskind O., Arpino P., Albrecht P., Ourisson G., Brooks P. W., Gaskell S. J., Kimble B. J., and Philp R. P. (1974) Degraded and extended hopane derivatives (C27 to C35) as ubiquitous geochemical markers. *Tetrahedron Lett.* **15,** 1349–1352.

Eglinton G. and Hamilton R. J. (1967) Leaf epicuticular waxes. *Science* **156, (***780***)**, 1322–1335.

Elstinow A. R., Schoonen M. A. A., and Strongin D. R. (2001) Aqueous geochemical and surface science investigation of the effect of phosphate on pyrite oxidation. *Environ. Sci. Technol.* **35,** 2252–2257.

Faure P. and Landais P. (2001) Rapid contamination screening of river sediments by flash pyrolysis-gas chromatography-mass spectrometry (PyGC-MS) and thermodesorption GCMS (TdGC-MS). *J. Anal. Appl. Pyrolysis* **57,** 187–202.

Franchini J. C., González-Vila F. J., and Rodriguez J. (2002) Decomposition of plant residues used in no-tillage systems as revealed by flash pyrolysis. *J. Anal. Appl. Pyrolysis* **62,** 35–43.

Gélinas Y., Baldock J. A., and Hedges J. I. (2001) Organic carbon composition of marine sediments: Effect of oxygen exposure time on oil generation potential. *Science* **294,** 145–148.

Griffioen J. (2001) Potassium adsorption ratios as an indicator for the fate of agricultural potassium in groundwater. *J. Hydrol.* **254,** 244–254.

Grimes S. T., Brock F., Rickard D., Davies K. L., Edwards D., Briggs D. E. G., and Parkes R. J. (2001) Understanding fossilization. Experimental pyritization of plants. *Geology* **29,** 123–126.

Grøn C., Wassenaar L., and Krog M. (1996) Origin and structures of groundwater humic substances from three danish aquifers. *Environ. Int.* **22,** 519–534.

Hansen L. K., Jakobsen R., and Postma D. (2001) Methanogenesis in a shallow sandy aquifer, Rømø, Denmark. *Geochim. Cosmochim. Acta* **65,** 2925–2935.

Hartnett H. E., Keil R. G., Hedges J. I., and Devol A. H. (1998) Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature* **391,** 572–574.

Hartog N., Van der Grift B., Griffioen J., and Van Liere H. (1998) Respiration of bulk organic matter in aquifer sediments with the Micro-Oxymax. *Min. Mag.* **62A,** 579–580.

Hartog N., Griffioen J., and Van Der Weijden C. H. (2002) Distribution and reactivity of O_2-reducing components in sediments from a layered aquifer. *Environ. Sci. Technol.* **36,** 2436–2442.

Hedges J. I. and Oades J. M. (1997) Comparative organic geochemistries for soils and marine sediments. *Org. Geochem.* **27,** 319–363.

Henrichs S. M. (1993) Early diagenesis of organic matter: The dynamics (rates) of cycling of organic compounds. In *Organic Geochemistry* (eds. M. H. Engel and S. A. Macko), pp. 101–117. Plenum Press.

Hulthe G., Hulth S., and Hall P. O. J. (1998) Effect of oxygen on degradation rate of refractory and labile organic matter in continental margin sediments. *Geochim. Cosmochim. Acta* **62,** 1319–1328.

Jakobsen R. and Postma D. (1994) In situ rates of sulfate reduction in an aquifer (Rømø, Denmark) and implications for the reactivity of organic matter. *Geology* **22,** 1103–1106.

Jenisch-Anton A., Adam P., Michaelis W., Connan J., Herrmann D., Rohmer M., and Albrecht P. (2000) Molecular evidence for biodegradation of geomacromolecules. *Geochim. Cosmochim. Acta* **64,** 3525–3537.

Kannenberg E. L. and Poralla K. (1999) Hopanoid biosynthesis and function in bacteria. *Naturwissenschaften* **86,** 168–176.

Karapanagioti H. K. and Sabatini D. A. (2000) Impacts of heterogeneous organic matter on phenanthrene sorption: Different aquifer depths. *Environ. Sci. Technol.* **34,** 2453–2460.

Keil R. G., Tsamakis E., Fuh C. B., Giddings J. C., and Hedges J. I. (1994) Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. *Geochim. Cosmochim. Acta* **58,** 879–893.

Keller C. K. and Bacon D. H. (1998) Soil respiration and georespiration distinguished by transport analyses of vadose CO2, (CO2)-C-13, and (CO2)-C-14. *Global Biogeochemical Cycles* **12,** 361–372.

Kleineidam S., Rügner H., Ligouis B., and Grathwohl P. (1999) Organic matter facies and equilibrium sorption of phenanthrene. *Environ. Sci. Technol.* **33,** 1637–1644.

Korom S. F. (1992) Natural denitrification in the saturated zone: A review. *Water Resources Res.* **28,** 1657–1668.

Kristensen E. and Holmer M. (2001) Decomposition of plant materials in marine sediment exposed to different electron acceptors (O_2, NO^{3-} and SO_4^{2-}), with emphasis on substrate origin, degradation kinetics, and the role of bioturbation. *Geochim. Cosmochim. Acta* **65,** 419–433.

Kuder T. and Kruge M. A. (1998) Preservation of biomolecules in sub-fossil plants from raised peat bogs —a potential paleoenvironmental proxy. *Org. Geochem.* **29,** 1355–1368.

Leenheer J. A., Nanny M. A., and McIntyre C. (2003) Terpenoids as major precursors of dissolved organic matter in landfill leachates,

surface water, and groundwater. *Environ. Sci. Technol.* **37,** 2323–2331.

Leo R. F. and Parker P. L. (1966) Branched-chain fatty acids in sediments. *Science* **152,** 649–650.

Lichtfouse E., Chenu C., Baudin F., LeBlond C., Da Silva M., Behar F., Derenne S., Largeaou C., Wherung P., and Albrecht P. (1998a) A novel pathway of soil organic matter formation by selective preservation of resistant straight-chain biopolymers: Chemical and isotope evidence. *Org. Geochem.* **28,** 411–415.

Lichtfouse E., Leblond C., Da Silva M., and Behar F. (1998b) Occurrence of biomarkers and straight-chain biopolymers in humin: Implication for the origin of soil organic matter. *Naturwissenschaften* **85,** 497–501.

Mayer L. M. (1994) Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* **58,** 1271–1284.

Miki K., Renganathan V., Mayfield M. B., and Gold M. H. (1987) Aromatic ring cleavage of a β-biphenyl ether dimer catalyzed by lignin peroxidase of phanerochaete chrysosporium. *FEBS Lett.* **210,** 199–203.

Moncaster S. J., Botrell S. H., Tellam J. H., Lloyd J. W., and Konhauser K. O. (2000) Migration and attenuation of agrochemical pollutants: Insights from isotopic analysis of groundwater sulphate. *J. Contaminant Hydrol.* **43,** 147–163.

Murphy E. M. and Zachara J. M. (1995) The role of sorbed humic substances on the distribution of organic and inorganic contaminants in groundwater. *Geoderma* **67,** 103–124.

Odier E. and Monties B. (1983) Absence of microbial mineralization of lignin in anaerobic enrichment cultures. *Appl. Environ. Microbiol.* **46,** 661–665.

Otto A. and Simoneit B. R. T. (2001) Chemosystematics and diagenesis of terpenoids in fossil conifer species and sediment from the Eocene Zeitz formation, Saxony, Germany. *Geochim. Cosmochim. Acta* **65,** 3505–3527.

Pauwels H., Kloppmann W., Foucher J.-C., Martelat A., and Fritsche V. (1998) Field tracer test for denitrification in a pyrite-bearing schist aquifer. *Appl. Geochem.* **13,** 767–778.

Pauwels H., Foucher J.-C., and Kloppmann W. (2000) Denitrification and mixing in a schist aquifer: Influence on water chemistry and isotopes. *Chem. Geol.* **168,** 307–324.

Pettersson C., Ephraim J., and Allard B. (1994) On the composition and properties of humic substances isolated from deep groundwater and surface waters. *Org. Geochem.* **21,** 443–451.

Pignatello J. J. (1998) Soil organic matter as a nanoporous sorbent of organic pollutants. *Adv. Colloid Interface Sci.* **76-77,** 445–467.

Postma D., Boesen C., Kristiansen H., and Larsen F. (1991) Nitrate reduction in an unconfined sandy aquifer: Water chemistry, reduction processes, and geochemical modeling. *Water Resources Res.* **27,** 2027–2045.

Qu D. G., Shi J. Y., and Xiang M. J. (1996) Novel extended side-chain-unsaturated hopenes released from the kerogen macromolecules under artificial conditions. *Org. Geochem.* **24,** 815–823.

Reiss C., Blanc P., Trendel J. M., and Albrecht P. (1997) Novel Hopanoid Derivatives Released by Oxidation of Messel Shale Kerogen. *Tetrahedron* **53,** 5767–5774.

Robertson W. D., Russell B. M., and Cherry J. A. (1996) Attenuation of nitrate in aquitard sediments of southern Ontario. *J. Hydrol.* **180,** 267–281.

Routh J., McDonald T. J., and Grossman E. L. (1999) Sedimentary organic matter sources and depositional environment in the Yegua formation (Brazos County, Texas). *Org. Geochem.* **30,** 1437–1453.

Routh J., Grossman E. L., Murphy E. M., and Benner R. (2001) Characterization and origin of dissolved organic carbon in Yegua ground water in Brazos County, Texas. *Ground Water* **39,** 760–767.

Rullkötter J. (1983) Gas chromatography/mass spectrometry of degraded triterpanes in fossil organic matter—A record of microbial action. *Int. J. Mass Spectr. Ion Phys.* **48,** 39–42.

Saiz-Jimenez C. and De Leeuw J. W. (1986) Chemical characterization of soil organic matter fractions by analytical pyrolysis-gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrolysis* **9,** 99–119.

Salloum M. J., Chefetz B., and Hatcher P. G. (2002) Phenanthrene sorption by aliphatic-rich natural organic matter. *Environ. Sci. Technol.* **36,** 1953–1958.

Sanchez-Monedero M. A., Roig A., Cegarra J., Bernal M. P., and Paredes C. (2002) Effects of HCl-HF purification treatment on chemical composition and structure of humic acids. *Eur. J. Soil Sci.* **53,** 375–381.

Schmidt M. W. I., Knicker H., Hatcher P. G., and KogelKnabner I. (1997) Improvement of C-13 and N-15 CPMAS NMR spectra of bulk soils, particle size fractions and organic material by treatment with 10% hydrofluoric acid. *Eur. J. Soil Sci.* **48,** 319–328.

Schmitter J. M., Arpino P., and Guiochon G. (1978) Investigation of high-molecular-weight carboxylic acids in petroleum by different combinations of chromatography (gas and liquid) and mass spectrometry (electron impact and chemical ionization). *J. Chromatogr. A* **167,** 149–158.

Schreiber M. E. and Bahr J. M. (1999) Spatial electron acceptor variability: Implications for assessing bioremediation potential. *Bioremediation J.* **3,** 363–378.

Simmleit N. and Schulten H.-R. (1989) Analytical pyrolysis and environmental research. *J. Anal. Appl. Pyrolysis* **15,** 3–28.

Smith R. L. and Duff J. H. (1988) Denitrification in a sand and gravel aquifer. *Appl. Environ. Microbiol.* **54,** 1071–1078.

Sollins P., Homann P., and Caldwell B. A. (1996) Stabilization and destabilization of soil organic matter: Mechanisms and controls. *Geoderma* **74,** 65–105.

Standley L. J. and Kaplan L. A. (1998) Isolation and analysis of lignin-derived phenols in aquatic humic substances: Improvements on the procedures. *Org. Geochem.* **28,** 689–697.

Starr J. L., Sadeghi A. M., and Parkin T. B. (1996) A tracer test to determine the fate of nitrate in shallow groundwater. *J. Environ. Quality* **25,** 917–923.

Sukhija B. S., Varma V. N., Nagabhushanam P., and Reddy D. V. (1996) Differentiation of palaeomarine and modern seawater intruded salinities in coastal groundwaters (of Karaikal and Tanjavur, India) based on inorganic chemistry, organic biomarker fingerprints and radiocarbon dating. *J. Hydrol.* **174,** 173–201.

Thurman E. M. (1985) *Organic Geochemistry of Natural Waters*. Kluwer Academic Publishers.

Tsai C.-S., Killham K., and Cresser M. S. (1997) Dynamic response of microbial biomass, respiration rate and ATP to glucose additions. *Soil Biol. Biochem.* **29,** 1249–1256.

Tyson R. V. (1995) *Sedimentary Organic Matter*. Chapman & Hall.

van Beek C. G. E. M. and Vogelaar A. J. (1998) *Pompstation Hengelo't Klooster—Geohydrologische, geochemische en hydrochemische beschrijving*. KIWA N.V.

van Bergen P. F., Nott C. J., Bull I. D., Poulton P. R., and Evershed R. P. (1998) Organic geochemical studies of soils from the Rothamsted Classical Experiments–IV. Preliminary results from a study of the effect of soil pH on organic matter decay. *Org. Geochem.* **29,** 1779–1795.

van den Berg M. W., van Houten C. J., and den Otter C. (2000) *Geologische Kaart van Nederland Blad Enschede West (34W) en Enschede Oost/Glanerbrug (34O/35)*. Nederlands Instituut voor Toegepaste Geowetenschappen TNO.

van Weert F. H. A., van Gijssel K., Leijnse A., and Boulton G. S. (1997) The effects of Pleistocene glaciations on the geohydrological system of Northwest Europe. *J. Hydrol.* **195,** 137–159.

Wassenaar L., Aravena R., Fritz P., and Barker J. (1990) Isotopic Composition (C-13, C-14, H-2) and Geochemistry of Aquatic Humic Substances from Groundwater. *Org. Geochem.* **15,** 383–396.

Weber W. J. Jr., Huang W., and Yu H. (1998) Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments; 2. Effects of soil organic matter heterogeneity. *J. Contaminant Hydrol.* **31,** 149–165.

Witter E. and Dahlin S. (1995) Microbial utilization of [U-^{14}C] [U-^{13}C]-labelled straw and [U-^{14}C] [U-^{13}C]-labelled glucose in soils of contrasting pH and metal status. *Soil Biol. Biochem.* **27,** 1507–1516.