



Supporting Online Material for

Ongoing Buildup of Refractory Organic Carbon in Boreal Soils During the Holocene

R. H. Smittenberg,* T. I. Eglinton, S. Schouten, J. S. Sinninghe Damsté

*To whom correspondence should be addressed. E-mail: smitten@u.washington.edu

Published 24 November 2006, *Science* **314**, 1283 (2006)
DOI: 10.1126/science.1129376

This PDF file includes:

Materials and Methods

Fig. S1

Table S1

References

MATERIALS AND METHODS

Setting and samples

A detailed account on the setting and sampling strategy is provided by Smittenberg *et al.* (S1). The *n*-alkanes were obtained by solvent extraction of freeze-dried sediments and isolated from the extract by column chromatography, urea adduction and preparative gas chromatography in quantities of 30-180 μ g. Purified samples were subsequently measured for radiocarbon content at the National Ocean Science AMS Facility, Woods Hole. $\delta^{13}\text{C}$ values of individual *n*-alkanes were determined by analysis of the alkane fractions on a Finnigan DELTA-isotope ratio gas chromatography mass spectrometry system, with samples typically run in triplicate. In addition to the samples described in Smittenberg *et al.* (S1) the following sections from ODP leg 169S were also used: 1034C, 3H-5, 5-140cm; 1034C, 6H-3, 69-109cm; 1033C, 8H-4, 5-145cm.

n-Alkane sources and estimation of fossil contribution

The C_{25} to C_{33} *n*-alkanes in Saanich Inlet sediments are inferred to be predominantly derived from terrestrial organic matter based on the high Carbon Preference Index (CPI) values and depleted $\delta^{13}\text{C}$ values. Bacterial and algal *n*-alkanes generally exhibit carbon-chain lengths $< \text{C}_{24}$, maximizing at C_{17} (S4) and the relatively low abundance of these *n*-alkanes (Fig. S1) points towards a minimal contribution of such a source. In agreement, measured $\delta^{13}\text{C}$ values (Table S1) indicate a predominant C3 vascular plant source (S2, S3) for the C_{25} to C_{33} *n*-alkanes. The CPI for living plant tissue ranges between 5 and 40 (S2, S3, S5, S6), but in soils and sediments values of 4-7 are typically observed (e.g. S5, S7). These lower CPI values are mainly attributed to mixing of the various plant inputs, but also to degradation of functionalized lipids like long chain alcohols and fatty acids to alkanes. Contributions of radiocarbon-dead (fossil) alkanes with a low CPI of 1 to 2 from mature weathered organic rich sediment rock (e.g. S8, S9, S10) also lowers soil and sediment CPI values. Indeed, previous research (S7) as well as local geology (S11) also suggests that the Saanich Inlet sediments receive at least some contribution of fossil *n*-alkanes from organic rich parent material.

Adopting a similar approach to Collister *et al.* (S10), the contribution of fossil *n*-alkanes was estimated by using an iterative mixing model that calculates the relative amounts and $\delta^{13}\text{C}$ values of individual *n*-alkanes by mixing a 'fresh' vascular plant and a fossil petrogenic source with different CPI's and $\delta^{13}\text{C}$ values. The fossil source was assumed to have a CPI of 1 and $\delta^{13}\text{C}$ values between -27‰ and -28‰ (S4, S9, S10 and references therein). The vascular plant *n*-alkane source was assumed have a CPI of 7 and $\delta^{13}\text{C}$ values that gradually decrease with increasing carbon chain length from -31.5‰ (C_{25}) to -33.0‰ (C_{35}) (S3, S10, S12). The modeling results in an estimated fossil *n*-alkane fraction of ca. 20% for $\Sigma(\text{C}_{25}\text{-C}_{35})$ for the laminated sediments, except the post-bomb (1984-1998 AD) sediment that is estimated to contain approximately 50% fossil *n*-alkanes, and 30% for the non-laminated sediments. The CPI of 2.7 of the post-bomb sediment is accompanied by a series of C_{36} - C_{46} *n*-alkanes, albeit in relatively low concentration, suggesting that this sediment received an additional contribution of fossil *n*-alkanes likely

derived from petroleum spillage from ships. Due to uncertainties in the end member values the estimates must be regarded with some caution. However, adjustments in the assumed CPI - and $\delta^{13}\text{C}$ values of the two sources do not lead to major changes in the estimates of the fossil contribution.

The abundant odd $\text{C}_{27}\text{-C}_{31}$ *n*-alkanes contain a relatively low fossil contribution when compared to the other homologues due to their abundance in vascular plant material (Fig. 1). The radio and stable carbon isotopic composition of these homologues thus likely reflects best the Holocene aged vascular plant derived *n*-alkanes and have therefore been used in our study. Consequently, the fossil contribution to the C_{27} , C_{29} and C_{31} *n*-alkanes is only approximately half compared to the $\Sigma(\text{C}_{25}\text{-C}_{35})$ *n*-alkanes, which translates into estimated fossil fractions of these homologues of $10\pm 5\%$ for the laminated sediments, around $15\pm 5\%$ for the non-laminated sediments, and around 20% for the post-bomb sediment (Table 1).

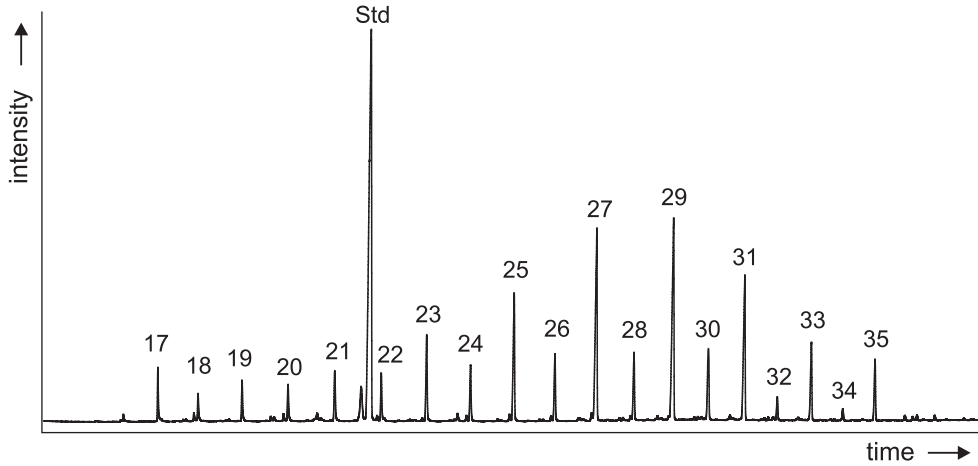
FIGURE S1

Figure S1. Gas chromatogram of the straight-chain hydrocarbon fraction obtained from the sediment of 568-465 BP. Numbers refer to the number of carbon atoms of the *n*-alkanes. Std=internal standard. The Carbon Preference Index (C_{25-33}) for this fraction is 4.3 (Table 1).

TABLE S1

Carbon number	Sediment age (cal BP)								
	1984 - 1998 AD	1932 - 1950 AD	465 - 568	977 - 1111	2533- 2707	3500 - 3600	4840 - 4940	6300 - 6500	11500 - 13000
23	-27.4	-27.7	-28.2	-28.4	-27.8	-28.2	-28.2		
24	-27.0	-27.8	-29.5	-29.4	-28.1	-27.6	-23.9		
25	-29.7	-28.7	-30.2	-30.1	-29.8	-30.1	-29.4		
26	-29.6	-29.2	-29.7	-29.9	-29.4	-30.0	-27.9		
27	-30.6	-30.1	-30.8	-31.3	-30.7	-30.6	-30.0		
28	-29.0	-30.6	-30.2	-31.1	-31.0	-29.6	-31.9		
29	-31.3	-32.0	-32.1	-32.3	-32.0	-31.6	-32.0	-30.8	-31.3
30	-28.7	-29.2	-31.0	-31.9	-31.7	-29.4			
31	-32.2	-32.2	-32.2	-32.6	-32.0	-32.6	-32.0	-32.7	-33.1
32	-27.5	-29.9			-30.5	-30.4			
33	-31.4	-31.0	-31.1	-31.7	-31.3	-31.8	-31.5	-32.1	-31.3

Table S1. $\delta^{13}\text{C}$ values of *n*-alkanes of the various sediments. Values are reported in ‰ VPDB. Typical standard deviation is 0.6‰ (n=3).

References

- S1. R.H. Smittenberg *et al.*, *Paleoceanogr.* **19**, (2004), doi:10.1029/2003PA000927
- S2. S.C. Brassell, G. Eglinton, J.R. Maxwell, R.P. Philp, in *Aquatic pollutants: Transformations and biological effects*, O. Hutzinger, W.H. van Lelyveld, B.C.J. Zoeteman eds. (Pergamon, Oxford, 1978), pp 69-86.
- S3. Collister, G. Rieley, B. Stern, G. Eglinton, B. Fry, *Org geochem.* **21**, 619 (1994)
- S4. G. Rieley *et al.* *Nature* **329**, 425 (1991).
- S5. P.A. Cranwell, *Prog. Lipid Res.* **21**, 271 (1982).
- S6. G. Eglinton, R.J. Hamilton, *Science* **156**, 1322 (1967).
- S7. M.B. Yunker, R.W. MacDonald, *Org Geochem.* **34**, 1429 (2003).
- S8. A. Pearson, T.I. Eglinton, *Org. Geochem.* **31**, 1103 (2000)
- S9. Killops, S & Killops, V. (eds) *Introduction to Organic Geochemistry 2nd ed.* (Blackwell, Oxford UK, 2005)
- S10. J.W. Collister, É. Lichtfouse, G. Hieshima, J.M. Hayes, *Org. Geochem.* **21**, 645 (1994).
- S11. British Columbia Geological Survey (2006)
<http://www.em.gov.bc.ca/mining/Geolsurv/default.htm>
- S12. M.J. Lockheart, P.F. van Bergen, R.P. Evershed, *Org Geochem* **26**, 137 (1997)