Bacteriohopanepolyol biomarker composition of organic matter exported to the Arctic Ocean by seven of the major Arctic rivers

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Introduction

The predicted amplified warming in the Arctic continental region, particularly in east Siberia [1], could result in an increase in summertime soil active-layer thickness and a reduction in the volume of the permafrost. This may have consequences for the release and degree of decomposition of the terrestrial organic matter in these regions and consequently could effect the composition of the terrestrial organic matter delivered to the Arctic Shelves. Several studies have been conducted on the OM at a molecular compositional level of rivers that discharge into the Arctic Ocean [2]. However none of the studies to date have investigated the bacteriohopanepolyol (BHP) component of OM in Arctic surface sediments.

In this study (Cooke et al., 2008, Bacteriohopanepolyol biomarker composition of organic matter exported to the Arctic Ocean by seven of the major Arctic rivers. Organic Geochemistry doi:10.1016/j.orggeochem.2009.07.014). we analysed estuary surface sediment samples obtained from the five Great Russian Arctic Rivers (GRARs; Ob, Yenisey, Lena, Indigirka, and Kolyma), and river sediments were obtained for two North American Rivers (Yukon and Mackenzie) [2], (Fig. 1)

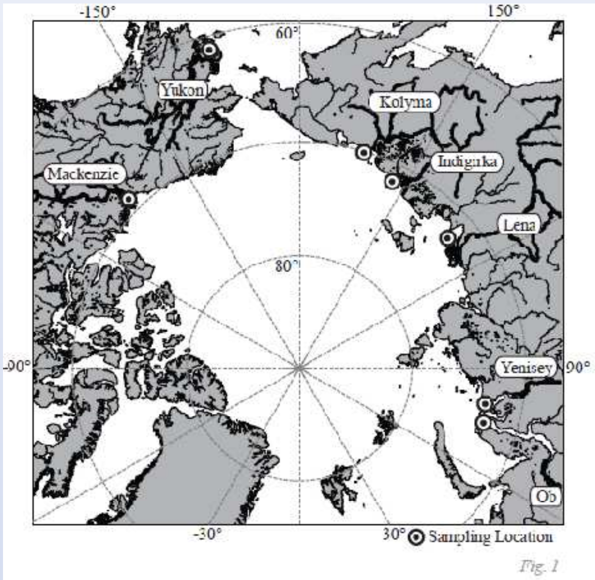
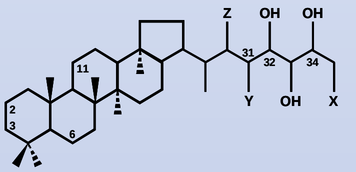


Fig. 1 Sampling Locations from the 5 GRARs and 2 North American Arctic Rivers

Bacteriohopanepolyols (BHPs)

BHPs are a diverse group of membrane lipids (Fig 2.) produced by a wide variety of bacteria [3], and can be used as molecular biomarkers for bacterial processes and populations in both modern and ancient environments [4].



Tetrafunctionalised
Z=H, Y=H, X=OH or NH_2 or composite group

Pentafunctionalised
Z=H, Y=OH, X=OH or NH_2 or cyclitol ether
Z=OH, Y=H, X=OH

Hexafunctionalised
Z=OH, Y=OH, X=NH_2

Side chain variants include a methyl group at C-31, a ketone group at C-32, -$OCONH_2$ at C-34, and structures with the side chain condensed into a cyclic ether form.
Variants in the ring system include methylation at either C-2 or C3, and a double bond at C-6 and/or C-11.

Fig.2 Generalised structure of bacteriohopanepolyols (BHPs). Most BHPs have four, five or six functional groups on the side chain, as indicated. Composite groups typically comprise sugar or amino acid derivatives.

A group of BHPs, including adenosylhopane (Fig 3) and related molecules, have been identified as being specific to soils [5], enabling the transport of terrestrial organic matter to the marine realm to be monitored. These soil markers (SM) have been identified as comprising approximately 28% of the total BHPs in a wide variety of global soils (Cooke et al.' unpublished data

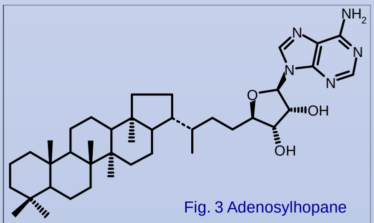


Fig. 3 Adenosylhopane

Methodology

•Sediment samples were freeze-dried, ground to a fine powder then extracted with a monophasic solution of water, methanol and chloroform (0.4:2:1) [4, 5]. Total lipid extracts were treated with pyridine/acetic anhydride (2 mL each) to form peracetate derivatives prior to analysis by LC-MS^n [6 and references therein].

• HPLC separation was achieved using a Phenomenex Gemini C18 column (150 mm x 3.0 mm i.d.) and a ternary gradient system from MeOH/water (90:10) to MeOH/propan-2-ol/water (59:40:1) and a flow rate of 0.5 mL/min.

References
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[5]} Cooke, M. P., et al., (2008) Org. Geochem. 39, 965-971. [6] Talbot , H. M., et al., (2007) Org Geochem 38, 1212-1225

Results

BHP levels were obtained by analysis of the chromatogram peaks and comparison with the standard. Results were calculated per g TOC (Table 1). The BHPs were subsequently grouped in to tetra-, penta-, hexa- and soil makers by relative % (Fig 4)

Abbreviated name	Ob River	Yenisey River	Lena River	Indigirka River	Kolyma River	Yukon River	Mackenzie River	Known Source organisms [a]
AnhydroBHT (IV)	bdl[b]	0.1	bdl	bdl	bdl	bdl	0.1	None
BHT (IV)	142	223	91	137	233	159	28	Various
2-methylBHT (IV)	9	15	11	9	17	6	2	Cyanobacteria, *Rhodopseudomonas palustris*
Aminotriol (IV)	24	18	63	14	32	81	9	Various
Adenosylhopane (SM)	29	50	65	84	120	104	10	Purple non-sulfur bactéria, Nitrogen & ammonia fixing bacteria
'*Adenosylhopane-type*' [c] (SM)	8	21	20	35	60	22	3	Purple non-sulfur bacteria
Aminotetrol (V)	4	1	9	2	bdl	16	0.6	Methanotrophs; *Desulfovibrio* sp.
'*2-methyl adenosyhopane -type*' [c] (SM)	bdl	3	3	7	6	bdl	bdl	None
2-methyl adenosylhopane (SM)	2	3	2	3	4	4	0.6	*Bradyrhizobium japonicum*
Aminopentol (VI)	1	1	6	1	7	4	0.8	Methanotrophs
BHT cyclitol ether (IV)	14	10	15	47	103	132	26	Various
2-methyl BHT cyclitol ether (IV)	bdl	bdl	bdl	3	5	0.4	0.1	Cyanobacteria
BHpentol cyclitol ether [d] (V)	bdl	bdl	3	4	10	15	8	Various
BHhexol cyclitol ether [d] (VI)	2	1	1	2	9	6	0.7	None
2-methylBHhexol cyclitol ether [d] (VI)	1	1	bdl	2	7	3	0.6	None
TOC (%)	9.2	19.4	4.8	14.6	17.3	12.4	20.2	
Total BHP (µg/g TOC)	**236**	**347**	**289**	**350**	**613**	**552**	**89**	

Table 1 BHP distribution for 7 arctic rivers BHP (µg/g TOC)

[a] Known hopanoid sources [4 and references therein]; [b] below detectable level; [c] structures in italics are tentative on basis of MS interpretation vs. spectra of authentic standards of other known BHP structures [6] [d] BH = bacteriohopane; IV = Tetra-functionalised; V = Penta-functionalised, VI = hexa-functionalised, SM = soil marker BHP

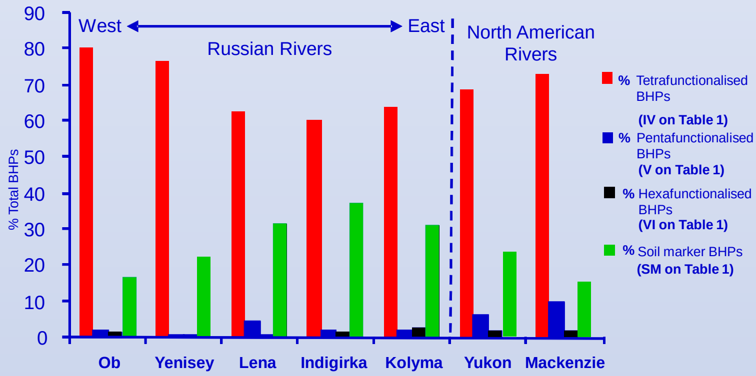

Fig.4. Histogram of relative abundance of BHPs groups in the studied pan-Arctic surface sediments. Note that the Indigirka River sample has the highest soil derived BHPs abundance decreasing along the Siberian east-west climosequence and towards Yukon and Mackenzie rivers.

Analyses of the BHP signatures, using HPLC-MS^n, indicated the presence of 15 different BHPs originating from a variety of different bacteria as well as a significant presence of terrestrially derived OM in the sediments as indicated by the soil marker (SM) BHPs (Table 1). The levels of BHPs were comparable to other estuary sediments [5], and generally lower than those found in soils [4]. The level of soil markers is comparable with those found in soils and estuary sediments. Total BHP abundance and the contribution of the "soil-marker" BHPs to the total BHP pool increased eastwards among the GRAR sediments (Fig. 4). The North American rivers showed greatly differing BHP levels between the Yukon and Mackenzie rivers, with a greater BHP input and thus a relatively higher soil OM contribution from the Yukon.

Conclusions

• The general increase in soil marker and overall BHP abundance towards the east indicates increasing terrestrial OM or increased preservation of OM due shorter periods of thawing and is in agreement with other biomarker information [2].

•The difference in BHP levels between the sediments of the YukonRiver, west of the Mackenzie Mountains, and the Mackenzie River to the east indicates that for Mackenzie, the low BHP level, coupled with the low proportion of soil markers, that there is a low terrestrial input to the sediment at this location or that the overall BHP-producing bacterial signal in this river is weak. The relatively high number of structures indicates that the reduction is unlikely to be a result of degradation of the BHP signature. For the Yukon the terrestrial OM and BHP signals are much higher.

•This benchmark study suggests that a general pan-Arctic BHP distribution pattern can be identified with the Indigirka River basin in the eastern Siberian Arctic being the epicentre with the highest soil marker BHPs but the lowest tetrafunctionalised BHPs [Fig. 1]. This trend is comparable to the distribution and abundance of permafrost in the Arctic region.

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