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Bacteriohopanepolyol distribution in Yenisei River and Kara Sea suspended particulate matter and sediments traces terrigenous organic matter input

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ABSTRACT

Bacteriohopanepolyols (BHPs) are ubiquitous bacterial membrane lipids, encountered in soils, river and marine suspended particulate matter (SPM) and sediments. Their abundance and distribution provides a direct means to identify bacterial inputs and can be used to trace soil-derived bacterial organic matter (OM) and in some cases the presence of bacterial groups and their activities in aquatic systems. We have studied the BHP distribution in the SPM of a major Siberian River (Yenisei River) that crosses a large latitudinal gradient, draining a large part of Mongolia and Siberian Russia. The Yenisei River is the main river to flow into the Kara Sea, a shelf sea of the Arctic Ocean. We show that the BHP distribution and concentration of SPM and surface sediments of the Yenisei Outflow in the Kara Sea allow to trace soil-marker BHPs and evaluate the performance of the R'_{soil} index, a proxy developed to trace bacterial soil-derived OM. Soil-marker BHPs are present in the Yenisei River, and their concentration decreases from the Yenisei River Outflow into the offshore marine sediments. The R'_{soil} correlates well with an independent proxy for bacterial OM, the BIT-index ($r^2 = 0.82$) and has a moderate correlation with the $\delta^{13}C_{org}$ values, a bulk OM proxy for terrigenous input ($r^2 = 0.44$). Consequently, the R'_{soil} index performs well in the Kara Sea, strengthening its application for tracing bacterial OM in the Arctic Ocean, both in modern and downcore sediments. Furthermore, a suite of BHPs that are characteristic for methanotrophic bacteria, i.e. 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol) and 35-aminobacteriohopane-31,32,33,34-tetrol (aminotetrol), is encountered in the Yenisei Outflow sediments. These components are partly sourced from terrigenous sources, but are likely also produced in-situ in the marine sediments. The distribution of the pentafunctionalized cyclitol ether BHP in the marine systems is noteworthy, and indicates that it can possibly be applied as a marker for cyanobacterial biomass in marine sediments.

1. Introduction

The study of the fate of organic carbon (OC) that is delivered to the marine environments by riverine sources is an important topic in environmental sciences (e.g. Blair and Aller, 2012). It is a critical component for models of carbon cycling in the modern coastal ocean and for models of atmospheric compositions over geologic time (Berner et al., 2004). The study of this process in the Arctic is especially important, as up to one half of global soil organic matter (OM) is stored in the Arctic terrestrial regions, predominantly in taiga and tundra soils (Tarnocai et al., 2009; Hugelius et al., 2014). This is one of the so-called global climate vulnerable carbon pools (Field and Raupach, 2004) and climate warming could cause transport of the terrestrial OC, that is now 'locked' in these pan-arctic tundra/taiga areas (Schuur et al., 2009), via the Arctic rivers to the Eurasian Arctic shelves. A second pool of vulnerable OC, that can contribute to atmospheric greenhouse gasses, is the large amount of submerged permafrost stored in the Kara Sea sediments, as reported by a number of authors (e.g. Portnov et al., 2013). As this permafrost is currently degrading, methane, a potent greenhouse gas that is found in permafrost layers near the surface (Rivkina et al., 2007), can be liberated as permafrost thaws (Portnov et al., 2013). Climate models forecast an amplification of global warming in the continental Arctic region (e.g. Zwiers, 2002), and there is already evidence for increasing river discharge and change in the hydrological regime in these regions (Peterson, 2002; Dittmar and Kattner, 2003; Benner et al., 2004). Within the context of the Arctic Ocean, which receives 11% of the freshwater and dissolved organic material globally (Aagaard and Carmack, 1989), the Kara Sea is of special importance, receiving about 50% (ca. 1500 km^3 $year^{-1}$) of the total river runoff discharged into the Eurasian Arctic (Gordeev et al., 1996; Holmes et al., 2002; Peterson, 2002; Stein and Macdonald, 2004). The Yenisei and Ob rivers are the major rivers contributing to this outflow, draining a large part of Mongolia and the Siberian continent (combined watersheds equal 5.6×10^6 km^2).

A fraction of the organic matter delivered to or produced in the marine system will be preserved in marine sediments. In these sediments, biomarkers, organic molecules with a characteristic and stable structure, can be analysed and traced back to a specific source. Sources include marine organisms such as algae, (cyano)bacteria and archaea and terrestrial organisms (plants, microbes). Biomarker distributions can reveal information about the environmental conditions, e.g. marine and continental environmental conditions, and the terrigenous supply of OM through time. One such group of biomarkers are the bacteriohopanepolyols (BHPs), membrane constituents that are synthesised by many bacteria (Ourisson and Albrecht, 1992; Pearson et al., 2007). These compounds are structurally diverse as they have polyfunctionalised side chains (e.g. Rohmer, 1993). Possible structures include tetra-, penta- and hexafunctionalised compounds according to the number of functional groups occupying positions C-30 to C-35 of the BHP structure (see Supp. Fig. 1 for structures). BHP derivatives have been observed in recent sediments and soils (e.g. Cooke et al., 2008; Cooke et al., 2009; Rethemeyer et al., 2010; Wagner et al., 2014) and older sediments (up to ca. 50 Ma; van Dongen et al., 2006; Cooke et al., 2008a; Handley et al., 2010; Talbot et al., 2014). Commonly occurring BHPs include bacteriohopane-

32,33,34,35-tetrol (BHT; **Id**; see Supp. Table 1 for used abbreviations), 35-aminobacteriohopane-32,33,34-triol (aminotriol; **Ig**) and BHT-cyclitol ether (**Ie**), which are found widespread among many bacterial species (Talbot et al., 2008 and references therein), while other BHPs are more source-specific. For instance 35-aminobacteriohopane-31,32,33,34-tetrol (aminotetrol, **Ij**; Talbot and Farrimond, 2007) and, especially, 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol, **Ik**; Talbot et al., 2014 and references therein) are produced almost exclusively by aerobic methanotrophic bacteria. Adenosylhopane (**Ia**) and up to five related BHPs (**IIa**, **Ib**, **IIb**, **Ic** and **IIc**) with a similar cyclized side chain have been observed to be particularly common in soils (e.g. Cooke et al., 2008b; Xu et al., 2009; Rethemeyer et al., 2010; Kim et al., 2011). They are therefore considered to be 'soil-markers', and have been used to trace soil transport to marine sediments, both in recent sediments and through time (e.g. Cooke et al., 2008a; Cooke et al., 2009; Handley et al., 2010; Taylor and Harvey, 2011). Recently Zhu et al. (2011) introduced a BHP-based proxy, R_{soil}, based on the relative abundance of soil marker BHPs against the end-member BHT (**Id**), to trace the soil input into surface sediments along a subtropical river–estuary-shelf transect. This ratio was simplified by Doğrul Selver et al. (2012), defining the R'_{soil}. In this ratio, the C-2 methylated soil-marker BHPs (**IIa**, **IIb**, **IIc**) were excluded due to their observed sporadic occurrence in Arctic materials. A few studies have been performed on BHPs in the Arctic Ocean. The BHP abundance and distribution has been studied in front of a set of Siberian rivers (Cooke et al., 2009), but this study did not allow for evaluation of changes that act on the BHPs before and during their outflow into the marine system and during sedimentation. Taylor and Harvey (2011) reported the BHP composition in surface sediments along two transects offshore two minor Alaskan Rivers (n = 8), in the Chukchi Sea, and compared the BHP signature within river sediments (n = 2) and watershed soils (n = 2). Doğrul Selver et al. (2015) discuss the BHP concentration along a transect in the East Siberian Sea (n = 9), downstream of the Siberian Kolyma River. However, it remains unclear how the Kara Sea compares with this setting.

This study describes, for the first time, the BHP distribution within riverine suspended particulate matter (SPM), over a large latitudinal gradient (Yenisei River, Siberia). The BHP signature is traced in the suspended material during its outflow in the Kara Sea, and compared with the signal preserved in the sediments. We quantify a suite of BHPs, which allows to trace the soil OM transport in the Yenisei River and in the Kara Sea system, and also evaluate the possibility of an *in-situ* produced BHP fingerprint of aerobic methanotrophic bacteria (Cvejic et al., 2000; Talbot and Farrimond, 2007; Talbot et al., 2014).

2. Geographical setting

The Yenisei River is the longest river in Russia and one of the longest rivers in Asia (Fig. 1A). The river starts in Northern Mongolia, draining a mountainous watershed. Further north, its most important tributary (25% of flow), the Angara River, joins the Yenisei River. Angara River drains Lake Baikal, a large freshwater lake that is fed dominantly (50% of flow) by the Selenga River that drains large parts of Mongolia, a watershed that is dominated by steppe vegetation (45 – 50 °N). The second important tributary for the Yenisei River is the Lower Tunguska (20% of flow), draining large areas of taiga (50 – 65 °N) and tundra (65 – 75 °N) soils. In the lower reaches of the river the Yenisei River flow rate decreases, the riverbed width reaching several kilometres. The Yenisei River is characterized by a pronounced discharge peak, the freshet, (>30% of annual discharge) in June associated with snowmelt and relatively low water flow between September and April (Stedmon et al., 2011). The Kara Sea (Fig. 1B), where the Yenisei River Mouth is located, is the second largest shelf area of the Arctic Ocean, partially enclosed to the west by the Novaya Zemblya and Franz Josef Land. To the southeast, it is confined by the Zevernaya Archipelago and the Taimyr Peninsula. About one third of the total freshwater discharge into the Arctic Ocean occurs through river run-off (Aagaard and Coachman, 1975). Here, the Kara Sea drains a fifth of the continental run-off of the Eurasian continent into the Arctic Ocean (Lammers et al., 2001). The resulting water discharges of the Ob and Yenisei River reach 400 and 630 $km^3.yr^{-1}$, ranking them thirteenth and sixth in the world in terms of water discharge (Bobrovitskaya et al., 1996). The Gydan Peninsula, where the narrow and deep Khalmyer Bay is situated, separates the Ob and Yenisei River estuaries. North of its shore are a number of islands; e.g the Oleniy and Sibiriakov Islands.

The Yenisei discharge and Kara Sea circulation are characterized by a strong seasonality. During the summer months, the surface currents in the Kara Sea follow a cyclonic circulation. The Greenland current enters the Kara Sea from the north, and passes along the east coast of Novaya Zemblya, flowing southwards. This water body is then joined by the discharge of the Ob and Yenisei Rivers, before flowing further to the northeast (Pavlov and Pfirman, 1995). From mid-October to mid-May, when only 10-15% of the river discharge happens, the Kara Sea and Yenisei River estuary are almost entirely ice-covered. The ice protects the uppermost water layers against wind mixing, and therefore the freshwater layer extends for a large distance under the ice, dispersing the little material delivered over a large distance (Lisitsyn, 1995). However, although less sediment is delivered to the Kara Sea in the winter months, Gaye et al. (2007) observed sedimentation increased with several orders of magnitude during ice-covered winter months, possibly because of sediment resuspension during months with a higher flow. The bulk of suspended load is deposited in front of the estuaries (Lisitsyn, 1995). This causes concentrations of suspended load to decrease by an order of magnitude compared to the estuary (Lisitsyn, 1995), between the surface isohaline of 2 and 20 psu. Between June and September, most of the discharge happens (ca. 80%, e.g. Pavlov and Pfirman, 1995). The high discharge period is characterized by a strong thermal stratification. Below the warm, fresh surface water, a salt-water tongue is present at 6-8 m in the inner Kara Sea, flowing onshore (Pavlov and Pfirman, 1995). Present sedimentation rates in the southern Kara Sea are estimated to range between approximately 0.2 to 1 $mm.yr^{-1}$, with the exception of shallow areas that are subjected to winnowing (Polyak et al., 2000). Sediment trap studies showed that sedimentation fluxes are highest in autumn and during the ice-covered months (Gaye et al., 2007).

The Kara Sea, like the other Arctic shelf seas, contains large amounts of submarine permafrost, that was submerged due to the eustatic sea-level rise (~120 m) since the last transgression (~7-15 ka). The submarine permafrost is composed of frozen sediments interlayered with flooded peatland (Romanovskii et al., 2005). The permanent permafrost is mapped to extend offshore in water depths < 20 m, and as it is expected to work as a 'seal' for methane release, no extensive methane release is expected above these depths (Shakhova et al., 2010). Discontinuous permafrost can be present in sediment underlying deeper water (>20 m, < 60 m), where large methane flares have indeed been described in the Kara Sea water column (Portnov et al., 2013).

3. Materials and methods

3.1. Collection of environmental samples

The suspended particulate matter (SPM) and sediment samples investigated in this study and location of the sampling stations (Fig. 1) are identical to those described in De Jonge et al. (2014, 2015 Briefly, surface water (<10 m depth; 1-300 L) was collected and filtered at 30 locations distributed throughout the Kara Sea and at 9 locations along the Yenisei River, from the R/V Sovetskaya Arktika (Aug and Sep 2009). At 15 sites, surface sediment samples were obtained by gravity coring. In September 2012, SPM (120-150 L) and surface sediments (obtained by box cores) were sampled at 9 sites, selected to sample conditions further offshore than the 2009 expedition, from the R/V Akademik Mstislav Keldysh. The SPM from both the 2009 and 2012 expeditions was collected with an in-situ pump (McLane Large Volume Water Transfer System Sampler), on 0.7 μm pore size GF/F glass fibre filters. In July 2010, three SPM samples were obtained in tributaries of the Angara and in the Selenga River. Surface water was collected in canisters after wading several meters into the river and filtered using the same type of filters, a peristaltic pump and a titanium tripod system.

3.2. BHP analysis

Freeze-dried sediments (2 g) and filters were extracted as described in De Jonge et al. (2015). In short, the samples were ultrasonically extracted three times for ten minutes using a single-phase solvent mixture of MeOH/DCM/phosphate buffer 10:5:4 (v/v/v). The total lipid extract (TLE) obtained from the sediments and an aliquot (5-10%) of the TLE obtained from the filters was used for BHP analysis. A known amount of internal standard (5α-pregnane- 3β,20β-diol) was added to the extracts. All lipid extracts were acetylated with acetic anhydride and pyridine (0.5 mL, 1:1 v/v) for 1 h at 50 °C and left at room temperature overnight. The solvent was removed under a continuous N_2 flow, on a 50°C heating block. The acetylated extract was dissolved in methanol:propan-2-ol (3:2, v/v) and filtered over 0.2 μm PTFE filters prior to HPLC–MS analysis.

Reversed-phase high-performance liquid chromatography (HPLC) analysis of the acetylated BHPs was modified after the method described in Cooke et al. (2008a). A Surveyor HPLC system (Thermo Finnigan, Hemel Hempstead, UK) was equipped with a Phenomenex (Macclesfield, UK)

Gemini C_{18} 5 μm HPLC column (150 mm, 3 mm internal diameter) and a Phenomenex Security Guard column of the same material. Separation over the column was achieved at a flow rate of 0.5 mL.min^{-1} at 30 °C with a solvent gradient profile starting at 90% A and 10% B (0–3 min), to 59% A, 1% B and 40% C at 25 min. Then elution was isocratic to 40 min, returning to starting conditions over a span of 5 min (with A = MeOH, B = water, C = propan-2-ol). The starting ratio was allowed to stabilize for 15 min before each run. For HPLC-MS, a Thermo Finnigan LCQ ion trap MS instrument equipped with an atmospheric pressure chemical ionization (APCI) source operated in positive ion mode was used. HPLC–MS was performed in data-dependent mode with two scan events. While SCAN 1 was performed over the whole spectrum (m/z 300–1300), SCAN 2 was a data-dependent MS^2 spectrum recorded for the most abundant ion from SCAN 1. Most intact BHPs were identified by comparison of the mass spectra to known BHP mass spectra (Talbot et al., 2001; Talbot et al., 2003; Talbot and Farrimond, 2007). A semi-quantitative estimate of the concentration was obtained, relative to the internal standard, as described in van Winden et al. (2012). The reproducibility of triplicate injections was 6% (relative standard error) for BHT and 8% for adenosylhopane (Doğrul Selver et al., 2014).

To trace the amount of soil-derived OM, the R'_{soil} was calculated, a ratio based on the relative abundances of soil-marker BHPs against BHT (Doğrul Selver et al., 2012):

$$R'_{\text{soil}} = (\mathbf{Ia}+\mathbf{Ib}+\mathbf{Ic})/(\mathbf{Ia}+\mathbf{Ib}+\mathbf{Ic}+\mathbf{Id}) \qquad \text{[Eq. 1]}$$

The structures **Ia**, **Ib** and **Ic** refer to soil-marker BHPs, while **Id** refers to BHT (see Supp. Fig. 1 for structures).

3.3. Bulk geochemical analysis

The bulk geochemical analysis was performed as in De Jonge et al. (2015), and the organic carbon content and δ^{13}C results have previously been reported by these authors. Briefly, the sediments were decalcified overnight with a surplus of 1.5 N HCl solution. The washed and freezedried sediments and the subsampled freezedried filters were then analysed using a Flash 2000 Organic Elemental Analyser.

4. Results

SPM samples from the Yenisei River (n = 13) and the SPM (n = 28) and sediments (n = 24) of its outflow into the marine system were analysed for BHPs (Fig. 1). A total of 22 BHP compounds were quantified (Supp. Tables 2 and 3). An overview of the abbreviations used and the chemical structures they refer to can be found in Supp. Table 1. The summed BHP concentration varied between 180 and 2300 μg.gTOC^{-1} in the sediments, with an average of 1100 μg.gTOC^{-1}. The BHPs in the SPM were present in lower absolute abundances, with concentrations varying between 0 and 1500 μg.gPOC^{-1}, with an average of 130 μg.gPOC^{-1}. The most abundant BHPs in the sediments were: BHT (**Id**), on average 410 μg.gTOC^{-1}, followed by adenosylhopane (**Ia**) and BHT cyclitol ether (**Ie**; both on average 160 μg.gTOC^{-1}). In the SPM these BHPs also have the highest concentration, although they are present in lower POC-normalized concentrations; BHT (on average 60 μg.gPOC^{-1}), adenosylhopane (15 μg.gPOC^{-1}) and BHT cyclitol ether (23 μg.gPOC^{-1}).

4.1. BHT, BHPentol, BHHexol

BHT (**Id**), and its C-2 methylated (**IId**) and unsaturated counterparts (**IIId** or **IVd**) are encountered both in the sediments and SPM. BHT is the most abundant compound in the Yenisei and Kara Sea environment, encountered in all sediments and the majority of SPM samples. In the Yenisei Mouth, Gulf and Outflow sediments, the TOC-normalized abundance of BHT (between 120 and 770 μg.gTOC^{-1}) remains constant downstream the Yenisei outflow (Fig. 2A). However, as the total amount of BHPs decreases downstream (Supp. Table 2), the fractional abundance of BHT increases in the sediments following the Yenisei River outflow (Fig. 2C). In the Yenisei River SPM, the absolute abundance is variable, but does not show a downstream trend (Fig. 3A, between 3 and 30 μg.gPOC^{-1}). In marine SPM, BHT is present in concentrations between 0 and 970 μg.gPOC^{-1}. Its fractional abundance varies between 0 and 1, but no downstream trend is obvious in the marine SPM (Fig. 2C). The unsaturated BHT is present in 71% of all sediments, in concentrations up to 120 μg.gTOC^{-1} (Supp. Table 2). It could be quantified in 14 SPM samples, in concentrations up to 70 μg.gPOC^{-1}. The methylated BHT is present in 22 sediments (0-34 μg.gTOC^{-1}) and 18 SPM samples (0-33 μg.gPOC^{-1}). The quantification of bacteriohopane-31,32,33,34,35-pentol (BHPentol; **If**) was problematic, as it co-elutes with the compound 35-aminobacteriohopane-32,33,34-triol (aminotriol; **Ig**), that is present in much higher abundance. We will thus refrain from discussing changes in the abundance of this BHP. The compound bacteriohopane-30,31,32,33,34,35-hexol (BHHexol; **Ih**) was present in the sediments at 15 sites, in concentrations up to 19 μg.gTOC^{-1}, and it was found in the SPM on two occasions (at a maximum abundance of 29 μg.gPOC^{-1}, Supp. Table 3). The BHP degradation product 32,35-anhydro-bacteriohopanetetrol (anhydroBHT; **Ii**) is observed in 14 sediments, in concentrations up to 10 μg.gTOC^{-1}. In the SPM it only amounts up to 5 μg.gPOC^{-1}.

4.2. Soil-marker BHPs

Adenosylhopane (**Ia**) is the most abundant component of a group of BHPs that is generally assumed to be derived of bacteria living in soil (e.g. Cooke et al., 2008a,b; Rethemeyer et al., 2011). It is present in all sediments (n = 24), in concentrations varying between 9 and 390 μg.gTOC^{-1}. Its methylated counterpart (2-methyladenosylhopane; **IIa**) is present in 50% of the sediments, although it is much less abundant (0-29 μg.gTOC^{-1}). The adenosylhopane type-2 (colloquially referred to as “soil group 2”; G2; **Ib**), is present in all but one sediment. It is less abundant than adenosylhopane at all sites, with concentrations varying between 0 and 110 μg.gTOC^{-1}. Its methylated counterpart (**IIb**) is present in 70% of the sediments, although the concentrations are never >22 μg.gTOC^{-1}. The “soil group 3”, G3 BHP (**Ic**), could be quantified in 18 sediments, and occurs in concentrations <47 μg.gTOC^{-1}. Its methylated form (**IIc**) is present less frequently (n = 9) and in even lower concentrations, with abundances that are in general below 25 μg.gTOC^{-1}, although one site (YG8) has a higher concentration of 92 μg.gTOC^{-1}. The non-methylated compounds are present in both river and marine SPM, in concentrations up to 240 μg.gPOC^{-1} (n = 30; Adenosylhopane), 110 μg.gPOC^{-1} (n = 30; G2) and 61 μg.gOC^{-1} (n = 5; G3). Their methylated counterparts could be quantified only in a few SPM samples, but they are encountered both in riverine and marine SPM. The highest concentration of the methylated (M; **IIa**, **IIb**, **IIc**) and non-methylated (NM; **Ia**, **Ib**, **Ic**) soil-marker BHPs are encountered in the Yenisei Mouth sediments (> 30 and >300 μg.gTOC^{-1}, respectively), decreasing towards the Yenisei Gulf (> 20 and between 300 and 150 μg.gTOC^{-1}, respectively), while the Yenisei Outflow and Kara Sea samples have concentrations <10 for M soil-marker BHPs and <150 μg.gTOC^{-1} (Fig. 2D) for NM soil-marker BHPs. The fractional abundance of the soil-marker BHPs, compared to the total amount of BHPs also decreases downstream in the SPM (Fig. 2E for NM soil-marker BHPs). Although not part of the Yenisei Outflow system, the Khalmyer Bay is also characterized by a high concentration of soil-marker BHPs (Fig. 2D; >20 μg.gTOC^{-1} for M soil-marker BHPs, >350 μg.gTOC^{-1} for NM soil-marker BHPs). In the Yenisei River SPM, higher abundances of NM soil-marker BHPs are encountered in the southern Selenga River, decreasing downstream in the Yenisei River, with the exception of YR5 (Fig. 3B). In the SPM of the marine system, the fractional abundance of the NM soil-marker BHPs is slightly increased in the Yenisei Gulf compared with the Yenisei Mouth (and Yenisei River), which is in contrast with the decrease observed in the underlying sediments (Fig. 2F). Also, the fractional abundance of the NM soil-marker BHPs is slightly increased compared to the riverine SPM samples, varying between 4 and 35% (Fig. 2F).

4.3. Composite BHPs

Composite BHPs contain an ether-linked functionality at the terminal position of the side-chain moiety (C-35) within the BHP structure. Cyclitol, glycosidic and carbapseudopentose moieties are produced by a variety of source organisms (Talbot et al., 2008 and references therein). Cyclitol ether-containing BHPs were encountered as tetra-, penta- and hexafunctionalized compounds. The tetrafunctionalized BHT cyclitol ether (**Ie**) was present in 18 sediments, with abundances up to 740 μg.gTOC^{-1}. It was present in the majority of the SPM samples (n = 18, up to 30 μg.gPOC^{-1}). Within the Yenisei River SPM, the concentration of this BHP was increased in the lowland, high latitude sites (Fig. 3C). The BHPentol cyclitol ether (**Il**) was less frequently observed (n = 13), with concentrations up to 100 μg.gTOC^{-1} (Supp. Table 2). However, it can be found with the same absolute abundances both in sediments with high and low riverine input (Fig. 4A), resulting in increased fractional abundances in the Kara Sea sediments (Supp. Table 2; Fig. 4B). It was present in 13 SPM samples (with a maximum concentration of 53 μg.gPOC^{-1}, Fig. 4A, crossed symbols). Even less common was the hexafunctionalized BHHexol cyclitol ether (**Im**). It was present in only a handful of sediments (n = 8), with low concentration, up to 51 μg.gTOC^{-1} (Supp. Table 2). It could be quantified in 5 SPM samples, albeit in relatively low concentration (up to 8 μg.gTOC^{-1}; Supp. Table 3).

BHT carbopseudopentose (BHT-pseudopentose; **In**) could be quantified in 10 sediment samples, in concentrations varying between 0 and 93 μg.gTOC^{-1}. In the SPM it could only be quantified at 5 locations, in concentrations up to 88 μg.gPOC^{-1}. Its unsaturated counterpart (**IIIn** or **IVn**) was present in a small number of sediments (n = 7), in a concentration between 21 and 89 μg.gTOC^{-1}. It was present in 4 SPM samples, albeit in low concentrations (up to 16 μg.gPOC^{-1}). The C-2 methylated BHT-pseudopentose (**IIn**) was present in 5 sediments (concentration up to 33 μg.gTOC^{-1}). It could be quantified in only 2 SPM samples, in relatively low concentration (up to 10 μg.gPOC^{-1}).

4.4. Aminopolyols

Aminobacteriohopanepolyol compounds were encountered as tetra-, penta- and hexafunctionalized compounds. Aminotriol (**Ig**) is present in all sediments (9 to 220 ug.gTOC^{-1}), while its unsaturated counterpart (**IIIg** or **IVg** or containing an unstauration in the side chain; van Winden et al., 2012) was present in much smaller quantities; it was present above detection limit in only 11 sediments (0 to 28 μg.gTOC^{-1}). The pentafunctionalized 35-aminobacteriohopanetetrol (aminotetrol, **Ij**) was present in the majority of the sediments (n = 16; 0-48 μg.gTOC^{-1}), with the highest abundances encountered in the Yenisei Gulf and Khalmyer Bay (Fig. 5A). The hexafunctionalized BHP 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol, **Ik**) was present in the sediment at 13 sites (0-54 μg.gTOC^{-1}), with the highest abundances again in the Yenisei Gulf and Khalmyer Bay (Fig. 5B). These BHPs are also present in the SPM, although the concentrations of the tetra-, penta- and hexafunctionalized aminopolyols only amount up to 67 μg.gPOC^{-1} (n = 21), 2 μg.gPOC^{-1} (n = 3) and 2 μg.gPOC^{-1} (n = 5), respectively.

5. Discussion

5.1. BHPs as tracers for soil organic matter in the Kara Sea

5.1.1. Using biomarker ratios to trace riverine export of Arctic carbon

The export of particulate and dissolved OC from the watershed of Arctic Rivers into the marine system is a major variable of the global carbon cycle. Here, the export of bacterial OM is an important constituent of this pool, as the DOC released in thawing permafrost soils is quickly respired by the bacterial community, and not exported to the marine system (e.g. Spencer et al., 2015). Besides being a specific marker for bacterial OM, lipid biomarkers find an application tracing this export through time, as their stable chemical structure allows their accumulation in marine sediments. In this geological archive, they can be (semi-) quantified to reconstruct past changes in the export of terrigenous bacterial OM. For this, ratios of terrigenous components and marine components are constructed (e.g. Hopmans et al., 2004). Employing a ratio instead of C-normalized concentrations, circumvents the impact of the degradation of OM, as degradation will affect the marine and terrigenous end-members to the same extent, as ideally, they will have a similar chemical structure. The downside of using a ratio, however, is that it is influenced both by the concentration of the terrigenous and marine end-members, in a non-linear way (Smith et al., 2012). The source of and mechanisms acting on the BHP distribution in the Yenisei River and Kara Sea are not constrained well. Therefore, their spatial distribution will be analysed in river SPM, marine SPM and recent surface sediments and compared with independent markers for bacterial and bulk terrigenous OM.

5.1.2. Provenance of R'_{soil} components

The R'_{soil} is an index, based on the abundance of three soil-marker BHPs relative to BHT, designed to trace soil-derived OM in a river outflow system (modified after Zhu et al., 2011 by Doğrul Selver et al., 2012). The BHP signature in soils has been identified over the last years; temperate soils and peats (Cooke et al., 2008b; Redshaw et al., 2008; Kim et al., 2011; van Winden et al., 2012a, 2012b), sub-tropical soils (Zhu et al., 2011), tropical soils (Pearson et al., 2009; Wagner et al., 2014; Spencer-Jones et al., 2015), subarctic soils (Xu et al., 2009) and high-latitudinal soil profiles (Rethemeyer et al., 2010; Höfle et al., 2015) have been studied. These studies have reported adenosylhopane (**Ia**) and G2 (**Ib**) BHPs (and their C-2 methylated homologues) as being present and abundant in all soils, typically averaging 29% of total BHPs in temperate and subarctic soils (Cooke et al., 2009; Cooke, 2010). These compounds have been identified in cultures of purple non-sulfur bacteria (Talbot et al., 2007 and references therein), while adenosylhopane is also known to be produced by other Proteobacteria including a dinitrogen-fixing bacterium (*Bradyrhizobium japonicum*; Bravo et al., 2001) and an ammonia-oxidizing bacterium (*Nitrosomonas europaea*; Seemann et al., 1999). In fact, adenosylhopane has been reported to be the precursor for all other side chain elongated BHPs (Bradley et al., 2010) and it is currently unknown why it appears to accumulate so readily in soils compared to other environments. G3 BHP (**Ic**) and its methylated counterpart (**IIc**) were first encountered in high latitude soils (Rethemeyer et al., 2010), where they comprised up to 15% of total BHPs. The microbial source of these compounds remains unknown.

BHT (**Id**) is a non-specific BHP, very common in both terrestrial and marine environments with a wide range of source organism (e.g. Talbot et al., 2008). Its use as an endmember (originally described as a pseudo-marine endmember; Zhu et al., 2011; Doğrul Selver et al., 2012) in the R_{soil} and R'_{soil} proxies is complicated by the fact that BHT is not exclusive for marine environments. However, it was selected as it was found to be the most and in many cases only significant BHP in marine sediments (Zhu et al., 2011; see also Blumenberg et al., 2010, Sáenz et al., 2011a). BHT was previously reported to account for an average of 20% of BHPs in soils (summarized in Zhu et al., 2011) although it can be significantly lower (e.g. as low as 1 % in some tropical soils; Spencer-Jones et al., 2015) or higher (average 31% in permafrost soil horizons from the Lena delta; Höfle et al., 2015). Little is known regarding marine sources of BHPs (e.g. Pearson et al., 2007) but potential sources of BHT do include sulfate reducing bacteria of the genus *Desulfovibrio* (Blumenberg et al., 2006, 2009, 2012), some anaerobic ammonia oxidising bacteria (anammox; Rush et al., 2014) and it was a trace component in the marine N-fixing cyanobacterium *Crocosphaera* sp. (Talbot et al., 2008).

5.1.3. Spatial patterns in R'$_{soil}$ components

5.1.3.1. NM soil-marker BHPs

To evaluate the transport and sedimentation of soil-derived OM delivered by the Yenisei River, we first discuss the abundance of the NM soil-marker BHPs (i.e. **Ia**, **Ib**, **Ic**; Cooke et al., 2010; Rethemeyer et al., 2011) in the sediments of the Yenisei Outflow in the Arctic Ocean. In marine sediments, the presence of soil-marker BHPs is generally interpreted to be derived from a terrigenous source, delivered to the marine system by riverine transport. Cooke et al. (2009) quantified four soil-marker BHPs in the estuaries of seven major rivers draining into the Arctic Ocean, where their concentration (between 10 and 190 μg.gTOC^{-1}) was found to increase eastwards along the Eurasian continent. Zhu et al. (2011) reported the seaward decrease in concentration of six soil-marker BHPs in front of the Yangtze River (400-40 μg.gTOC^{-1}) and Doğrul Selver et al. (2012) evaluated seaward trends in concentration changes (500-80 μg.gTOC^{-1}) of six soil-marker BHPs in the Baltic Sea, in front of the Kalix River. In the East Siberian Sea, Doğrul Selver et al. (2015) report a seaward decreased in the abundance of six soil-marker BHPs (300-150 μg.gTOC^{-1}), in front of the Kolyma River. In line with these previous studies, and supporting the riverine transport mechanism of the soil-marker BHPs, we find the full suite of six soil-marker BHPs in the Yenisei River Mouth sediments (Supp. Table 2). The concentration of the six soil-marker BHPs reported for the Yenisei River outflow in this study (between 10 and 550 μg.gTOC^{-1}) compares well with the concentrations encountered in the Kolyma, Kalix and Yangtze River systems. However, in these studies, the concentration of soil-marker BHPs (between 250 and 550 μg.gTOC^{-1}) is high compared to the 77 μg.gTOC^{-1} reported for soil-marker BHPs in the Yenisei River estuary in Cooke et al. (2009), which indicates there is localized heterogeneity within this region. The observed offshore decrease in the concentration of soil-marker BHPs (Fig. 2D) in the Kara Sea, is in agreement with the suggested riverine-derived terrigenous source. Indeed, following the delivery of soil-derived OM to the marine system, the concentration of soil-derived OM in the marine system will decrease, because of dilution with marine organic matter and degradation.

The concentration of NM soil-marker BHPs can be compared with previously published data (De Jonge et al., 2015) on the presence of terrigenous OM in the Yenisei River and Kara Sea (Fig. 6A-C). Firstly, the results are compared with the relative abundance of branched glycerol dialkyl glycerol tetraethers (brGDGTs). The BIT-index is a ratio that contrasts the abundance of five major brGDGTs against the marine isoprenoid GDGT crenarchaeol (modified after Hopmans et al., 2004). It was found to trace the presence of terrigenous OM (river- and soil-derived; De Jonge et al., 2015) in the Kara Sea. The summed concentrations of sedimentary NM soil-marker BHPs possess a good linear correlation (r^2 = 0.78) with the concentration of river and soil-derived brGDGTs (Fig. 6A; full line). This good correlation reflects that both sets of compounds are derived from a comparable source: bacterial membranes. However, a deviation from a linear regression can be observed in the lower abundances, which results in a slightly better fit ($r^2 = 0.81$) when plotting the summed NM soil-marker BHPs as a logarithmic function [$y = \log(x)+z$] against the brGDGT concentration (Fig. 6A; dotted line). This indicates that the concentration of brGDGTs approaches 0 between the Yenisei Gulf and Kara Sea, whereas the soil-marker BHPs are still present and decreasing in these offshore sediments (Fig. 6A). The presence of a recalcitrant pool of brGDGTs agrees with the observed difference in degradation by Zhu et al. (2013) in the East China Sea, who describes a stronger resilience of brGDGTs to degradation, compared to soil-marker BHPs. The pattern in the decrease in abundance of both classes of biomarkers is thus likely to be explained by degradation and dilution (by freshly produced organic matter) in the marine system. As both the brGDGT and BHP lipid classes seem to be controlled by the same mechanisms, the correlation between the BIT values and the concentration of NM soil-marker BHPs ($r^2 = 0.74$, $p<0.05$; Fig. 6B) is good.

A second proxy for the presence of terrigenous OM is the stable carbon isotopic composition of organic matter ($\delta^{13}C_{org}$), a bulk proxy for the presence of terrigenous organic matter in the marine system, measured on the same samples (De Jonge et al., 2014, 2015). $\delta^{13}C_{org}$ has been frequently used for tracing terrigenous OM transport in the Kara Sea (Fernandes and Sicre, 2000; Krishnamurty et al., 2001; Vetrov and Romankevich, 2011; Lein et al., 2012). However, there is only a moderate correlation between the $\delta^{13}C$ org values and the soil-marker BHPs concentration ($r^2 = 0.38$, $p<0.05$; Fig. 6C) suggesting they trace different pools of OM (bulk terrigenous OM versus bacterial OM).

In contrast to many other coastal seas, the shoreline of the Kara Sea is composed of an extensive system of coastal cliffs that are subjected to thermal and wave erosion. Recently Doğrul Selver et al. (2015) suggested that the erosion of coastal cliffs may be the major source of BHPs in the Kolyma River region, although riverine transport was not excluded as a potential secondary source. A contribution from coastal cliff erosion will likely be even more significant in those settings where no major rivers drain. In the Kara Sea, the Khalmyer Bay is a good example of such a setting, where the high concentration of soil-marker BHPs encountered (Fig. 2D; >350 $\mu g.gTOC^{-1}$) is probably not only derived from riverine transport, as was previously observed for other organic biomarkers (De Jonge et al., 2015).

5.1.3.2. BHT

The fractional abundance of BHT in the surface sediments of the Yenisei River mouth varies between 20 and 43% (Fig. 2C) and probably reflects that of the watershed soils (cf. average of 31% in permafrost soils from the Lena delta; Höfle et al., 2015). In contrast to the distribution of the soil-marker BHPs (Fig. 2D), the BHT concentration in marine sediments does not change substantially downstream of the Yenisei Outflow (Fig. 2A), and it does not correlate significantly with the BIT, $\delta^{13}C$ and C/N values ($p>0.05$). The absence of a downstream trend can be based on two mechanisms; i) the simultaneous degradation of terrigenous BHT with marine in-situ production, or ii) a better preservation of BHT compared to the soil-marker BHPs. Handley et al. (2010) observed better preservation of BHT, compared to the soil-marker BHPs, in downcore sediments from the Congo deep sea fan. This was, however, only evident in sediments with an age >500 ka, and has not been observed in more recent sediments (e.g. Wagner et al., 2014), suggesting that differences in preservation cannot explain the trend observed. On the other hand, in-situ production of BHT in the marine system was observed to occur in many modern marine coastal systems. For instance, Pearson et al. (2009), Rethemeyer et al. (2011) and Zhu et al. (2011) observed an increase of the BHT concentration in increasingly marine conditions, and attributed this to in-situ production. Based on this dataset, we cannot conclusively state which mechanism is dominant in controlling the observed pattern in the Yenisei outflow BHT concentrations.

5.1.4. Performance of R'_{soil} in Kara Sea sediments

The R_{soil} is an index, based on the abundance of six soil-marker BHPs relative to BHT, designed to trace soil-derived OM in a river outflow system (Zhu et al., 2011). The R'_{soil} [Eq. 1] is a similar, but simplified index that excludes three minor C-2 methylated (M) compounds, without losing the source-specific nature of the original ratio (Doğrul Selver et al., 2012). As BHT is also present in soils, this results in R_{soil} and R'_{soil} values that are below unity in soils. Zhu et al. (2011) report that R_{soil} values in soil globally vary between 0.4 and 0.9, with an average value of 0.7 ± 0.1 (n = 30). This variability within the soil end-member is similar to the BIT-index (Hopmans et al., 2004) that uses crenarchaeol, a tetraether membrane lipid typical for marine Thaumarchaeota as the marine end-member. Crenarchaeol occurs typically in substantially lower concentrations than the brGDGTs, resulting in BIT-values that are generally vary between 0.7 and 1 in soils and peat with an average of 0.9 ± 0.14 (n = 224) (Schouten et al., 2013). The R_{soil} and R'_{soil} values are strongly correlated in our dataset ($r^2 = 0.99$, both for SPM and sediments), caused by the low abundance of the M soil-marker BHPs (Supp. Tables 2 and 3). Although the presence of the M soil-marker BHPs does not introduce any variation in the index, as observed in Doğrul Selver et al., (2012), the R'_{soil} has typically been applied in northern river systems, and so we will thus discuss variations in the R'_{soil} index only. After soil erosion and transport to the marine system, the R'_{soil} values in the Yenisei River Mouth sediments amounts up to 0.62 (Fig. 7A), with slightly lower values in the overlying SPM (up to 0.57; Fig. 7B). These values exceed the R'_{soil} values reported by Doğrul Selver et al. (2012) for the subpolar Kalix outflow (up to 0.30), and for the tropical Yangtze River outflow (0.43), but are comparable to the values in the Arctic Kolyma river outflow (up to 0.57; Doğrul Selver et al., 2015). The spatial pattern in the R'_{soil} values reflects a high input of soil-marker BHPs in the Yenisei Mouth that decreases downstream (Fig. 7A). Although not part of the Yenisei outflow system, the Khalmyer Bay is characterized by similar R'_{soil} values.

In the Kara Sea, the variations in R'_{soil} values correlate with the concentration of soil-marker BHPs ($r^2 = 0.83$, $p<0.05$; Fig. 7C), and not with changes in the concentration of BHT ($r^2 = 0.05$; Fig. 7D). In the Kara Sea system, R'_{soil} values can thus be interpreted as a tracer for soil-marker BHPs in the marine system, without being influenced by changes in the concentration of BHT. The R'_{soil} values show a slightly improved correlation with independent terrigenous OM proxies compared to the absolute and fractional abundances of the soil-marker BHPs (Fig. 6). It shows a moderate linear correlation with $\delta^{13}C_{org}$ ($r^2 = 0.44$, $p<0.05$; Fig. 7E) and a good linear correlation with the BIT ratio ($r^2 = 0.82$, $p<0.05$; Fig. 7F). Both lipid-based tracers for OM thus show a slightly different pattern compared to the bulk $\delta^{13}C_{org}$ values, which reflects the heterogeneous nature of the terrigenous OM delivered to the marine system. This contrasts with a recent study performed in the Arctic Kolyma river outflow, where a much stronger linear correlation was observed between R'_{soil} and bulk $\delta^{13}C$ in ($r^2 = 0.96$; Doğrul Selver et al., 2015), whilst a strong but non-linear correlation was identified for the BIT vs. $\delta^{13}C$ values. This suggests that the R'_{soil} values better reflect bulk OM in the Kolyma system. As the watershed of the Kolyma river is exclusively continuous permafrost, the soil types in the watershed possibly influence the source and behavior of the lipid biomarkers in their outflow.

5.1.5. R'_{soil} values in riverine and marine SPM

The proposed concept of the R'_{soil}, tracing soil-derived OM after soil run-off and transport through a riverine system, implies the presence of soil-marker BHPs in the riverine SPM. As the Yenisei is one of the longest rivers in Asia (5550 km), it allows evaluation of the BHP distribution in river water crossing several climatic zones (latitudinal range = 46-73°N). Furthermore, this study allows comparison of upstream and lowland BHP distributions. We have identified 17 individual BHPs in the Yenisei River SPM (Supp. Table 3), although the maximum diversity of BHPs encountered in a single sample was nine compounds. To date, only one description of BHPs in riverine SPM has been published (Sáenz et al., 2011), for a small river in Panama. They described the BHP distribution at one site, quantifying 11 compounds. The total BHP abundance encountered in this setting ($0.18\ \mu g.L^{-1}$) is slightly lower than the highest abundance found in our dataset ($0.31\ \mu g.L^{-1}$; SR), but higher than the majority of the upstream and lowland sites investigated ($1–3 \,.\, 10^{-5}\ \mu g.L^{-1}$).

Both BHT and soil-marker BHPs can be quantified in the Yenisei River SPM, both in upstream and downstream rivers (Fig. 3A, B). The resulting R'_{soil} values are low in the Yenisei River SPM, between 0 and 0.35 (Fig. 3A, B) and are only weakly controlled by changes in the concentration of the NM soil-marker BHPs ($r^2 = 0.17$, $p = 0.2$). No correlation is observed for R'_{soil} values and the concentration of BHT. Although the variation in R'_{soil} values in the river SPM are substantial, we cannot infer what causes these shifts without further knowledge of the watershed soils BHP distribution. However, different soil types possibly deliver different amounts of soil-marker BHPs, as is exemplified by the higher concentration of soil-marker BHPs in the (single) measurement in the Selenga river that drains the Mongolian steppe soils. Nonetheless, the presence of soil-marker BHPs supports the riverine transport of soil-marker BHPs, as part of the Yenisei River SPM. In the Yenisei Mouth and Gulf, a slightly increased amount of soil-marker BHPs is observed, compared to the SPM of the Yenisei River (Fig. 2F). However, taking the average and variance within these groups into account, these small increases are not significant (student t-test, $p>0.05$). As the fractional abundance of BHT shows no significant increase in the Yenisei Mouth and Gulf (Fig. 2C), the resulting average *R'*soil values in the SPM of the Yenisei Mouth (0.31), is higher than the average *R'soil* values in the Yenisei River SPM (0.21). This increase in soil-derived OM in the marine system has also been recognized based on brGDGT concentrations and was discussed in the study by De Jonge et al. (2015). There, it was postulated that it can be due to the presence of an SPM signal that records the signal delivered during the freshet that is possibly increased in soil-derived OM, as the main settling fluxes only occur during the calmer winter months (Gaye et al., 2007). Furthermore, the contribution of coastal-cliff derived soil-marker BHPs may also influence their abundance in the Yenisei River Mouth. Further downstream in the Yenisei Outflow and Kara Sea, soil-marker BHPs are below detection limit in many samples, resulting in *R'soil* index values that equal 0.

5.2. Other BHPs derived from terrigenous sources

As reported previously (Zhu et al. 2011; Sáenz et al., 2011a; Doğrul Selver et al., 2012), the diversity of BHP compounds is larger in riverine and soil samples, compared to the marine environment (e.g. Blumenberg et al., 2010; Sáenz et al., 2011b), indicating that, in addition to the soil-marker BHPs, an additional suite of BHP compounds is produced in the terrigenous system and transported to the marine system. In this section we identify those compounds that are delivered to the marine system via the Yenisei River or coastal erosion, based on their presence in the Yenisei River SPM and on having a similar geographical distribution in the Kara Sea as the soil-marker BHPs, i.e. with the largest concentrations in the Yenisei River mouth and Khalmyer Bay.

The BHPs BHT-pseudopentose (**In**) and its unsaturated (**IIIn** or **IVn**) and methylated (**IIn**) counterparts are present in the Yenisei mouth and gulf outflow sediments, with the highest abundance in YM3. Originally shown to be produced by an Arctic cyanobacterium (*Gloeocapsa* sp.; Talbot et al., 2008), they have subsequently been described in the surface layers of peat bogs (van Winden et al., 2012), and also in Arctic soils, where they were found to be particularly abundant in the overlying surface vegetation (organic mat) and river sediments (Rethemeyer et al., 2010). The fractional abundance of the three BHT pseudopentoses is highest in the upstream river SPM samples (Supp. Table 3) that have the highest *R'soil* signal. This pattern fits a dominant source in soils and/or overlying vegetation.

The tetra- and hexafunctionalized BHP cyclitol ethers (**Ie** and **Im** respectively) show an increased abundance in the Yenisei Mouth sediments, indicating a likely predominantly terrigenous source for these BHPs. This agrees with the presence of BHT CE in near-shore river fan sediments in the East Siberian Sea (Doğrul Selver et al., 2015). Additionally, the BHHexol cyclitol ether also shows an increased abundance in the upstream rivers and Yenisei outflow SPM, both sites characterised by high *R'soil* values (Supp. Table 3). This BHP has been observed in temperate soils (e.g. Cooke et al., 2008b) but has yet to be identified in bacterial cultures although a related BHHexol mannosamide has been reported from a culture of *Alicyclobacillus acidoterrestris* (Řezanke et al., 2011). The BHT cyclitol ether

(**Ie**) is an abundant BHP in both temperate (e.g. Cooke et al., 2008b) and Arctic soils (Rethemeyer et al., 2010). It is produced by a variety of organisms, including cyanobacteria, purple non-sulfur bacteria, N_2-fixing bacteria, *Geobacter* sp. and others (e.g. Talbot et al., 2008; Eickhoff et al., 2013). However, the increase in absolute abundance of BHT cyclitol ether (Fig. 3C) results in their large fractional abundance (between 60 and 70% of all BHPs) in lowland river SPM samples. This points to *in-situ* production in the river water, although input of high-latitude permafrost soils cannot be excluded. Indeed, a recent study on the BHP distribution in Arctic polygons (Höfle et al., 2015), shows that BHT cyclitol ether is a common compounds in Arctic polygon environments, where it is apparently produced in the polygon depression. Polygons, that are associated with massive ground ice bodies have, however, not been described in the Yenisei River watershed.

The hexafunctionalized BHHexol (**Ih**) is observed in highest abundance in the Khalmyer Bay and Yenisei Gulf. It has been described to be the dominant BHP in an enrichment culture of *Methylomirabilis* sp. (Kool et al., 2014), an autotrophic methanotroph. Furthermore, Řezanka et al. (2011) have found BHHexol to be present in the thermophilic bacterium *Alicyclobacillus acidoterrestris*, in abundances up to half of the commonly occurring BHT. This BHP has only occasionally been reported in low abundances in the environment, including lake sediments of Loch Ness, UK (Talbot and Farrimond, 2007), soils (Cooke et al., 2008b), and Amazon shelf and fan sediments (Wagner et al., 2014). This compound has also been encountered in near-shore marine river fan sediments by Doğrul Selver et al. (2015). Although this BHP could not be quantified in the Yenisei River SPM, we infer a soil source for this minor BHP in the Kara Sea, based on its presence in Yenisei River Mouth sediments.

5.3. Possible marine sources of BHPs

5.3.1. Possible cyanobacterial markers produced in the marine system

The pentafunctionalized BHP cyclitol ether (**Il**) is present in similar concentration in marine sediments with high and low riverine input, resulting in increased fractional abundances in the Kara Sea sediments (Supp. Table 2; Fig. 4A, B). This indicates that this BHP is possibly produced in-situ in the marine system. This is confirmed by its presence in marine SPM, where it can be present in a high fractional abundance (up to 70% in one sample, on average 30%). This is remarkable, as this compound was to date reported to dominate BHP distributions only in environmental samples from a terrestrial geothermal vent (Champagne Pool; Gibson et al., 2014). The possible source organism in that environment are chemolithotrophic organisms such as *Acidithiobacillus* sp. Other known source organisms include the acetic acid bacteria (*Acetobacter* spp., *Gluconacetobacter* spp.; Talbot et al., 2007b and references therein). However, these organisms also make the unsaturated and C-3 methylated cyclitol ethers that were not present in the studied sediments. In the acetic acid bacterium *Frateuria aurantica* (Joyeux et al., 2004), the BHPentol cyclitol ether was shown to be the most abundant BHP, although its abundance increased with increased growth temperature, a condition that does not reflect the Arctic Ocean. Furthermore, both the acetic acid bacteria and *Frauteuria* sp. thrive at low pH conditions, and are thus unlikely to occur in the high pH Arctic marine system. In polar environments, BHPentol cyclitol ether (**Il)** was previously described as a minor compound in an Antarctic lake sediment and microbial mat (Talbot et al., 2008). As BHPentol cyclitol ether has been encountered in a cyanobacterial culture (*Chlorogloeopsis* sp.; Talbot et al., 2003b), we postulate that the most probable source organism of this compound in the Kara Sea is a cyanobacterium. This results in a dominance of BHPentol cyclitol ether especially in those sediments that receive almost no terrigenous OM (e.g. KS1).

5.3.2. Methanotrophic markers in the marine system

Large amounts of submerged, degrading permafrost are present in the Kara Sea and East Siberian Sea sediments (Romanovskii et al., 2005; Portnov et al., 2013). This permafrost was formed on-land during the sea-level lowstand of the last glacial period and inundated with marine water 7-15 ky ago. Substantial amounts of methane are present (trapped in frozen material) or being formed in these sediments. Since the inundation, this permafrost has been thawing, and methane gas can be expelled as large flares of methane bubbles that have been reported to be present between the 20 and 60 m isobaths, where pathways are present within the degrading permafrost that allow the escape of methane (Portnov et al., 2013). Aerobic methanotrophic bacteria have been described to be present and active in permafrost environments (Trotsenko and Khmelenina, 2005, and references therein). As methanotrophic bacteria have the capacity to mitigate CH_4 emissions from thawing permafrost, the response of microbial communities to thawing permafrost will determine whether permafrost environments will be a net source of greenhouse gasses in the coming decades (Graham et al., 2012). The presence of active aerobic methanotrophs in the Kara Sea sediments is to be expected, as methane oxidation was described to occur in the upper sediments throughout the Kara Sea (Galimov et al., 2006; Savvichev et al., 2010) and in the water column of the East Siberian Sea (Shakhova et al., 2015).

Aerobic methanotrophy can be traced using specific BHPs that are known to be markers for methanotrophic bacteria. Aminopentol (**Ik**) is a marker for type I methanotrophs (gammaproteobacteria; Talbot et al., 2014 and references therein) although there is one report of trace levels in one species of sulfate-reducing bacteria (Blumenberg et al., 2012). Aminotetrol (**Ij**) also may reflect the presence of both type I and type II (alphaproteobacteira) methanotrophs, as it was found in most methanotrophs from the alpha- and gammaproteobacteria (Talbot and Farrimond, 2007). Type I methanotrophs (using the ribulose monophosphate carbon assimilation pathway) are generally associated with freshwater and marine aquatic systems, although they have also been shown to dominate Arctic soils (e.g. Martineau et al., 2010; Yergeau et al., 2010), while Type II methanotrophs (employing the Serine pathway for carbon assimilation) are widespread in terrestrial settings, (e.g. Hanson and Hanson, 1996).

While aminopolyols have been shown to be present in cultures of anaerobic sulfate-reducing bacteria, where present, aminotetrol and in one case only aminopentol account for only low to trace amounts compared to aminotriol. This is unlike the distribution encountered in these marine sediments, which is much more consistent with an aerobic, methanotrophic source. It is possible for aminotriol to be produced under anaerobic conditions (e.g. *Desulfovibrio* spp. Blumenberg et al., 2006, 2009, 2012), but the production of aminotetrol and particularly aminopentol is still widely accepted as indicating aerobic methanotrophy (e.g. Berndmeyer et al., 2013; Talbot et al., 2014; Höfle et al., 2015). Thus, previous research on the distribution of the BHPs aminopentol and aminotetrol in the freshwater and marine realm identified two possible methanotrophic sources. Firstly, the signal can be derived from the continent, as methanotrophy is a process that will occur in the aerobic zones of methanogenic soils, peats and wetlands (e.g. Talbot et al., 2014 and references therein). Van Winden et al. (2012a, 2012b) described the presence of both aminotetrol and aminopentol in UK and Belgian *Sphagnum* peat, amounting up to 3 and 0.5% of all BHPs quantified, respectively. This is comparable to the fractional abundances encountered in the marine sediments in this study. Bacterial methanotrophy has also been described in the Yenisei River water column (Namsaraev et al., 1995), and the biomarker signal may thus also be produced in-situ in the Yenisei River. At least part of the methanotrophic signal encountered in the marine system is derived from the Yenisei River or its watershed, as aminopolyols were detected in the Yenisei River SPM (Supp. Table 3). Aminotetrol is present in both the Yenisei River and the Yenisei Gulf. The fractional abundance of aminopentol is highest in lowland Yenisei River SPM, and in the Yenisei River Mouth (Supp. Tables 2 and 3). A terrigenous source is in line with previous studies (Talbot et al., 2014, Wagner et al., 2014, Höfle et al., 2015; Spencer-Jones et al., 2015), where the presence of aminopentol in marine river fan sediments was shown to derive from terrestrial wetland systems and soils in the Congo River catchment, in the Amazon Basin and in Siberian permafrost soils.

However, the increase in concentration of all aminopolyols in the Yenisei Gulf sediments, compared to the upstream Yenisei River Mouth (Supp. Table 3; illustrated for aminotetrol and aminopentol in Figs. 5A-B) contrasts with the decrease observed for soil-marker BHPs (Fig. 2D). A possible explanation for the increase of the concentration of all four aminopolyols is the in-situ production of these BHPs in the marine sediments. Based on the presence of aminopentol, we postulate that they are produced by a salt-tolerant clade of Type I methanotrophic Bacteria. *Methylovulum sp.* isolated from an acidic peat has been shown to produce all four of these BHPs (van Winden et al., 2012). The aminopolyol signature thus reflects a typical methanotrophic signature that would be expected for a *Methylovulum*-like organism. Also, Taylor and Harvey (2011) describe the presence of aminotetrol and aminopentol in the surface sediments of the Chukhi Sea, a shallow shelf sea comparable to the Kara Sea, although these BHPs were absent from river sediments (n = 2) and watershed peat samples (n = 2). These data are in favour of an *in-situ* source for these BHPs in the Yenisei Gulf sediments.

Moving further downstream, to the Yenisei River outflow, both the unsaturated and saturated aminotriol compounds and aminotetrol are still present in similar maximum abundances as observed in the Yenisei River mouth sediments (Fig. 5A). However, as aminopentol is not present at these sites, this BHP distribution possibly reflects the in-situ production by a methanotrophic community that is dominated by Type II methanotrophs, potentially including *Methylocella* sp., which produces high levels of aminotriol and also BHT (van Winden et al., 2012). In truly marine systems where methanotrophy is encountered, e.g. those associated with methane seeps, aminopentol has not been observed (Jahnke et al., 1995; Burhan et al., 2002; Pancost et al., 2005; Birgel et al., 2011), which has led to the speculation that at least some of these environments are dominated by Type II methanotrophs (e.g. Birgel et al., 2011). However, Coolen et al. (2008) reported 16S ribosomal RNA gene sequences from Type I species in sediments from an Antarctic meromictic lake in which the only aminoBHPs observed were aminotriol and aminotetrol, indicating that some Type I species may not produce aminopentol. Therefore, it is possible that the absence of aminopentol, whilst potentially indicating a change in the methanotroph community, does not necessarily indicate a shift to Type II species. Although the presence of methanotrophic biomarkers does not necessarily indicate that the source organisms are active in the environment, it does highlight the potential for methanotrophic bacteria to mitigate the export of methane stored and produced within submerged permafrost.

6. Conclusion

This study reports the BHP distribution and abundance in a major Siberian river that spans a large latitudinal gradient, and its outflow in the Kara Sea, a shallow Arctic Ocean shelf sea. In this setting, the R'_{soil} index can be used as a tracer for the delivery of terrigenous OM to modern marine sediments, indicated by its good correlation with the BIT-index ($r^2 = 0.82$). Although the presence of both soil-marker BHPs and BHT in the Yenisei River SPM supports the proposed riverine transport mechanism of BHPs to the marine system, it is unclear to what extent the R'_{soil} values in the River SPM reflect the R'_{soil} values in the watershed soils, as no BHPs were measured on soils in the Yenisei watershed. The increased abundance of soil-marker BHPs in the Khalmyer Bay, where no major rivers drain, is probably derived from coastal cliffs erosion. Soil-marker BHPs can thus have two sources in shallow Arctic Seas. The diversity of BHPs was found to decrease from the Yenisei River Mouth into the marine system. The distributions of the BHPs BHT-pseudopentose (**In**), its unsaturated (**IIIn** or **IVn**) and methylated (**IIn**) counterparts, tetra- and hexafunctionalized BHP cyclitol ethers (**Ie** and **Im** respectively) and BHHexol (**Ih**) in the marine sediments mimics that of the soil-marker BHPs in the outflow of the Yenisei River. This suggests that these BHPs are also terrigenous-derived, and delivered to the marine system by riverine transport. The distribution of BHTetrol CE (**Ie**) in the river SPM indicates that it is possibly produced in-situ in the lowland Yenisei River, or derived from high-latitude soils. The increased fractional abundance of BHPentol CE in offshore marine samples indicates a marine source, possibly from cyanobacteria. The spatial distribution of biomarkers for methanotrophic activity (aminotetrol (**Ij**), and especially aminopentol (**Ik**)) in the Kara Sea sediments indicates a mixture of terrigenous and marine sources. Their downstream increase is a strong indication for an in-situ produced methanotrophic signal. As the methane in the marine sediments is probably derived from submerged permafrost in the Kara Sea sediments, methanotrophic markers can possibly be used as tracer for submerged, thawing permafrost. To extrapolate the observed export of soil-marker BHPs up to a yearly, watershed-wide flux of bacterial OM, more research is needed on the concentration of soil-marker BHPs in the Yenisei River watershed, and their concentration in the river water during the freshet, when the majority of the terrigenous organic matter is exported. Overall, the study of riverine and marine BHPs in the Yenisei River/Kara Sea system confirms the potential of BHPs to identify the dominant source of the OM encountered, and even identify specific bacterial groups.

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Figure legends

Fig. 1. Map with the sampling locations of A) the Siberian mainland and B) the Kara Sea, with the outflow of the Yenisei and Ob Rivers and Khalmyer Bay indicated. Background colours divide the stations in geographical zones, according to the legend.

Fig. 2. Box plots showing the variation in the concentration (A-D) and fractional abundances (FA: relative to the total suite of 22 BHPs quantified) of bacteriohopanetetrol (BHT; panels A, B,C) and of the summed concentration of the non-methylated (NM) soil-marker BHPs (Adenosylhopane, G2 and G3 BHPs; Ia, Ib, Ic; panels D, E, F) in sediments (panels A-B, D-E) and SPM (panels C and F). Data are summarized per geographical zone (as defined in Fig. 1), where the vertical lines indicate different areas of freshwater inputs in the Kara Sea. Within each section the order of boxplots agrees with the direction of the outflowing water. MR = Mountainous upstream rivers, YR = Selenga and Yenisei River, YM = Yenisei Mouth, YG = Yenisei Gulf, YO = Kara Sea sites in Yenisei Outflow, KS = Kara Sea sites distinct from Yenisei outflow, KB = Khalmyer Bay, KG = Khalmyer Gulf, OO = Kara Sea sites in Ob Outflow.

Fig. 3. River SPM BHP distributions showing the concentration of BHT (**Id**; A), of the sum of the non-methylated (NM) soil-marker BHPs (**Ia** + **Ib** + **Ic**; B), and of BHT CE (**Ie**; C). The R'_{soil} values are plotted in panel A and B in a red line. The grey bars indicate mountainous rivers, while the black bars indicate lowland river settings, reflecting the zones in Fig. 1.

Fig. 4. Occurrence of the BHP CE (**Il**) in the Yenisei/Kara Sea system. A) Geographical variation in the concentration of BHP CE (**Il**) in the sediments. The symbol colour refers to the legend, while a blank symbol indicates a concentration below detection limit (b.d.l.). Crossed symbols indicate the sites where BHP CE (**Il**) was encountered in the SPM. B) Box plots showing the variations in fractional abundance (relative to the summed amount of 22 BHPs) of BHP CE, summarized per geographical zone (see Fig. 1), where YM = Yenisei Mouth, YG = Yenisei Gulf, YO = Kara Sea sites in Yenisei Outflow, KS = Kara Sea sites not directly influenced by the Yenisei outflow, KB = Khalmyer Bay, KG = Khalmyer Gulf, OO = Kara Sea samples in Ob Outflow.

Fig. 5. Box plots showing the variation in concentrations of the BHPs aminotetrol (**Ij**) (A) and aminopentol (**Ik**) (B) per geographical zone (defined as in Fig. 1), where YM = Yenisei Mouth, YG = Yenisei Gulf, YO = Kara Sea sites in Yenisei Outflow, KS = Kara Sea sites not directly influenced by the Yenisei outflow, KB = Khalmyer Bay, KG = Khalmyer Gulf, OO = Kara Sea samples in Ob Outflow.

Fig. 6. The concentration (in μg.gTOC^{-1}) of the sum of non-methylated soil-marker BHPs (Sum NM Soil BHPs; **Ia** + **Ib** + **Ic**) in surface sediments plotted against A) the concentration of brGDGTs, B) BIT-index values and C) $\delta^{13}C_{org}$ values . The squared correlation coefficients (r^2) values are reported. The values for the brGDGT concentrations, BIT-indices and $\delta^{13}C_{org}$ values are from De Jonge et al. (2015). Symbol colours indicate geographical zones, as shown in the legend and defined in Fig. 1.

Fig. 7. Geographical distribution of the R'_{soil} index values in (A) surface sediments and (B) SPM of the Yenisei/Kara Sea system. The symbol colours refer to the legend in panel B. B.d.l = below detection limit. The R'_{soil} values of the sediments are plotted against (C) the concentration of the summed non-methylated (NM) soil-marker BHPs (**Ia** + **Ib** + **Ic**), (D) the concentration of BHT (**Id**), (E) the $\delta^{13}C_{org}$, and (F) the BIT-index values, a brGDGT-based biomarker proxy for terrigenous material. BIT and $\delta^{13}C_{org}$ values are reported by De Jonge et al., 2015. For Panel C-F, the symbol colours indicate geographical zones, as reflected in the legend and in Fig. 1.

Tables

Supp. Table 1. Overview of the BHP names used in the manuscript, the corresponding structure number, that refers to Supp. Fig. 1, and the dominant base peak ion that is formed analyzing the samples when using the method described in section 3.

BHP name	**Structure number**	**Base peak ion (*m/z*)**
Adenosylhopane	Ia	788
Meth. Adenosylhopane	IIa	802
G2	Ib	761
Meth. G2	IIb	775
G3	Ic	802
Meth. G3	IIc	816
BHT	Id	655
Meth. BHT	IId	669
Unsat. BHT	IIId or Ivd	653
AnhydroBHT	Ii	613
BHPentol	If	713
BHHexol	Ih	771
Aminotriol	Ig	714
Unsat. Aminotriol	IIIg or Ivg	712
Aminotetrol	Ij	772
Aminopentol	Ik	830
BHT cyclitol ether	Ie	1002
BHPentol cyclitol ether	Il	1060
BHHexol cyclitol ether	Im	1118
BHT Comp	In	943
Meth. BHT Comp	IIn	957
Unsat. BHT Comp	IIIn or IVn	941

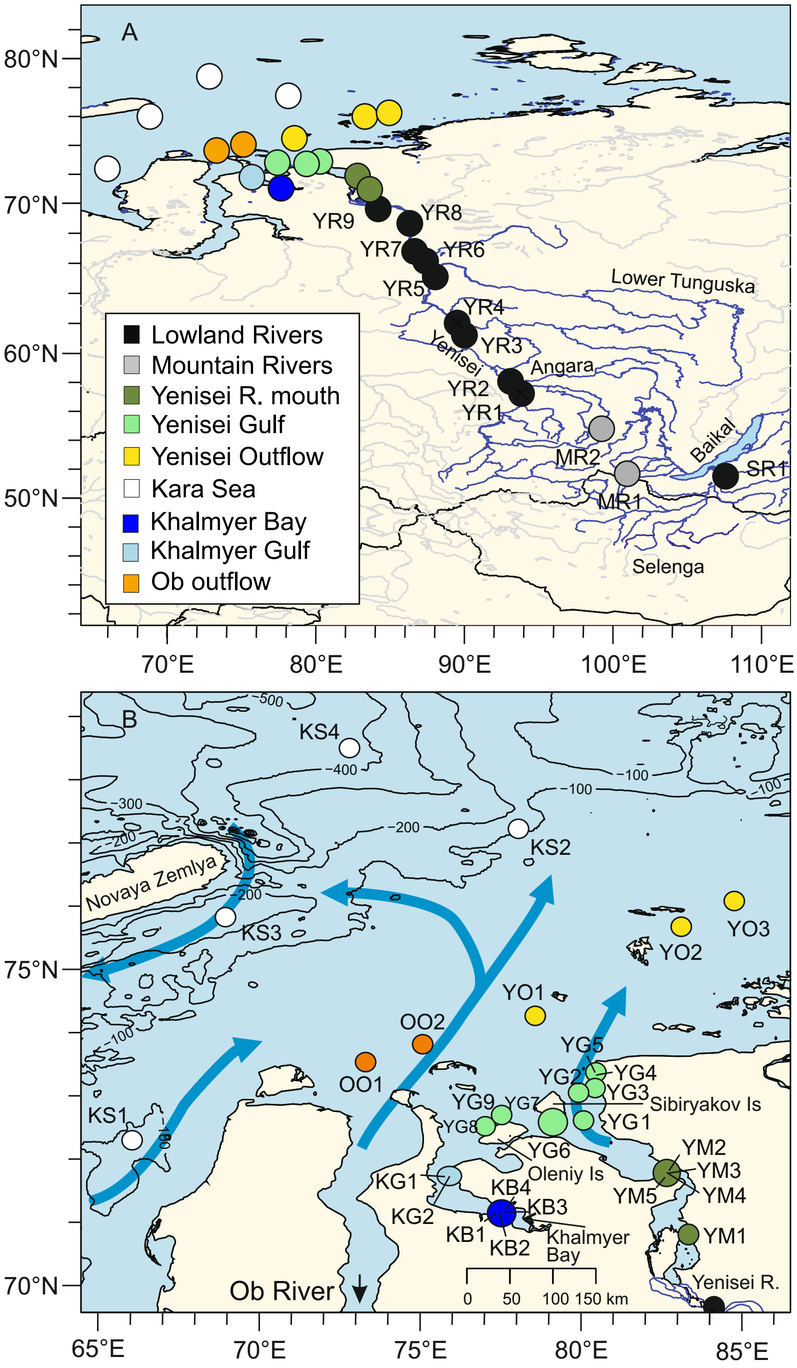
Supp. Table 2. Concentration of the individual and summed sedimentary BHPs (µg.gTOC^{-1}). The *R'*$_{\text{soil}}$ values are calculated [Eq. 1], based on the concentrations of the compounds indicated in bold. B.d.l. indicates that the concentration was below detection limit.

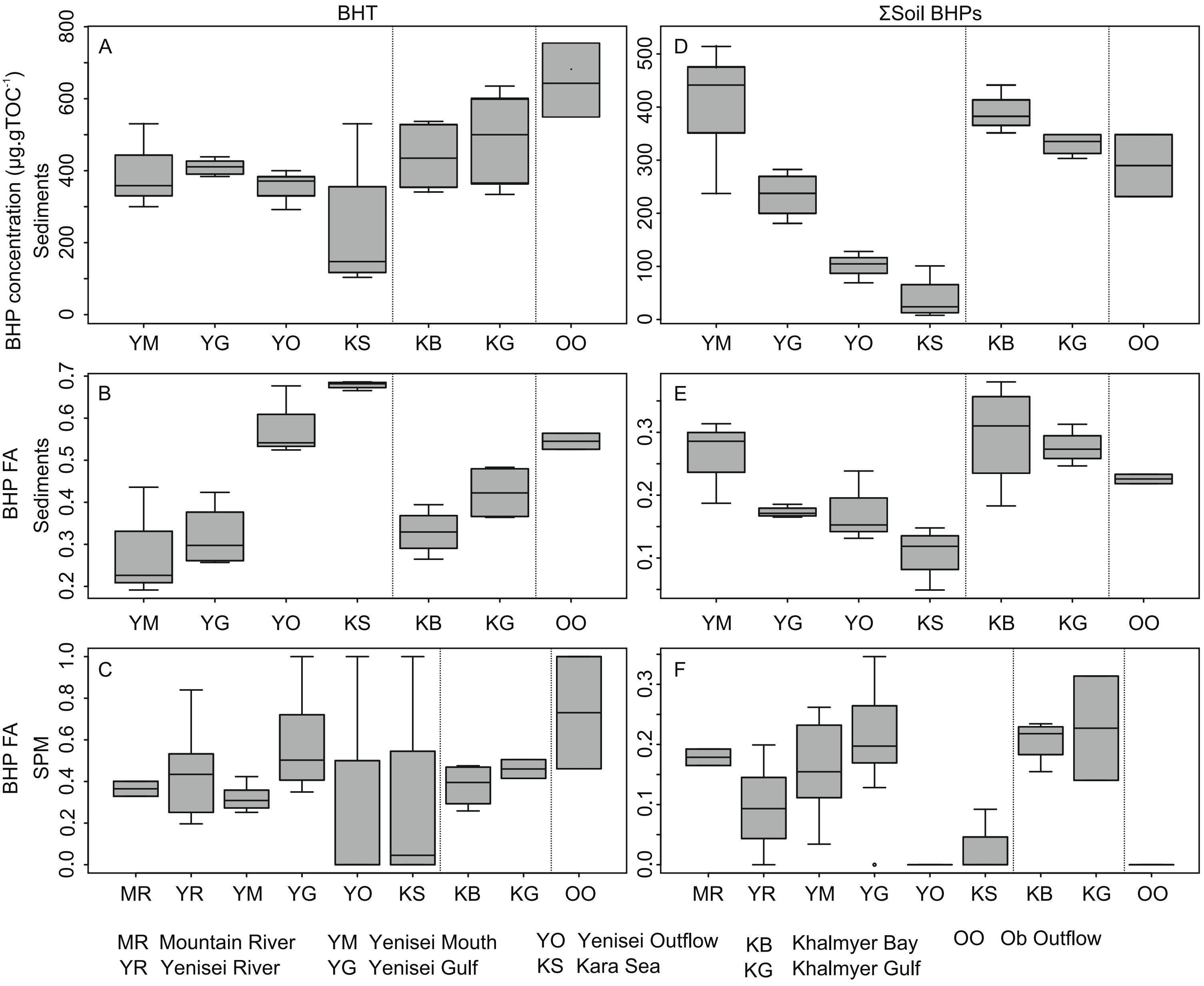
	Absolute abundance (µg.gTOC-1)																						
	Ii	IIId or IV d	**Id**	IId	Ih	IIIg or IVg	Ig	Ij	Ik	**Ia**	**IIa**	**Ib**	**IIb**	**Ic**	**IIc**	IIIn or IVn	In	IIn	Ie	Il	Im	Sum BHPs µg.gTOC^{-1}	*R'*$_{\text{soil}}$
m/z	*613*	*653*	*655*	*669*	*771*	*712*	*714*	*772*	*830*	*788*	*802*	*761*	*775*	*802*	*816*	*941*	*943*	*957*	*1002*	*1060*	*1118*		
Site																							
YM2	9.1	120	310	25	9	b.d.l	70	15	6.8	390	27	71	12	47	b.d.l	21	33	b.d.l	310	100	13	1600	0.62
YM3	b.d.l	52	530	34	13	9.6	110	19	27	300	21	110	22	30	b.d.l	89	93	33	740	37	51	2300	0.45
YM4	b.d.l	27	360	31	11	b.d.l	32	b.d.l	6.8	150	8.9	60	14	26	9.0	33	37	21	b.d.l	b.d.l	b.d.l	830	0.40
YG1	2.9	20	400	30	10	23	160	35	33	170	11	80	13	31	11	44	57	19	290	24	25	1500	0.41
YG2	2.5	22	440	29	11	11	82	16	10	100	b.d.l	56	14	25	11	29	36	11	110	7.6	10	1000	0.29
YG3	3.5	24	410	24	12	24	130	30	22	130	b.d.l	54	11	20	9.0	31	42	b.d.l	210	20	16	1200	0.33
YG7	b.d.l	33	380	28	18	28	220	48	34	150	11	76	15	26	10	35	47	16	240	26	23	1500	0.40
YG8	5.9	28	570	27	13	b.d.l	70	b.d.l	b.d.l	220	b.d.l	79	11	30	93	b.d.l	b.d.l	b.d.l	55	b.d.l	b.d.l	1200	0.36
YG9	b.d.l	b.d.l	640	b.d.l	b.d.l	b.d.l	57	b.d.l	b.d.l	220	b.d.l	100	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	200	98	b.d.l	1300	0.34
YO1	4.8	14	290	14	6.4	5.5	31	5.5	b.d.l	69	b.d.l	44	8.0	19	b.d.l	b.d.l	b.d.l	b.d.l	31	b.d.l	b.d.l	540	0.31
YO2	7.4	13	410	25	b.d.l	24	77	9.5	b.d.l	68	b.d.l	46	8.4	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	40	25	b.d.l	750	0.22
YO3	8.3	b.d.l	370	23	b.d.l	9.9	37	b.d.l	b.d.l	39	b.d.l	33	3.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	24	b.d.l	550	0.16
KS1	9.6	14	530	25	b.d.l	b.d.l	69	13	b.d.l	66	b.d.l	32	b.d.l	17	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	780	0.18
KS2	b.d.l	b.d.l	190	14	b.d.l	b.d.l	22	b.d.l	b.d.l	24	b.d.l	12	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	24	b.d.l	290	0.16
KS3	b.d.l	b.d.l	120	b.d.l	b.d.l	3.3	16	6.2	b.d.l	13	b.d.l	7.4	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	11	b.d.l	180	0.14
KS4	b.d.l	b.d.l	130	6.7	b.d.l	b.d.l	9.3	b.d.l	b.d.l	9.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	17	17	b.d.l	190	0.07
KB1	8.8	61	530	34	19	b.d.l	120	46	54	230	19	100	10	33	b.d.l	b.d.l	54	b.d.l	610	b.d.l	24	2000	0.41
KB2	6.1	59	360	27	9	b.d.l	38	b.d.l	9.0	260	29	92	8.8	23	b.d.l	b.d.l	44	b.d.l	170	b.d.l	b.d.l	1100	0.51
KB3	9.3	b.d.l	340	19	9	b.d.l	26	b.d.l	b.d.l	220	19	69	13	40	12	b.d.l	b.d.l	b.d.l	79	b.d.l	b.d.l	860	0.49
KB4	b.d.l	b.d.l	520	30	15	b.d.l	44	13	11	290	20	110	b.d.l	35	b.d.l	b.d.l	52	b.d.l	350	13	10	1500	0.46
KG1	b.d.l	22	330	11	b.d.l	b.d.l	43	13	11	200	21	53	8.0	33	16	b.d.l	b.d.l	b.d.l	150	b.d.l	b.d.l	910	0.46
KG2	7.6	30	390	14	b.d.l	b.d.l	89	35	14	190	18	71	11	34	25	b.d.l	b.d.l	b.d.l	130	b.d.l	b.d.l	1100	0.43
OO1	6.1	29	770	30	16	9.6	110	18	16	210	16	77	20	32	b.d.l	b.d.l	b.d.l	b.d.l	96	b.d.l	b.d.l	1500	0.29
OO2	b.d.l	27	530	28	12	15	95	14	b.d.l	130	b.d.l	56	b.d.l	34	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	940	0.29

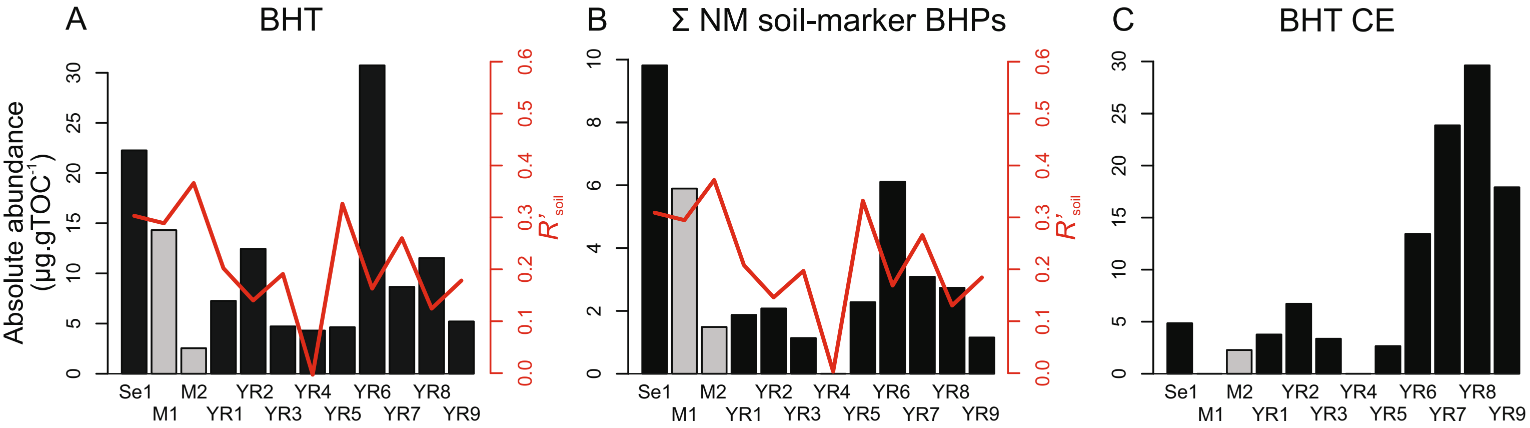
Supp. Table 3. Concentration of the individual and summed BHPs of the suspended particulate matter (µg.gPOC^{-1}). The R'_{soil} values are calculated [Eq. 1], based on the concentrations of the compounds indicated in bold. B.d.l. indicates that the concentration was below detection limit.

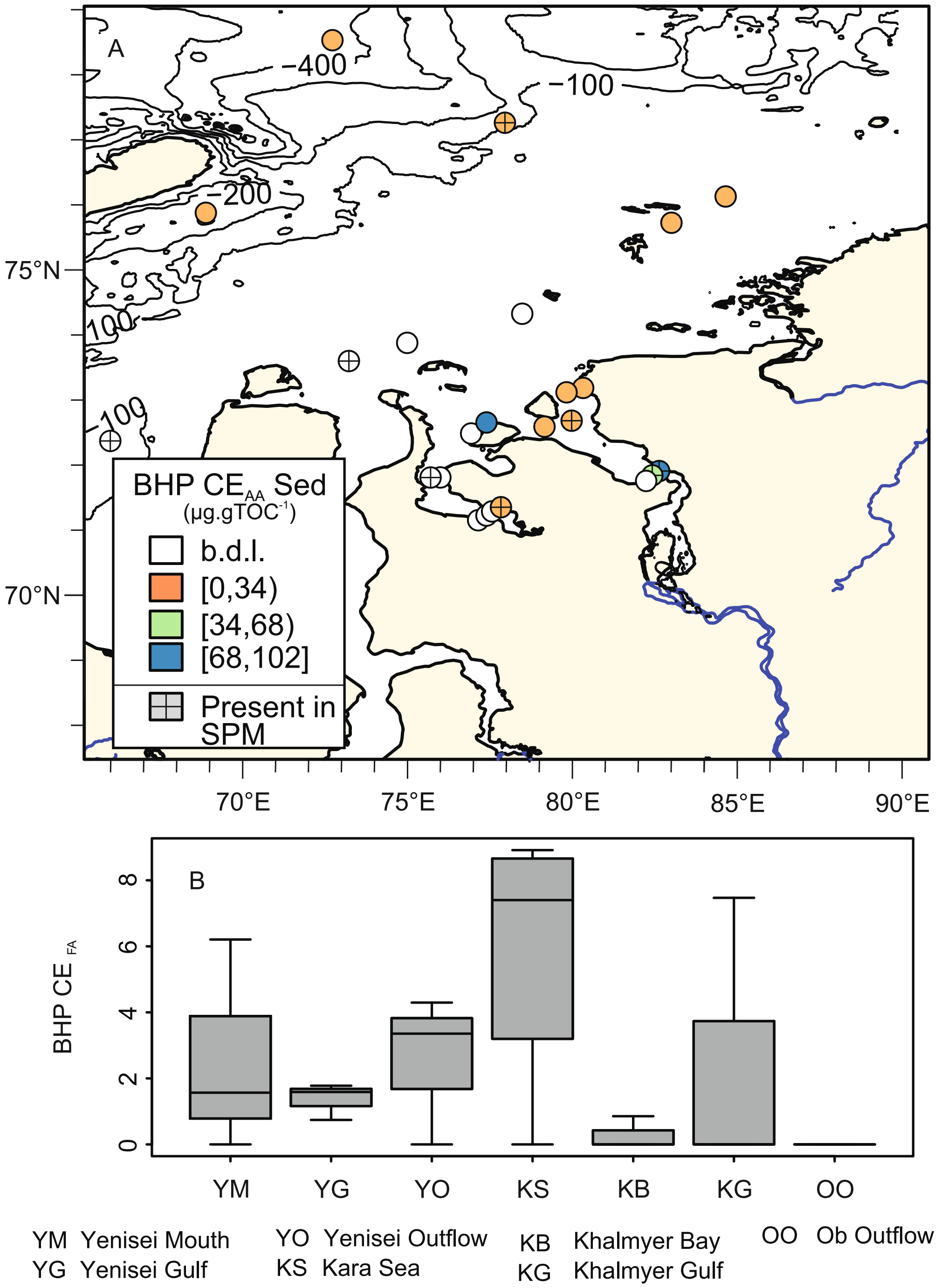
	Absolute abundance (µg.gTOC-1)																					
	Ii	IIId or IV d	**Id**	IId	Ih	IIIg or IVg	Ig	Ij	Ik	**Ia**	**IIa**	**Ib**	**IIb**	**Ic**	**IIc**	IIIn or IVn	In	IIn	Ie	Il	Im	Sum BHPs µg.gPOC^{-1}	R'_{soil}
m/z	*613*	*653*	*655*	*669*	*771*	*712*	*714*	*772*	*830*	*788*	*802*	*761*	*775*	*802*	*816*	*941*	*943*	*957*	*1002*	*1060*	*1118*		
Site																							
M1	b.d.l	b.d.l	14	1.8	b.d.l	b.d.l	1.3	b.d.l	b.d.l	3.0	b.d.l	2.9	1.1	b.d.l	b.d.l	3.0	5.7	2.5	b.d.l	b.d.l	b.d.l	35	0.29
M2	b.d.l	b.d.l	2.5	b.d.l	0.2	b.d.l	0.1	b.d.l	b.d.l	1.0	b.d.l	0.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.3	0.5	0.5	7.6	0.37
SR1	b.d.l	3.5	22	1.8	b.d.l	b.d.l	5.1	b.d.l	b.d.l	6.4	b.d.l	3.4	2.0	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	4.9	b.d.l	b.d.l	49	0.31
YR1	b.d.l	b.d.l	7.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.2	b.d.l	0.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	3.8	b.d.l	b.d.l	13	0.20
YR2	0.6	b.d.l	12	2.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.6	b.d.l	0.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	6.7	b.d.l	b.d.l	24	0.14
YR3	b.d.l	0.6	4.7	0.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.9	b.d.l	0.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	3.4	0.6	b.d.l	11	0.19
YR4	5.1	b.d.l	4.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	10	0.00
YR5	0.1	1.1	4.6	0.8	b.d.l	b.d.l	0.4	b.d.l	b.d.l	1.8	b.d.l	0.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.7	b.d.l	b.d.l	12	0.33
YR6	b.d.l	b.d.l	31	6.2	b.d.l	b.d.l	1.2	b.d.l	b.d.l	6.1	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	13	b.d.l	b.d.l	58	0.17
YR7	b.d.l	1.0	8.7	0.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.4	b.d.l	0.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	24	1.4	b.d.l	39	0.26
YR8	b.d.l	b.d.l	12	b.d.l	b.d.l	b.d.l	0.7	b.d.l	b.d.l	1.2	1.1	0.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	30	1.3	b.d.l	47	0.13
YR9	b.d.l	1.0	5.2	b.d.l	b.d.l	b.d.l	0.3	b.d.l	b.d.l	0.9	b.d.l	0.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	18	0.9	b.d.l	27	0.18
YM1	b.d.l	b.d.l	16	b.d.l	b.d.l	b.d.l	0.8	b.d.l	b.d.l	b.d.l	b.d.l	1.6	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	27	b.d.l	b.d.l	45	0.09
YM2	b.d.l	3.1	21	1.9	b.d.l	b.d.l	1.8	b.d.l	1.6	6.9	b.d.l	3.8	0.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	25	1.6	b.d.l	68	0.33
YM3	b.d.l	2.3	22	2.0	b.d.l	b.d.l	2.0	b.d.l	b.d.l	7.8	b.d.l	2.1	0.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	46	2.6	1.2	89	0.31
YM4	b.d.l	6.9	100	8.7	b.d.l	3.2	6.6	b.d.l	1.9	65	5.5	23	5.3	8.8	4.00	16	22	11	71	7.0	3.5	370	0.49
YM5	b.d.l	b.d.l	20	1.7	b.d.l	b.d.l	b.d.l	b.d.l	0.5	6.8	1.0	3.7	0.8	0.70	b.d.l	b.d.l	b.d.l	b.d.l	13	b.d.l	b.d.l	48	0.35
YG1	1.3	b.d.l	25	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	7.8	b.d.l	3.7	1.3	b.d.l	b.d.l	3.6	6.3	b.d.l	14	6.8	b.d.l	70	0.32
YG2a	b.d.l	b.d.l	7.4	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	3.3	b.d.l	1.0	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	9.4	b.d.l	b.d.l	21	0.37
YG2b	1.4	b.d.l	22	1.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	5.2	b.d.l	3.5	0.9	b.d.l	b.d.l	2.0	2.2	b.d.l	2.9	b.d.l	b.d.l	42	0.29
YG3	b.d.l	b.d.l	6.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	7.1	0.13
YG4	b.d.l	b.d.l	7.1	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.1	b.d.l	0.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	3.9	b.d.l	1.0	15	0.28
YG5	b.d.l	b.d.l	5.6	b.d.l	b.d.l	b.d.l	0.5	0.2	0.6	2.2	b.d.l	1.0	b.d.l	0.6	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	11	0.40
YG6	b.d.l	b.d.l	4	b.d.l	b.d.l	b.d.l	0.5	b.d.l	b.d.l	1.8	b.d.l	0.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.6	b.d.l	b.d.l	10	0.39
YG7	b.d.l	b.d.l	970	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	970	0.00
YG8	b.d.l	69.0	600	34	29	20	68	b.d.l	b.d.l	240	b.d.l	110	b.d.l	62	b.d.l	b.d.l	88	b.d.l	160	b.d.l	b.d.l	1500	0.41
YG9	b.d.l	b.d.l	5.30	0.2	b.d.l	b.d.l	0.5	b.d.l	b.d.l	0.7	b.d.l	0.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	7.4	0.21
YO1	b.d.l	b.d.l	0.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.5	0.00
YO2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	NA

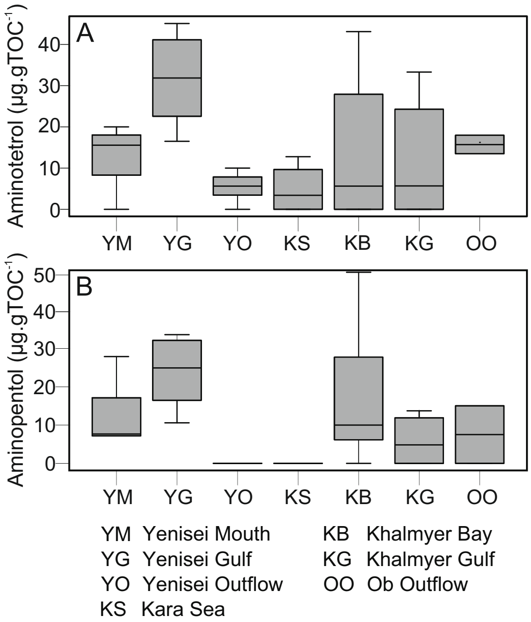
YO3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	NA
KS1	b.d.l	0.5	0.6	b.d.l	b.d.l	b.d.l	0.3	b.d.l	b.d.l	0.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.9	4.1	b.d.l	7.1	0.50
KS2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.4	b.d.l	0.6	NA
KS3	b.d.l	b.d.l	0.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.8	0.00
KS4	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.2	NA
KB1	b.d.l	5.3	38	1.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	13	b.d.l	4.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	18	b.d.l	b.d.l	81	0.32
KB2	b.d.l	15.0	47	4.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	25	b.d.l	6.7	b.d.l	2.70	b.d.l	b.d.l	b.d.l	b.d.l	43	b.d.l	b.d.l	140	0.42
KB3	b.d.l	16.0	99	4.0	b.d.l	b.d.l	6.4	b.d.l	b.d.l	24	b.d.l	9.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	56	b.d.l	b.d.l	220	0.25
KB4	b.d.l	31.0	230	17	b.d.l	19	17	b.d.l	b.d.l	150	b.d.l	41	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	330	53	7.9	900	0.45
KG1	b.d.l	b.d.l	35	b.d.l	b.d.l	b.d.l	5.2	2.1	b.d.l	7.1	b.d.l	4.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	13	17	b.d.l	84	0.25
KG2	b.d.l	b.d.l	34	b.d.l	b.d.l	b.d.l	4.3	b.d.l	b.d.l	15	b.d.l	5.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	7.7	b.d.l	b.d.l	67	0.38
OO1	b.d.l	b.d.l	1.6	b.d.l	b.d.l	b.d.l	0.5	0.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.9	0.2	b.d.l	3.4	0.00
OO2	b.d.l	b.d.l	0.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.3	0.00

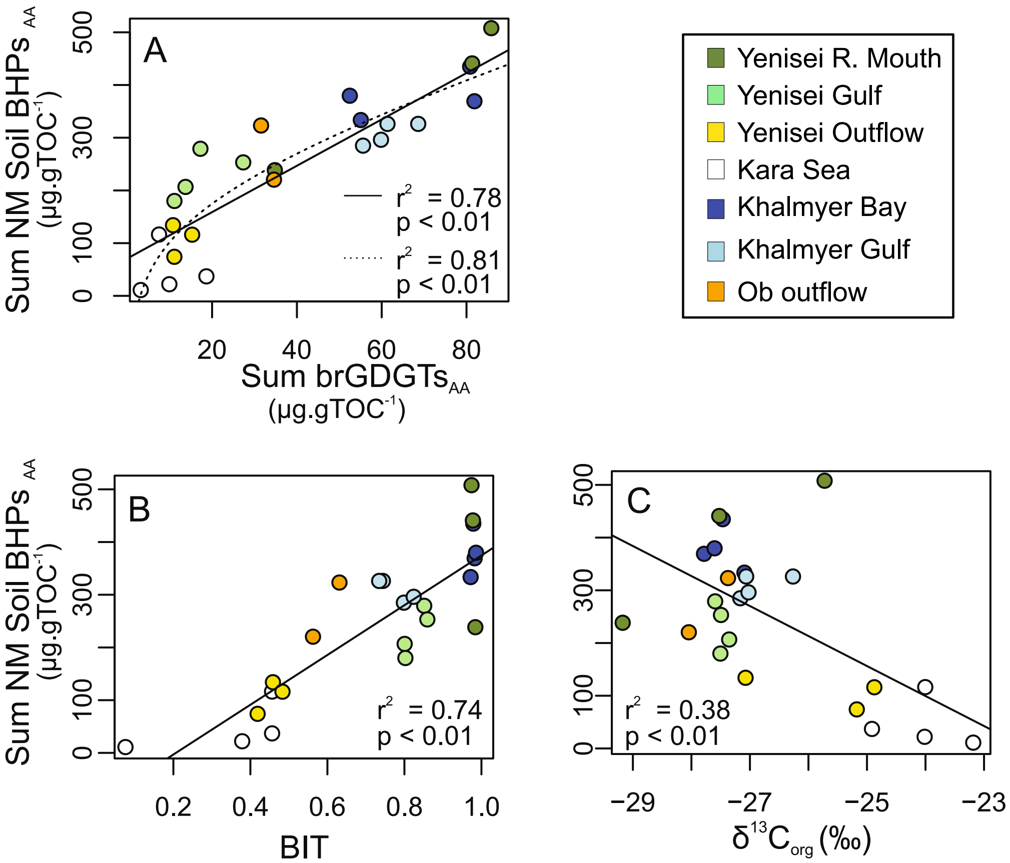

A
80°N
70°N
60°N
50°N
70°E
80°E
90°E
100°E
110°E
YR9
YR8
YR7
YR6
YR5
YR4
YR3
YR2
YR1
Yenisei
Angara
Lower Tunguska
MR2
MR1
Baikal
SR1
Selenga
■ Lowland Rivers
■ Mountain Rivers
■ Yenisei R. mouth
■ Yenisei Gulf
■ Yenisei Outflow
□ Kara Sea
■ Khalmyer Bay
■ Khalmyer Gulf
■ Ob outflow
B
-500
KS4
-400
-100
-100
-100
-300
-200
-200
KS2
Novaya Zemlya
-200
KS3
YO3
YO2
75°N
YO1
OO2
-100
YG5
OO1
YG2
YG4
YG3
Sibiryakov Is
KS1
-180
YG9
YG7
YG8
YG1
YG6
YM2
Oleniy Is
YM3
KG1
KB4
YM5
YM4
KB3
KG2
KB1
Khalmyer Bay
YM1
KB2
0
50
100
150 km
Yenisei R.
70°N
Ob River
65°E
70°E
75°E
80°E
85°E

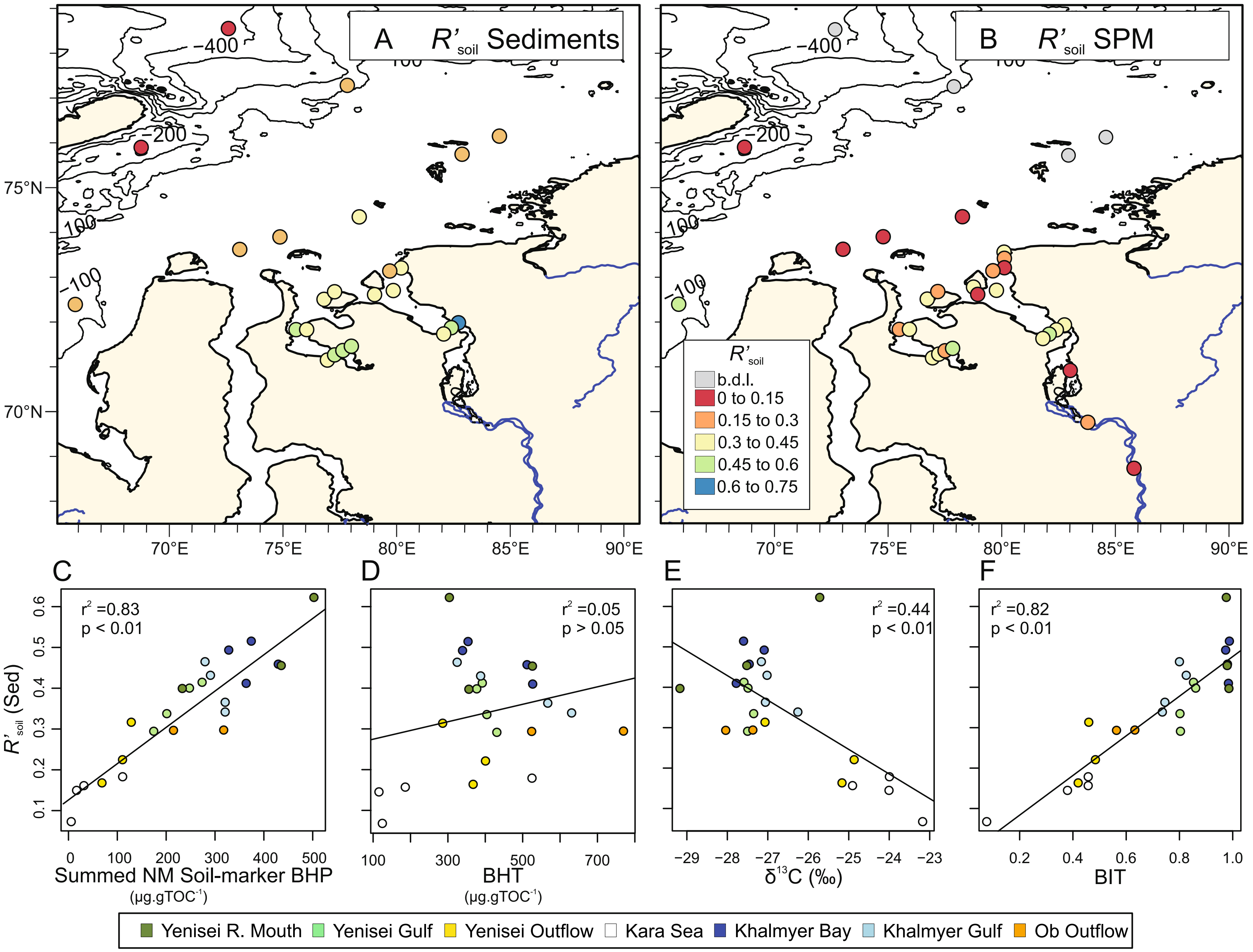

BHT
ΣSoil BHPs
BHP concentration (µg.gTOC-1)
Sediments
BHP FA
Sediments
BHP FA
SPM
A
B
C
D
E
F
0
200
400
600
800
100
300
500
0.2
0.3
0.4
0.5
0.6
0.7
0.1
0.0
0.8
1.0
YM
YG
YO
KS
KB
KG
OO
MR
YR
MR Mountain River
YR Yenisei River
YM Yenisei Mouth
YG Yenisei Gulf
YO Yenisei Outflow
KS Kara Sea
KB Khalmyer Bay
KG Khalmyer Gulf
OO Ob Outflow


A
BHT
B
Σ NM soil-marker BHPs
C
BHT CE
Absolute abundance (μg.gTOC-1)
R'soil
0
5
10
15
20
25
30
0
2
4
6
8
10
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Se1
M1
M2
YR1
YR2
YR3
YR4
YR5
YR6
YR7
YR8
YR9


A
−400
−100
−200
100
100
BHP CE$_{AA}$ Sed
(µg.gTOC^{-1})
b.d.l.
[0,34)
[34,68)
[68,102]
Present in SPM
75°N
70°N
70°E
75°E
80°E
85°E
90°E
B
BHP CE $_{FA}$
0
2
4
6
8
YM
YG
YO
KS
KB
KG
OO
YM Yenisei Mouth
YG Yenisei Gulf
YO Yenisei Outflow
KS Kara Sea
KB Khalmyer Bay
KG Khalmyer Gulf
OO Ob Outflow


A
Aminotetrol (µg.gTOC⁻¹)
0
10
20
30
40
YM
YG
YO
KS
KB
KG
OO
B
Aminopentol (µg.gTOC⁻¹)
0
10
20
30
40
50
YM
YG
YO
KS
KB
KG
OO
YM Yenisei Mouth
YG Yenisei Gulf
YO Yenisei Outflow
KS Kara Sea
KB Khalmyer Bay
KG Khalmyer Gulf
OO Ob Outflow

A
Sum NM Soil BHPs AA (µg.gTOC-1)
0
100
300
500
20
40
60
80
Sum brGDGTsAA (µg.gTOC-1)
r2 = 0.78
p < 0.01
r2 = 0.81
p < 0.01
Yenisei R. Mouth
Yenisei Gulf
Yenisei Outflow
Kara Sea
Khalmyer Bay
Khalmyer Gulf
Ob outflow
B
Sum NM Soil BHPs AA (µg.gTOC-1)
0
100
300
500
0.2
0.4
0.6
0.8
1.0
BIT
r2 = 0.74
p < 0.01
C
0
100
300
500
−29
−27
−25
−23
δ13Corg (‰)
r2 = 0.38
p < 0.01


A R'_{soil} Sediments
B R'_{soil} SPM
-400
-200
-100
100
75°N
70°N
70°E
75°E
80°E
85°E
90°E
R'_{soil}
b.d.l.
0 to 0.15
0.15 to 0.3
0.3 to 0.45
0.45 to 0.6
0.6 to 0.75
C
D
E
F
R'_{soil} (Sed)
r^2 =0.83
$p < 0.01$
r^2 =0.05
$p > 0.05$
r^2 =0.44
$p < 0.01$
r^2 =0.82
$p < 0.01$
0.1
0.2
0.3
0.4
0.5
0.6
0
100
200
300
400
500
Summed NM Soil-marker BHP
(µg.gTOC^{-1})
100
300
500
700
BHT
(µg.gTOC^{-1})
−29
−28
−27
−26
−25
−24
−23
δ^{13}C (‰)
0.2
0.4
0.6
0.8
1.0
BIT
Yenisei R. Mouth
Yenisei Gulf
Yenisei Outflow
Kara Sea
Khalmyer Bay
Khalmyer Gulf
Ob Outflow