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Pan-Arctic Patterns in Black Carbon Sources and Fluvial Discharges Deduced From Radiocarbon and PAH Source Apportionment Markers In Estuarine Surface Sediments

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Pan-Arctic patterns in black carbon sources and fluvial discharges deduced from radiocarbon and PAH source apportionment markers in estuarine surface sediments

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[1] A pan-arctic geospatial picture of black carbon (BC) characteristics was obtained from the seven largest arctic rivers by combining with molecular combustion markers (polycyclic aromatic hydrocarbons) and radiocarbon (^{14}C) analysis. The results suggested that the contribution from modern biomass burning to BC ranged from low in the Yukon (8%) and Lena (5%) Rivers to high in the Yenisey River (88%). The Mackenzie River contributed almost half of the total arctic fluvial BC export of 202 kton a^{-1} (kton = 10^9 g), with the five Russian-Arctic rivers contributing 10–36 kton a^{-1} each. The ^{14}C-based source estimate of fluvially exported BC to the Arctic Ocean, weighted by the riverine BC fluxes, amount to about 20% from vegetation/biofuel burning and 80% from ^{14}C-extinct sources such as fossil fuel combustion and relict BC in uplifted source rocks. Combining these pan-arctic data with available estimates of BC export from other rivers gave a revised estimate of global riverine BC export flux of 26×10^3 kton a^{-1}. This is twice higher than a single previous estimate and confirms that river export of BC is a more important pathway of BC to the oceans than direct atmospheric deposition.

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1. Introduction

[2] Black carbon (BC) particles are released from incomplete combustion of organic matter and are believed to have a large impact on both regional and global climate through their effect on Earth's radiative balance [e.g., *Charlson et al.*, 1991; *Jacobson*, 2001; *Lelieveld et al.*, 2001; *Andreae et al.*, 2005]. However, the current level of understanding of BC is still "Very Low" [*Solomon et al.*, 2007]. BC further plays an important but poorly constrained role in the global biogeospheric carbon cycle [e.g., *Goldberg*, 1985; *Kuhlbusch and Crutzen*, 1995; *Suman et al.*, 1997; *Druffel*, 2004] as recalcitrance gives it a high preservation potential in sediments [e.g., *Smith et al.*, 1973; *Goldberg*, 1985; *Gustafsson and Gschwend*, 1998; *Masiello and Druffel*, 1998; *Dickens et al.*, 2004] and yields long residence times in soils [e.g., *Skjemstad et al.*, 1996; *Glaser and Amelung*, 2003].

[3] BC may be classified based on whether it originates from fossil fuel combustion or vegetation fires and biofuel combustion. This distinction is important as these two BC source classes have different impacts on the global carbon cycle. Sequestration of biogenic carbon as BC is a direct sink of carbon from the rapidly cycling atmosphere-biosphere reservoirs whereas burial of petrogenic/fossil BC is simply a conversion of one form of geological carbon to another. A second important BC classification is the distinction between soot-BC and char-BC. BC particles formed in the combustion vapor phase (soot-BC) is generally of sub-micron size [e.g., *Ishiguro et al.*, 1997; *Schmidt and Noack*, 2000; *Gustafsson et al.*, 2001; *Stanmore et al.*, 2001] and subject to long-range atmospheric transport, whereas the partly burned residue of original, often solid, fuel phase left after combustion (char-BC) is much larger and thus less prone to atmospheric transport [e.g., *Hamins*, 1993; *Kuhlbusch and Crutzen*, 1995; *Fernandes et al.*, 2003]. It has recently been demonstrated that soot-BC is more resistant to oxidation than char-BC, suggesting that soot-BC is also more environmentally recalcitrant [*Nguyen et al.*, 2004; *Elmquist et al.*, 2006].

[4] The pan-arctic landmass may be an important source region for coastal export of BC due to a combination of large and frequent vegetation fires and the characteristics of the regional atmospheric transport. Nevertheless, the river export dynamics of BC in the Arctic region remain poorly understood. Natural wildfires in the Arctic region, especially in the Far East Siberia, are common in the summer

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due to specific climate and vegetation characteristics [e.g., *Davidenko and Eritsov*, 2003] (see www.fire.uni-freiburg. de). For instance, the forest fires in Russia in 1998 are estimated to have contributed about 14–20% of the average global carbon emissions from forest fires [*Conard et al.*, 2002]. In addition, air pollution produced at lower latitudes is frequently transported into the Arctic region. During the winter months, when the prevailing high-pressure cell in Siberia produces stable weather conditions, the air is transported from Europe and South Asia into the Arctic, whereas at the same time it is transported out of the Arctic region into North America [e.g., *Rahn*, 1981; *Barrie*, 1986; *Hansen et al.*, 1997; *Polissar et al.*, 1999; *Macdonald et al.*, 2000]. While poorly constrained, riverborne transport is believed to be a globally significant conduit for large-scale BC transport from land to ocean [e.g., *Suman et al.*, 1997; *Kuhlbusch*, 1998; *Masiello and Druffel*, 2001; *Mitra et al.*, 2002]. The many large Arctic rivers draining onto the world's largest continental shelf (the Arctic) may play a particularly important role in the large-scale fluvial BC export.

[5] There are currently debate around several significant aspects of the BC cycle in the Arctic, including the BC contribution to total carbon in both soil and sediment as well as the geospatial trends in BC sources. One study conducted in Siberian Scots pine forest did not detect BC as a major fraction of the soil OC pool [*Czimczik et al.*, 2003]. However, it should be noted that the wet chemical oxidation BC method used in that soil study may only detect the char-BC and miss the soot-BC [e.g., *Elmquist et al.*, 2006; *Hammes et al.*, 2007]. In contrast, *Guo et al.* [2004] found that the soot-BC fraction, isolated with the chemothermal oxidation approach [*Gustafsson et al.*, 1997, 2001; *Hammes et al.*, 2007], which quantifies ambient soot-BC but less of char–BC, comprised 1-17% of the terrestrial OC deposited off the Great Russian Arctic Rivers (GRARs), with drainage basins covering a large part of the Eurasian Arctic landmass [*Guo et al.*, 2004]. Furthermore, *Guo et al.* [2004] found a geospatial trend of consistently increasing ^{14}C age of sedimentary organic carbon (SOC) from west (Ob) to east (Kolyma) that was well correlated with the BC:SOC ratio. However, their study was unable to directly test whether the high reservoir age of the SOC was due to ^{14}C-depleted BC as they did not measure the radiocarbon composition of the BC. Finally, there is also a debate in the literature regarding the BC sources in the Arctic region and different atmospheric modeling experiments have led to discrepant results, especially concerning the extent of the south Asian influence [e.g., *Koch and Hansen*, 2005; *Stohl*, 2006].

[6] The objectives of the present study were to (1) elucidate the geospatial patterns of the soot-BC contribution to the composition and age of SOC in Arctic shelf estuaries, (2) elucidate the large-scale features of soot-BC export fluxes from the pan-arctic rivers and (3) to deduce the relative contributions of fossil versus biomass burning to soot-BC in the Arctic. To this end, we use the seven largest Arctic Rivers to provide an integrated signal of the soot-BC deposited in their respective drainage basins and subjected to fluvial export to the Arctic Ocean. The BC isolated with a broadly applied and tested chemothermal oxidation method

is dominated by recalcitrant soot-BC that resembles atmospherically transported BC [e.g., *Gustafsson et al.*, 1997, 2001; *Reddy et al.*, 2002; *Elmquist et al.*, 2006; *Hammes et al.*, 2007; *Zencak et al.*, 2007a]. Further, the relative abundance of different combustion-derived PAHs was utilized to shed light on the relative contribution of different combustion sources. A combination of these source-diagnostic molecular combustion markers and radiocarbon is used to apportion the soot-BC between biomass burning (modern radiocarbon signal) and fossil fuel combustion (extinct radiocarbon signal).

2. Methods

2.1. Study Area

[7] The pan-arctic study area includes five Siberian and two North American estuaries (Figure 1). The Eurasian study sites stretch over a climosequence with decreasing annual precipitation and surface air temperatures when moving from west to east across northern Siberia [*AMAP Assessment Report: Arctic Pollution Issues*, 1998]. Because of meteorological conditions and mountainous orology, the Lena basin acts as a transition zone between Atlantic and Pacific influence on the water budget over northern Eurasia [*Barrry and Serreze*, 2000; *Semiletov et al.*, 2000]. On the western side of the Lena, vapor from the nortern Atlantic Ocean is transported over Eurasia leading to decreasing annual precipitation further away from the Ocean (600–800 mm a^{-1} in the northwest to 300 mm a^{-1} nearer the mid-lower Lena). On the eastern side of the Lena, the precipitation increases again due to the humid air masses from the North Pacific. Therefore the Eurasian study area can be divided into two regions predominantly influenced by two separate atmospheric circulation patterns: the area located to the west of the Lena watershed, where BC and PAH are provided by the Atlantic air mass, while the area east of the Lena watershed is under the Pacific influence. Both regions are naturally influenced by local vegetation burning.

[8] The average summer temperature is roughly the same throughout the studied area (+7°C to +9°C), whereas the average winter temperature is about −20°C in West Siberia and North American Arctic, but reaches below −40°C in the Far East Siberia. The Arctic Rivers may flow through non-frozen ground as well as through discontinuous or continuous permafrost depending on their locations (see below). The rivers studied here that have their headwaters south of the Arctic region (defined as the area north of the 10°C July isotherm) include the Ob, Yenisey, Lena, Yukon and Mackenzie Rivers.

[9] The vegetation also varies along the Siberian transect [http://www.terranorte.iki.rssi.ru]. The Ob flows through mostly taiga (boreal forest; 40% of total area), bogs and marshes (27%) at lower latitudes and a tundra landscape (52%) at higher latitudes. The upper Yenisey landscape mostly consists of deciduous shrubs (42%) and then dominated by tundra vegetation (79%) further to the north. Most of the Siberian wildfires occur in the southern Far East Siberia and is thus outside the studied drainage basins (Figure 1). Carbonaceous aerosols from forest fires in these areas may be atmospherically transported northward and
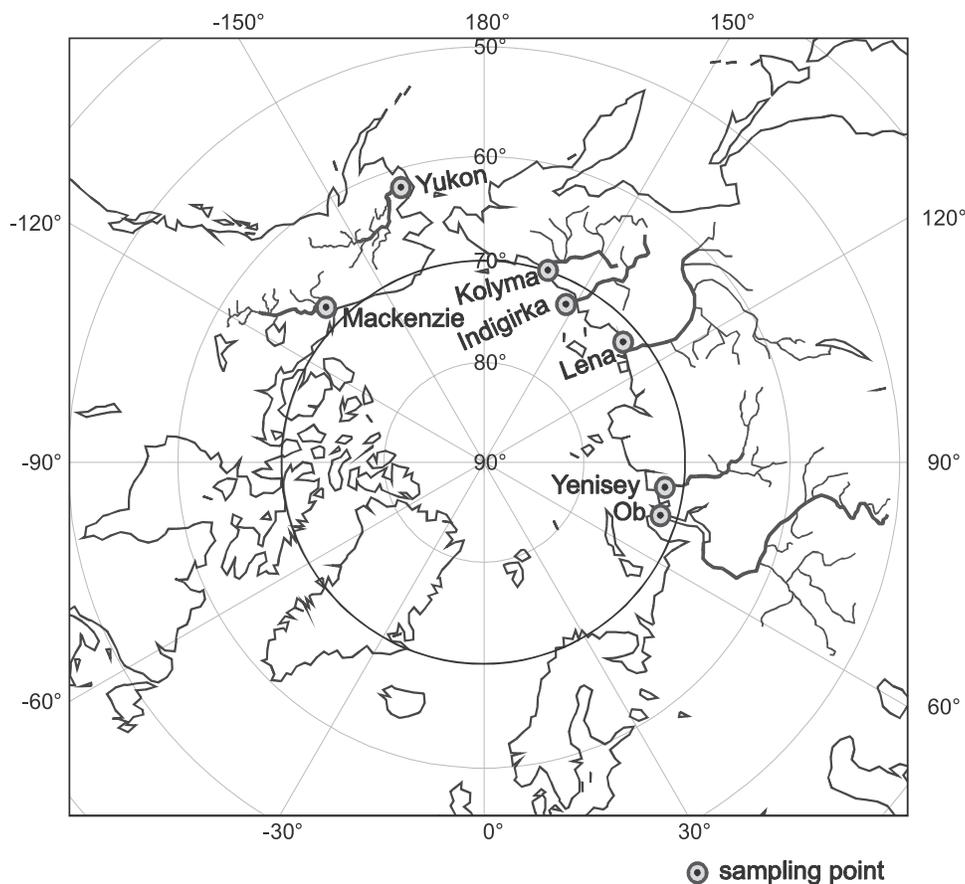
Figure 1. Map of pan-arctic sampling locations in or near the rivers Ob, Yenisey, Lena, Indigirka and Kolyma in Siberia, the Yukon in Alaska and the Mackenzie in northwestern Canada.

thus deposit in the Kolyma and Indigirka watersheds. The Lena flows through a landscape mostly consisting of taiga (48%) and tundra vegetation (26%), whereas the drainage basins of Indigirka and Kolyma overwhelmingly consist of taiga and tundra. The North American Cordillera rivers flow through boreal forest at lower latitudes and tussock tundra at higher latitudes (e.g., *Goni et al.* [2005] and references therein).

2.2. Sampling and Sediment Handling

[10] The locations of the five Siberian river mouths span over 4000 km along the Eurasian rim of the Arctic Ocean (Figure 1). Surface sediment samples of the Lena, Indigirka and Kolyma estuaries were collected using a van Veen grab sampler (dimensions 20 × 30 cm), a light weight sampler designed to take large samples in soft bottoms [e.g., *Riddle*, 1989], during the R/V Ivan Kireev September 2004 cruise in the East-Siberian and Laptev Seas. Typically, kg sized sediment samples were collected to have enough material for compound-specific radiocarbon analysis to be performed in parallel projects. For this reason, sediments from four locations were combined for the Indigirka estuarine sample to provide a sufficiently large sample (detailed in Table 1 footnote). Surface sediment samples of the Ob and Yenisey estuaries were similarly obtained during the R/V Ivan

Kireev September 2005 cruise in the Kara Sea. The sediments were all taken from a central location of the river plume. The pooled Indigirka sediments were obtained from 8–11 m water depths whereas the samples from the four other rivers were obtained from below 1–2 m water depths using a small boat deployed from the mother ship. Detailed sampling locations and bulk organic matter sediment characteristics are listed in Table 1. In all cases sediment integrity was first visually inspected for undisturbed sediment-water interface before approximately 0–2 cm was carefully sub sampled manually from the van Veen sampler into pre-combusted glass jars; the rest was discarded. The samples were initially kept frozen at −20°C and then dried in a oven at 60°C followed by homogenization into a fine powder with an automatic ball grinder.

[11] Sediments from the Mackenzie and Yukon rivers were collected and sub sampled from the riverbed about 5–10 m away from the riverbank using a stainless steel hand shovel during June and July 2004, respectively, as described elsewhere [*Guo et al.*, 2007]. The Mackenzie River sediment was collected near the Arctic Red River (Canada) and the Yukon River sample was obtained near the town of Pilot Station (Alaska, USA) with exact location listed in Table 1. Sediment samples were stored frozen and then freeze dried for further analysis.

Table 1. Geochemical and Geospatial Characteristics of the Studied Surface Sediments of Seven Pan-Arctic Rivers

	Ob	Yenisey	Lena	Indigirka	Kolyma	Yukon	Mackenzie
Latitude; Longitude	72°65′N/ 73°41′E	72°61′N/ 79°86′E	71°96′N/ 129°54′E	71°02′N/ 150°46′E[a]	70°00′N/ 163°70′E	61°56′N/ 162°53′W	67°26′N/ 130°45′W
Geological and physiographic regions (AMAP)	West Siberian Lowlands	West Siberian Lowlands	Central Siberian Upland	East Siberian Highlands	East Siberian Highlands	North American Cordillera	North American Cordillera
SOC (mg g^{-1})	9.2 ± 0.2	19.4 ± 0.3	5.7 ± 0.3	18.1 ± 2.5	19.2 ± 0.8	12.4 ± 0.5	20.2 ± 0.3
Soot-BC (mg g^{-1})	0.47 ± 0.01	1.2 ± 0.03	0.17 ± 0.07	1.4 ± 0.5	1.5 ± 0.1	1.2 ± 0.08	1.0 ± 0.5
f_M ^{14}C-SOC[b]	0.691 ± 0.003	0.831 ± 0.003	0.395 ± 0.003	0.476 ± 0.003	0.501 ± 0.003	0.576 ± 0.003	0.371 ± 0.003
f_M ^{14}C-BC	0.340 ± 0.002	1.051 ± 0.003	0.064 ± 0.001	0.332 ± 0.002	0.370 ± 0.003	0.095 ± 0.001	0.185 ± 0.003
ΣPAH (ng g^{-1})[c]	23.8	129	79.6	84.6	91.1	85.0	454
ΣMP/P[d]	1.02	0.71	0.77	1.24	1.22	1.57	2.09
Flu/(Flu+Pyr)[e]	0.63	0.60	0.43	0.47	0.48	0.32	0.32
IP/(IP+BgP)[f]	0.53	0.51	0.35	0.36	0.36	0.18	0.17
1,7-DMP/(1,7-DMP+2,6-DMP)[g]	0.66	0.60	0.42	0.71	0.70	0.74	0.71

[a]The bulk sample represented combined samples taken between 71°02′–72°06′N/150°46′–152°60′E.

[b]f_M – fraction modern where the definition is described elsewhere [*Stuiver and Polach*, 1977; *McNichol et al.*, 1992] and the uncertainty represents the statistical error calculated using the number of counts measured from each individual AMS target.

[c]Including phenanthrene, anthracene, methyl-phenanthrenes, dimethyl-phenanthrenes, fluoranthene, pyrene, methyl-pyrenes, retene, benzo(*ghi*)fluoranthene, cyclo(*cd*)pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*e*)pyrene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, benzo(*ghi*)perylene and coronene.

[d]Methylphenanthrenes to phenanthrene.

[e]Fluoranthene to fluoranthene and pyrene.

[f]Indeno(1,2,3-*cd*)pyrene to indeno(1,2,3-*cd*)pyrene and benzo(*ghi*)perylene.

[g]1,7-dimethylphenanthrene to 1,7-dimethylphenanthrene and 2,6-dimethylphenanthrene.

2.3. Quantification of Soot-BC and SOC

[12] Soot black carbon was analyzed in triplicates with the chemothermal oxidation (CTO) method that has been described and tested in detail elsewhere [e.g., *Gustafsson et al.*, 1997, 2001; *Reddy et al.*, 2002; *Elmquist et al.*, 2004; *Hammes et al.*, 2007]. Briefly, about 10 mg of dry, ground sediment was weighed into Ag capsules (5 × 9 mm, Säntis Analytical AB, Uppsala, Sweden) and placed in a homebuilt aluminum boat. The boat was put into a tube furnace and combusted at 375°C for 18 h under an active airflow (200 mL min^{-1}). When the sample had cooled off, small volumes of 1 M HCl (25 + 50 μL) were added to the sample to remove carbonates. The sample was then dried (60°C) and the residual carbon, defined as soot-BC, was then analyzed with an isotope ratio mass spectrometer (Europa Hydra 20/20, Stable Isotope Facility, UC Davis, USA). The SOC pool was measured in the same way as the soot-BC pool without the 375°C treatment.

2.4. Radiocarbon Measurements of SOC and Soot-BC

[13] For the SOC radiocarbon measurements, about $1-2$ g of dry, fine-ground sediment was weighed into crucibles and about 2 mL of 1M HCl was added. The acid was allowed to react with any carbonates in the sediment for at least 60 min and dried (60°C). To harvest enough carbon for the soot-BC radiocarbon measurements, four-six identical runs, exact number depending on BC concentration, of 10 mg sub-portions of sediments were combusted (375°C, 18 h). The combusted sediment portions were pooled together, put into a pre-combusted glass scintillation vial and about 1 mL of MilliQ water was added to each sample. The scintillation vials were then placed for 48 h inside a dessicator with a beaker containing concentrated HCl (12 M). The SOC and soot-BC samples were dried (60°C), re-ground and sent to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution (USA) for radiocar-

bon content analyses following a previously described protocol [e.g., *McNichol et al.*, 1992; *Pearson et al.*, 1998].

2.5. Black Carbon Source Apportionment With Radiocarbon

[14] Technical definitions of radiocarbon metric has been described elsewhere [e.g., *Stuiver and Polach*, 1977; *McNichol et al.*, 1992; *Pearson et al.*, 1998; *Zencak et al.*, 2007b]. Radiocarbon values in this study are reported as fraction modern (f_M), according to the following equation:

$$f_{M(sample)} = \frac{S - B}{M - B} \times \left(\frac{1 - \frac{25}{1000}}{1 + \frac{\delta^{13}C}{1000}} \right)^2 \qquad (1)$$

where S, B and M represent the ^{14}C/^{12}C ratios of the sample, the blank and the modern reference, respectively. The ^{14}C/^{12}C ratio of the "modern reference" is defined as 95% of the radiocarbon concentration of NBS Oxalic Acid I in AD 1950 normalized to δ^{13}C$_{VPDB}$ of -19‰ (blank corrected). Results were calculated using the internationally accepted modern ^{14}C/^{12}C ratio of $1.176 \pm 0.010 \pm 10^{-12}$ [*Stuiver and Polach*, 1977]. The second term on the right-hand side of the equation corrects for ^{14}C/^{12}C isotope fractionation that may have occurred either in nature or during sample preparation. Radiocarbon data used for dating measurements are therefore by convention corrected to the ratio they would have if they had an original δ^{13}C of -25‰ in order to ensure comparability between different samples [*Stuiver and Polach*, 1977].

[15] The f_M signal in the atmosphere almost doubled in the 1950s and 1960s due to extensive aboveground nuclear weapon testing, but the radiogenic signal has since then decreased primarily due to dispersal through the biogeosphere and due to increased input of CO_2 from fossil fuel combustion [e.g., *Levin et al.*, 1985; *Levin and Kromer*, 1997].

[16] A simple isotopic mass balance equation was used to derive the modern (i.e., contemporary) biomass fraction in the measured samples using equation (2).

$$f_{M,SOC;BC} = (f_{M,biomass}) \times (F_{biomass}) + (f_{M,fossil}) \times (1 - F_{biomass})$$
(2)

where $f_{M,SOC;BC}$ is the measured ^{14}C signature of the SOC or the soot-BC fraction, $f_{M,biomass}$ is the characteristic ^{14}C signature of modern biomass material ($f_{M,biomass}$ = 1.23), $f_{M,fossil}$ is the characteristic ^{14}C signature of fossil material ($f_{M,fossil}$ = 0) and $F_{biomass}$ is the fraction of the SOC or the soot-BC isolate that is derived from modern biomass combustion. It is not straightforward what $f_{M,biomass}$ end-member value to select for at least two reasons: (1) The f_M of atmospheric CO_2, used in photosynthesis, has varied substantially over the life-span of many trees standing today [e.g., *Levin et al.*, 2003] and (2) the integrated f_M of the biomass contributing to the BC in the Arctic is unknown.

[17] The $f_{M,biomass}$ value used in this study (1.23) is the average value for wood logged in the 1990s [*Klinedinst and Currie*, 1999]) and was recently found to be consistent with the $f_{M,biomass}$ values obtained both in the particulate emissions from domestic wood-fuel burning in Sweden ($f_{M,biomass}$ = 1.23) [*Zencak et al.*, 2007a, 2007b] and in ambient wood combustion derived aerosols in Switzerland ($f_{M,biomass}$ = 1.24) [*Szidat et al.*, 2007]. An $f_{M,biomass}$ of 1.23 therefore seems reasonable as an end-member value of burning of slow-growing arctic vegetation and long-range atmospheric transport of wood-fuel combustion into the Arctic.

[18] There are several potentially important sources of the BC found in arctic surface sediments contributing to the integrated BC radiocarbon signal: (1) combustion of fossil fuel (extinct radiocarbon), (2) combustion of recently synthesized biomass/vegetation during fires (modern radiocarbon), (3) combustion of semi-relict biomass as in peat (intermediate radiocarbon signal depending on age) or (4) erosion of geologically recycled fossil BC in uplifted rocks. When moving around the pan-arctic geospatially distributed estuarine systems, the contribution of anthropogenic burning of fossil fuels varies along the way. It is obviously not possible to quantitatively apportion between these four sources based solely on equation (2). Radiocarbon is able to provide information on the relative contribution from combined source classes of modern versus extinct signatures. In this study, radiocarbon is accompanied with similarly combustion-derived polycyclic aromatic hydrocarbons (PAHs) as source-diagnostic molecular combustion markers.

2.6. Quantification of PAHs

[19] PAHs were analyzed by well-established methods commonly used in our laboratory [*Bandh et al.*, 1996; *Elmquist et al.*, 2007]. Wet sediments (ca. 15–90 g) were weighed into cellulose extraction thimbles (Whatman Inc., Florham Park, NJ, USA) and spiked with an internal standard consisting of 5 deuterated PAHs (D_{10}-phenanthrene, D_{10}-fluoranthene, D_{10}-pyrene, D_{12}-benzo[a]pyrene, D_{12}-benzo[ghi]perylene; Ultra Scientific Inc.). The samples were extracted in 100–150 mL Soxhlet apparati with toluene (glass-distilled quality, Burdick & Jackson, Fluka Chemie

AG, Buchs, Switzerland) for 24 h. The extracts were then reduced in volume by rotary evaporation and further purified by chromatography on silica gel (deactivated with 10% H_2O) in a column of 3.0 cm height and 0.5 cm I.D. The samples were eluted with 15 mL *n*-hexane (glass-distilled quality, Burdick & Jackson, Fluka Chemie AG). Thereafter, the *n*-hexane extracts were reduced with copper to remove any elemental sulfur and treated with a dimethylformamide-pentane partitioning procedure according to the protocol described by *Mandalakis et al.* [2004] to remove aliphatic components. The extracts were further cleaned with a second column (silica gel deactivated with 10% H_2O, height 3.0 cm, I.D. 0.5 cm), which was topped with sodium sulfate to remove any water residues and eluted with 15 mL of *n*-hexane.

[20] The extracts were finally concentrated and spiked with the recovery standard D_{12}-chrysene and injected onto an 8060 GC interfaced to a MD 800 mass spectrometer (Fisons Instruments, Manchester, UK) operating in selected ion monitoring mode. The analytes were separated on a PTE-5 (Supelco Inc., Bellefonte, PA, USA) capillary column (5% - diphenyl-dimethylpolysiloxane, length 30 m, I.D. 0.25 mm, film thickness 0.25 μm) and the oven was temperature programmed from 70°C (2 min isothermal) to 200°C at 20°C min^{-1} and to 310°C at 5°C min^{-1} (15 min isothermal).

2.7. PAHs as Source-Diagnostic Molecular Combustion Markers

[21] The relative abundances of many different polycyclic aromatic hydrocarbons (PAH), co-formed with BC during incomplete combustion, also hold useful information to differentiate among different sources (i.e., a molecular source fingerprint). Source-diagnostic PAH ratios used in this study are summarized in Table 1. The methylphenan-threnes to phenanthrene (ΣMP/P) and the fluoranthene to fluoranthene plus pyrene (Flu/(Flu + Pyr)) ratios are used to distinguish between petrogenic (ΣMP/P >5 and Flu/(Flu + Pyr) <0.5) and pyrogenic sources (0.4 < ΣMP/P < 0.7 and Flu/(Flu + Pyr) > 0.5) [e.g., *Youngblood and Blumer*, 1975; *Gustafsson and Gschwend*, 1997; *Yunker et al.*, 2002]. To distinguish between wood and fossil fuel combustion we used indeno(1,2,3-*cd*)pyrene to indeno(1,2,3-*cd*)pyrene plus benzo(*ghi*)perylene (IP/(IP + B*g*P)) and 1,7-dimethylphe-nanthrene to 1,7- plus 2,6-dimethylphenanthrene (1,7/(1,7 + 2,6-DMP)) ratios [*Benner et al.*, 1995; *Yunker et al.*, 2002]. For the IP/(IP + B*g*P) ratio, a value below 0.20 indicate petroleum source whereas combustion of wood and coal, and grass fires usually have values over 0.50 although the transition line between petroleum and combustion for this ratio is not well established [*Yunker et al.*, 2002]. For the 1,7/(1,7 + 2,6-DMP) ratio, values ≤0.45 indicate vehicle emissions, values of 0.65–0.68 may come from coal burning, and values ≥0.90 are characteristic of softwood combustion (e.g., spruce, pine and larch) [*Benner et al.*, 1995; *Yunker et al.*, 2002].

3. Results and Discussion

3.1. Ob and Yenisey in the West Siberian Lowlands

[22] Both the Ob and Yenisey Rivers have their head-waters south of the Arctic region and flow mainly on non-

Table 2. Estimated Annual Fluvial Fluxes of Soot-BC From Arctic Rivers

	Ob	Yenisey	Lena	Indigirka	Kolyma	Yukon	Mackenzie	TOTAL
Water discharge (km^3 a^{-1})	404[a]	620[a]	523[a]	54.2[a]	122[a]	200[b]	330[a]	2253
POC flux (kton a^{-1})	360[a]	170[a]	1200[a]	170[a]	310[a]	12[b]	2100[a]	4322
Soot-BC export (kton a^{-1})	18	10	36	13	24	1.1	99	202
Soot-BC yield (kg a^{-1} km^{-2})	7.2	3.9	15	36	36	1.3	56	-
Modern soot-BC export (kton a^{-1})	5.2	9.0	1.9	3.5	7.3	0.086	15	42
Fossil soot-BC export (kton a^{-1})	13	1.3	34	9.3	16	1.0	84	159

[a]Data from [*Stein and Macdonald*, 2004].
[b]Data from [*Guo and Macdonald*, 2006].

permafrost ground (Figure 1). Furthermore, the Yenisey is one of the world's largest rivers with a water discharge of over 600 km^3 a^{-1} (Table 2). The soot-BC concentrations were 0.47 and 1.2 mg/gdw in the surface sediments of the estuaries of Ob and Yenisey (Table 1), respectively, yielding a BC:SOC ratio of 0.05 for the Ob and 0.06 for the Yenisey.

[23] The soot-BC flux from each river was also estimated. It is advantageous to compare fluxes rather than concentrations of minor components such as BC as the former is not affected by varying inputs of major matrix components. The soot-BC flux was estimated by multiplying the surface sediment BC:SOC ratio (calculated from Table 1) with the reported POC flux of each river [*Stein and Macdonald*, 2004; *Guo and Macdonald*, 2006]. This is a similar approach as employed for fluvial fluxes of terrestrial OC by *Burdidge* [2005]. Since arctic river DOC has been shown to be transported nearly conservatively with salinity during estuarine mixing [*Cauwet and Sidorov*, 1996; *Andersson*, 2002], we assumed that river POC was more likely than DOC a carrier of the river-borne BC that accumulates in the estuarine sediments [e.g., *Stein and Macdonald*, 2004; *Guo et al.*, 2007]. Further, hydrophobic BC particles exist overwhelmingly as grape-like clusters of supramicron sizes [e.g., *Hamins*, 1993; *Gustafsson et al.*, 2001], which are thus likely to reside as part of POC aggregates, as defined by one-micron-sized filter cut offs. The estimated fluvial export flux of soot-BC was 18 kton a^{-1} for the Ob and only 10 kton a^{-1} for the Yenisey (Figure 2c and Table 2). This translated into drainage-basin normalized fluvial export yields of 7 and 4 kg km^{-2} a^{-1}, respectively, which are the lowest yields among the five Great Siberian Rivers (Table 2).

[24] The SOC in these two estuaries had the highest contribution from modern biomass among all seven analyzed surface sediments, with 58% for the Ob and 69% for the Yenisey (Figure 2b and Table 1). The relatively younger SOC from this West Siberian Lowland basin is consistent with the fact that these two rivers also drain substantial sub-Arctic and temperate areas [*Brown et al.*, 1997; *Guo et al.*, 2004] as well as the low relief of these river meanders, which leads to less erosion of old uplifted rocks [e.g., *Raymond et al.*, 2004]. Hence relatively more recently synthesized biomass can be leaking out from the surrounding topsoil and eventually be incorporated into river-exported estuarine sediments.

[25] Compared with the total SOC, the isolated soot-BC had a less modern origin for the Ob (28%), whereas the soot-BC had a more modern origin for the Yenisey (88%).

The more depleted ^{14}C signal for the soot-BC fraction in the Ob sediments may reflect that this westernmost drainage basin is influenced by atmospheric deposition of soot-BC from Europe where fossil fuels dominate as a combustion source [e.g., *Mandalakis et al.*, 2005]. It has been shown that the air is frequently transported from Europe into the Arctic region during the wintertime [e.g., *Rahn*, 1981; *Barrie*, 1986]. Such a radiocarbon signal of the soot-BC may also reflect burning of peatlands. The western Siberian region contains vast areas of peatlands (about 900,000 km^2), which has been estimated to represent 30% of the world total peat stock [*Kremenetski et al.*, 2003]. The peatlands are important for long-term carbon storage and sequestration. Further, peatland fires are common and would lead to a less than modern soot-BC signal in western Siberia (www.fire.uni-freiburg.de) [*Davidenko and Eritsov*, 2003]. Coincidentally, in 2002, a large fire was burning in West Siberian peatlands and the Krasnoyarsk region east of the Yenisey River experienced large forest fires. Both of these events may have contributed to the relatively modern soot-BC radiocarbon signal (www.fire.uni-freiburg.de) [*Sukhinin et al.*, 2003].

[26] Source-diagnostic PAH ratios such as ΣMP/P in the Ob and Yenisey sediments show that the PAHs indeed are mainly combustion-derived (Figure 3 and Table 1). The IP/(IP + BgP) and the Flu/(Flu + Pyr) ratios further suggests that the PAHs in the Ob and Yenisey sediments primarily come from grass fires, wood or coal combustion whereas the 1,7/(1,7 + 2,6-DMP) indicates mixed combustion sources (Figure 3). Petroleum seepage does not seem to be a significant PAH source to this region.

### 3.2. Lena River in the Central Siberian Uplands

[27] The Lena River has the largest catchment area in the Central Siberian Uplands, with results quite different from the other GRARs (Figure 1). Lena had a comparatively low BC:SOC ratio of 0.03 (Table 1). However, due to its large POC export fluxes, the Lena has the highest estimated fluvial soot-BC export of the five GRARs with 36 kton a^{-1} (Figure 2c and Table 2). The soot-BC yield of the Lena drainage basin (Table 2) was intermediate among the GRARs, with higher yields than the Ob and Yenisey to the west and lower than the Indigirka and Kolyma to the east, consistent with continent-scale trends of increasing relief, and changing atmospheric circulation patterns, to the east. The observed low soot-BC concentration in the Lena sediment may have been caused by sediment dilution due to the intensive coastal erosion along the Laptev Sea border
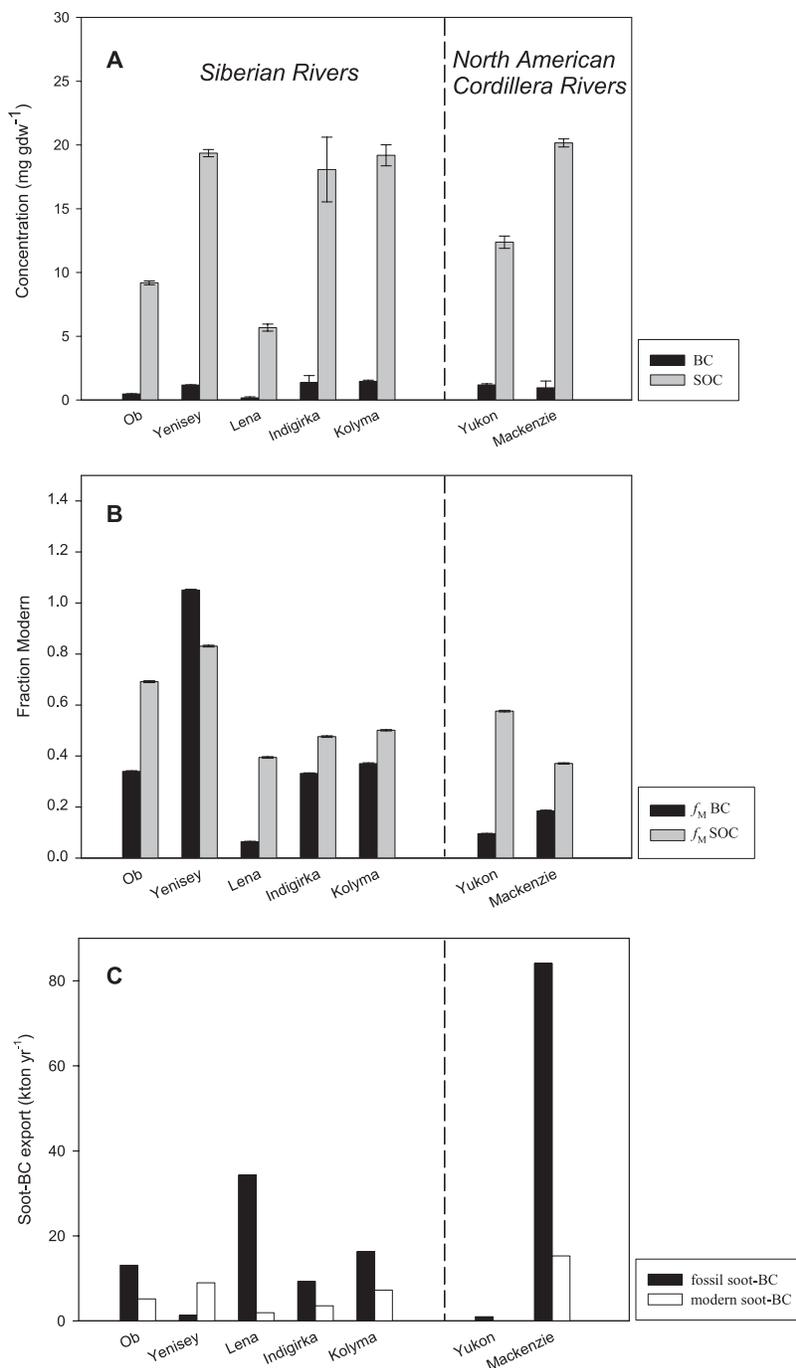
Figure 2. The geospatial distribution, source classification and estimated export fluxes of soot-BC in or near pan-arctic rivers: (a) surface sediment concentrations of soot-BC (black bars) and SOC (grey bars) (n = 3, 1 s.d.), (b) radiocarbon signature of soot-BC (black bars) and SOC (grey bars) (error bars represent an internal statistical error of the ^{14}C counts, an external error from reproducibility tests and the statistical error associated with the δ^{13}C correction) and (c) proportion of soot-BC export fluxes originating from fossil (black bars) and modern biomass (white bars) sources.

that is common in the area [*Rachold et al.*, 2000]. Erosion of coastal sea ice complexes is consistent with a low contribution from modern biomass in the surface SOC pool of only 33%. Our previous study of the SOC phase in another estuarine surface sediment sample from the Lena

River also showed a low contribution from modern biomass of 38% (f_M = 0.451 ± 0.002) [*Guo et al.*, 2004]. The soot-BC was extremely depleted in radiocarbon with only a 5% modern source, indicating an overwhelmingly fossil/petro-genic origin, perhaps in combination with a reservoir ageing
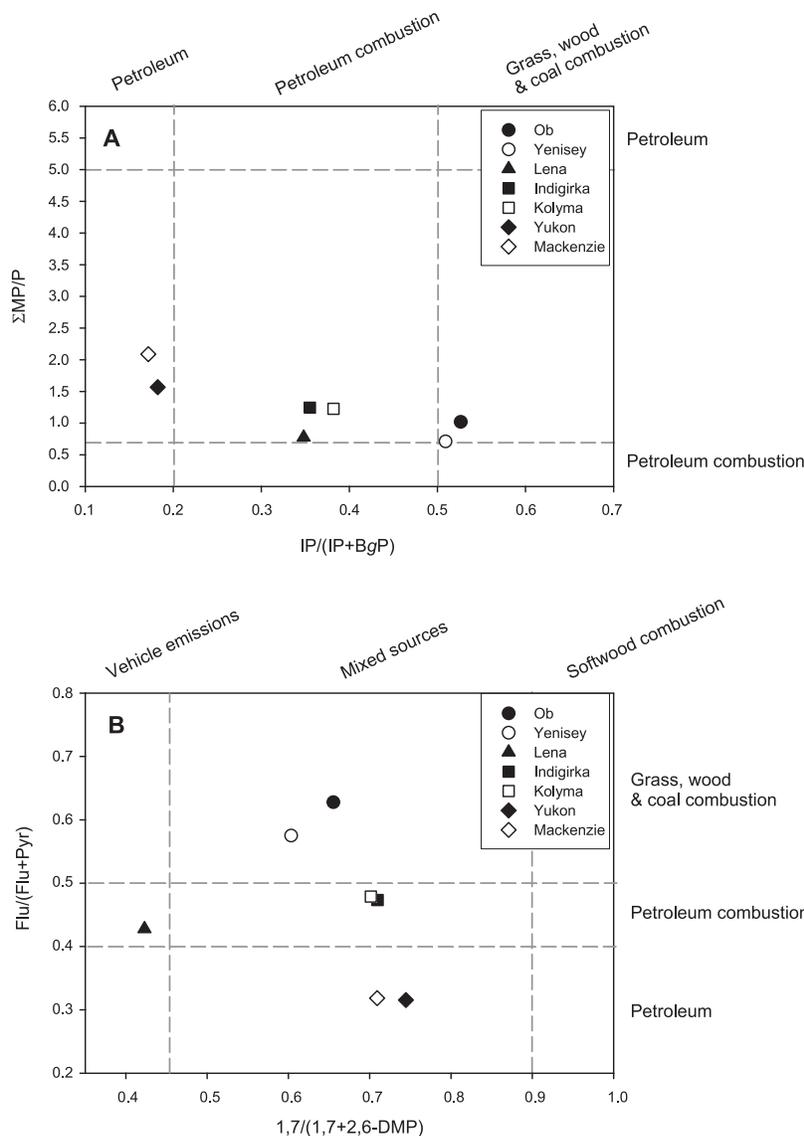
Figure 3. Source-diagnostic PAH combustion marker analysis: (a) methylphenanthrene to phenanthrene (ΣMP/P) ratio and indeno(2,3-cd)perylene to the indeno(2,3-cd)perylene plus benzo(*ghi*)perylene (IP/(IP + B*g*P)) ratio (dashed lines separate PAHs from different sources; end-member values detailed elsewhere [e.g., *Gustafsson and Gschwend*, 1997; *Yunker et al.*, 2002]); (b) 1,7-dimethylphenanthrene to the 1,7- plus 2,6-dimethylphenanthrene (1,7/(1,7 + 2,6-DMP)) ratio and the fluoranthene to fluoranthene plus pyrene (Flu/(Flu + Pyr)) ratio (end-member values from *Benner et al.* [1995] and *Yunker et al.* [2002]).

effect from long-term storage of some soot-BC in coastal ice complexes and permafrost (Table 1).

[28] The ΣMP/P ratio suggests that the Lena estuary PAHs are combustion-derived rather than from petroleum seeps (Figure 3a and Table 1). The lack of petroleum seeps/spill/contamination is also confirmed by a low ΣPAH concentration from the Lena that is comparable to the PAH levels from the other arctic rivers (Table 1). Furthermore, the IP/(IP + B*g*P) and the Flu/(Flu + Pyr) show a signal of input from petroleum combustion and the 1,7/(1,7 + 2,6-DMP) point toward vehicle emissions, presumably long-range transported, as the main PAH source (Figure 3). The long-range transport may be further constrained by the benzo(*a*)pyrene to benzo(*e*)pyrene ratio [*Mandalakis et al.*, 2004]. For the Lena estuary sample,

this ratio is comparatively low at 0.12 (data not shown), which is consistent with distant sources. The low fraction modern for the soot-BC phase and the source-diagnostic PAH ratios together suggest anthropogenic burning of fossil fuels as strong sources of particulate combustion products in the Lena River Basin. In addition to long-range atmospheric transport, a contribution of soot-BC from fossil fuel combustion may also stem from mining activities in the Aldan and Vilyui tributaries of the Lena River.

3.3. Indigirka and Kolyma Rivers in the East Siberian Highlands

[29] The Indigirka and Kolyma Rivers are located in the eastern Siberian region (Figure 1). The soot-BC concentrations

were the highest in these two of the seven pan-arctic river/delta systems, with a BC:SOC ratio of 0.08 for both sediments (Table 1). These rivers are the smallest drainage basins of the GRARs and drain mostly continuous permafrost. Nevertheless, their fluvial soot-BC-export fluxes, 13 kton a^{-1} for the Indigirka and 24 kton a^{-1} for the Kolyma (Table 2), were as high as those for the other large Siberian rivers. The high soot-BC export yields from these smaller basins may come from the higher relief for these East Siberian Highlands areas, making the river erode deeper into the old uplifted rocks [e.g., *Dickens et al.*, 2004; *Raymond et al.*, 2004]. The radiocarbon signals for SOC were fairly similar for the two (40 and 42% modern biomass, respectively). The lower fraction modern biomass of the SOC in these easterly parts of Siberia than in western Siberia may stem from a combination of carbon with high reservoir ages stored in the exclusively permafrost drainage basin [*Guo et al.*, 2004] and ^{14}C-depleted and geologically recycled soot-BC [e.g., *Dickens et al.*, 2004] in the uplifted rocks of the East Siberian Highlands. The contribution from modern biomass for soot-BC of 28% for Indigirka and 31% for Kolyma was consistently lower than for the SOC phase. These values for soot-BC could indicate a combination of vegetation fires and fossil fuel combustion within the region or soot-BC imported via long-range atmospheric transport from highly polluted Asian regions to the south [e.g., *Bond et al.*, 2004; *Koch and Hansen*, 2005]. The benzo(*a*)pyrene to benzo(*e*)pyrene ratio confirms long-range transport of PAHs to the area with values ranging between 0.22–0.25 for the two sediments (data not shown). Model studies suggest that the southern Asian contribution represent only 1.6% of the European contribution to BC in the entire Arctic, even if the emissions in southern Asia are 2.5 times higher than in Europe [*Stohl*, 2006]. However, another study pointed toward a 20–25% contribution of lower altitude BC by southern Asia to the whole Arctic region [*Koch and Hansen*, 2005].

[30] The ΣMP/P ratio shows a pyrogenic origin of the PAHs in the Indigirka/Kolyma basins where the slightly higher ΣMP/P ratios indicate lower-temperate combustion processes (e.g., wood) (Figure 3a and Table 1) [*Youngblood and Blumer*, 1975; *Elmquist et al.*, 2007]. Both the IP/(IP + BgP) and the Flu/(Flu + Pyr) signal for petroleum combustion whereas the 1,7/(1,7 + 2,6-DMP) ratio suggests a somewhat greater influence from wood combustion (Figure 3b). These Far East Siberian Highlands experience high fire frequency due to their specific climate and vegetation characteristics [e.g., *Davidenko*, 2000; *Shvidenko and Goldammer*, 2001]. Furthermore, ^{14}C measurements of carbon monoxide (CO) samples taken from air between the Chita and Khabarovsk regions in the Far East Siberia, showed that biomass burning contributed to the elevated CO concentrations and hence point toward forest fires as an important source in this region [*Bergamaschi et al.*, 1998]. The East Siberian Highlands thus appears to receive contributions from both natural vegetation fires and anthropogenic combustion of fossil fuels, but with a weaker signal than for the Lena River catchment area.

3.4. Yukon and Mackenzie Rivers in the North American Cordillera

[31] The BC:SOC ratios were 0.10 for the Yukon and 0.05 for the Mackenzie surface sediments (Table 1). The Mack-

enzie River had the highest fluvial soot-BC export whereas the Yukon had the lowest soot-BC export flux (Table 2). The high value for the Mackenzie River may be related to the fact that this river has its headwaters south of the Arctic region and thereby covering an area with more pronounced anthropogenic BC influences. The modern biomass contribution of the SOC was 48% for the Yukon and 31% for the Mackenzie (Figure 2b and Table 1). The Mackenzie River has the largest OC and BC load, and studies have shown that more than 60% of the organic carbon in its estuary sediment comes from the surrounding soil storages rather than from marine sources [*Goni et al.*, 2005]. In addition, the Mackenzie River has been shown to contain *n*-alkanes and other hydrocarbons of petrogenic origin such as from oil seeping out from the underlying rocks to the river [*Yunker et al.*, 2002]. Furthermore, the two N. American rivers have a more erosive nature than the five Siberian Rivers and therefore tend to undercut their banks and create large braided channels [*AMAP Assessment Report: Arctic Pollution Issues*, 1998]. These natural petroleum source rocks could therefore contribute to older ^{14}C ages for the SOC compartment. Very low contributions from modern biomass were found for the soot-BC isolates with just 8% for Yukon and 15% for Mackenzie. Integrity testing of the CTO-375 method has shown that important constituents of petroleum source rocks (e.g., kerogen, coal, asphaltenes) are quantitatively removed during the thermal oxidation treatment [*Gustafsson et al.*, 1997, 2001; *Hammes et al.*, 2007]. Therefore weathered petroleum source rocks may affect the radiocarbon signal of SOC, and the PAH ratios, but not the radiocarbon signal of the soot-BC phase. However, the eroding petroleum source rocks may also contain geologically preserved macerals such as pyrofusinites and other pyrogenic particle facies [e.g., *Schmidt and Noack*, 2000; *Cornelissen et al.*, 2004] and such fossil BC may contribute to the low ^{14}C in the BC [e.g., *Cornelissen et al.*, 2004; *Dickens et al.*, 2004]. Fossil fuel combustion-derived soot-BC would also be consistent with the depleted ^{14}C signals and may be from combustion within the region, or coming from areas further south. Furthermore, dust particles traveling all the way from the Asian continent have been detected in snow sampled in the Yukon region [e.g., *Welch et al.*, 1991; *Zdanowicz et al.*, 2006], which may explain the high fossil fuel combustion input in this region. The slightly higher fraction biomass in soot-BC measured for the Mackenzie River may imply some influence of forest fires. High wild fire frequency has been reported with large amounts of BC emitted every year in the North American Cordillera [e.g., *Lavoue et al.*, 2000; *Kim et al.*, 2005].

[32] In vivid contrast to the GRARs, but consistent with the discussion above, the high ΣMP/P ratio and the low Flu/(Flu + Pyr) and IP/(IP + BgP) ratios for the two North American Cordillera rivers indicate significant petrogenic origin of PAHs (Figure 3 and Table 1).

3.5. Geospatial Patterns in Contribution of Soot-BC to the Total Sedimentary Organic Carbon

[33] The Pan-Arctic BC:SOC ratio reported here ranges between 3.0–9.6%. The highest values were found in the high permafrost region (i.e., possibly due to lower SOC

leakage) compared to rivers that also drain non-permafrost regions. Earlier studies in Siberia have shown BC:SOC ratios spanning between 3.9–17% [*Guo et al.*, 2004]. In sediments on the New England continental shelf, the BC:SOC ratio were between 2.8% and 15% [*Gustafsson and Gschwend*, 1998] and solid particles collected in the Mississippi River had values of 1.9% to 17% [*Mitra et al.*, 2002]. The BC:SOC ratios found in this study for the Arctic Rivers are thus comparable with values found with similar BC quantification techniques for other locations.

[34] The results here only partly agree with the bulk SOC ages reported by *Guo et al.* [2004] for a similar coastal Siberian transect, likely due to different sampling time and locations. A significant relationship between geospatial ^{14}C-SOC and the BC:SOC ratio, as was noted by *Guo et al.* [2004] would imply that old soot-BC may govern the bulk SOC age trend, could now be tested with our ^{14}C data (Table 1). A similar linear regression of f_M-SOC versus BC.SOC, as reported by *Guo et al.* [2004] showed here a statistically insignificant linear relationship at 95% confidence interval ($r^2 = 0.046$; p-value = 0.64; data not shown).

3.6. Fluvial Soot-BC Fluxes to the Arctic Ocean

[35] It is important to get more information of the different transport pathways of BC from land to the Arctic Ocean to be able to estimate their contribution to the larger-scale biogeospheric carbon cycle. For the global BC cycle, one study has suggested that, globally, the fluvial BC deposition onto the continental shelf is 2 to 3 times more important than the aeolian transport to such waters [*Suman et al.*, 1997]. Here, the calculated riverine soot-BC fluxes for the seven Pan-Arctic Rivers are compared with the Mississippi River, and a revised global soot-BC riverine export is also estimated.

[36] The total Pan-Arctic soot-BC river export of 200 kton a^{-1} is of the same scale as the soot-BC flux determined for the Mississippi River of 500 kton a^{-1} [*Mitra et al.*, 2002] and the 24 kton a^{-1} exported from the comparatively minor drainage areas emptying into the more polluted Delaware Bay of the Atlantic Ocean [*Mannino and Harvey*, 2004]. The Mississippi River has a large drainage basin that stretches from its source at Lake Itasca in northern Minnesota to the Gulf of Mexico. Both the high fossil fuel usage and the higher anthropogenic impacts in the two temperate North American river systems may explain the somewhat higher BC flux in the Mississippi River than in the seven Arctic Rivers. The only available estimate of the global riverine BC export flux suggested a value of 12×10^3 kton a^{-1} [*Suman et al.*, 1997]. Their assessment was the product of a rough estimate that 0.1% of soils is BC [*Goldberg*, 1985] multiplied by global river discharge of suspended material at 12×10^6 kton a^{-1} [e.g., *Milliman and Meade*, 1983]. The combined BC river discharge of the Mississippi and the Pan-Arctic rivers represent a soot-BC concentration in the river SPM of 0.2% (=2 mg BC g^{-1}). If this is taken as representative for global rivers and combined with the global river SPM export, an estimate of 26×10^3 kton BC a^{-1} is deduced for the global fluvial discharge of BC. This is an upward revision of the *Suman et al.* [1997] estimate by a factor 2 due to the higher soot-BC determined

for these sediments. Probably, it is not the sedimentary soot-BC that is overestimated since the CTO-375 method used to deduce the soot-BC concentrations in the Mississippi and Arctic River studies only detects the most refractory part of the combustion continuum [*Elmquist et al.*, 2004, 2006; *Hammes et al.*, 2007].

[37] It is stressed that we interpret these crude global BC river fluxes with caution. Nevertheless, such estimates are, combined with global BC fluxes across other major interfaces in the global biogeosphere (such as atmospheric BC deposition, sediment burial, and degradation), an important first step in the construction of a global biogeospheric BC budget [e.g., *Suman et al.*, 1997; *Druffel*, 2004]. The global BC emissions have been estimated to span between 4.3×10^3 and 22×10^3 kton BC a^{-1} [*Liousse et al.*, 1996; *Bond et al.*, 2004]. Therefore the global riverine BC flux estimated in this study is in the higher end of the estimated BC emissions to the atmosphere. This can come from either overestimation of the suspended matter transported by the rivers, extra input to the fluvial BC pool from weathering of rocks containing ancient BC, or an underestimation of the global BC emissions to the atmosphere. In addition, the BC emitted from biomass burning such as in forest fires has a large uncertainty [e.g., *Bostrom et al.*, 2002; *Bond et al.*, 2004].

3.7. Source Apportionment of Soot-BC Found in the Arctic Region

[38] The Pan-Arctic perspective from the seven drainage-integrated river systems affords the possibility to investigate the large-scale source contributions of BC currently found in recently deposited Arctic sediments. An average contribution from biomass burning processes was estimated by using the measured ^{14}C-BC values for each sediment weighted by the corresponding riverine soot-BC flux to the Arctic basin. This yields a ^{14}C-based pan-arctic soot-BC source apportionment corresponding to 21% contribution from modern biomass burning and 79% from ^{14}C-extinct sources such as fossil fuel combustion and relict BC in uplifted source rocks. If the BC contributions from peat and permafrost-derived organic carbon, both being of intermediate ^{14}C ages, are significant compared to fossil fuel combustion and erosion of petroleum source rock, then the contribution from modern biomass burning to the pan-arctic soot-BC pool will be even lower (<21%).

[39] For comparison, we also estimated the source apportionments of soot-BC in the Arctic atmosphere based on data from atmospheric modeling studies. Using the amount of BC from biomass burning versus fossil fuel combustion for each continent as described elsewhere [*IPCC*, 2001; *Bond et al.*, 2004], we could estimate the corresponding modern-biomass contribution suggested by two recent atmospheric chemical-transport models. The first estimate was based on the output from a model suggesting a low influence of South Asia on the BC phase [*Stohl*, 2006] and the second with a predicted higher South Asian influence [*Koch and Hansen*, 2005]. The input from both the low and high South Asian influence models yielded an estimated biomass-burning contribution of nearly 60%.

[40] The factor of three discrepancy between the river-basin integrated radiocarbon signal and estimated from the

two atmospheric models may reflect a number of factors: (1) current BC emission factors from biomass burning carry large uncertainties [e.g., *Bostrom et al.*, 2002; *Bond et al.*, 2004]; (2) the 50% contribution of Mackenzie River to the pan-arctic river soot-BC radiocarbon signal have attenuated the total ^{14}C signal as this river system delivers source-rock eroded relict BC, which obviously has not passed through the recent Arctic atmosphere. Excluding the Mackenzie and performing the pan-arctic soot-BC source apportionment for just six rivers increased the estimate of the modern biomass combustion from 21 to 26%. (3) Given an uncertainty in the proper value for the modern biomass combustion ^{14}C end-member, a sensitivity calculation of this factor was performed. End-member values of $f_{M,biomass}$ in the range 1.1–1.3 resulted in estimated contributions to pan-arctic river soot-BC from modern biomass sources in the range of 19–23% (i.e., not very sensitive); and finally, (4) the surface sediment samples constitute an integrated record of several years of BC input and therefore could also represent times when the BC emissions from fossil fuel burning were different from today [e.g., *Elmquist et al.*, 2007]. Taken together, the integrated source signal in the total biogeo-sphere may not be expected to be identical to the minor BC reservoir residing in the atmosphere. Apparently, both biomass burning, some occurring in the Arctic itself, and fossil fuel combustion, overwhelmingly taking place outside the Arctic, are important contributors to the Arctic BC pool. Further studies should seek to investigate the quantitative contribution from peatland fires where molecular combustion markers may prove rewarding. The powerful receptor-based source apportionment with radiocarbon and molecular combustion markers that have been demonstrated in this paper could favorably also be applied directly to BC-containing atmospheric aerosols collected in the Arctic.

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