GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 22, GB2018, doi:10.1029/2007GB002994, 2008

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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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Received 13 April 2007; revised 11 January 2008; accepted 31 January 2008; published 29 May 2008.

[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.

Citation: Elmquist, M., I. Semiletov, L. Guo, and Ö. Gustafsson (2008), Pan-Arctic patterns in black carbon sources and fluvial discharges deduced from radiocarbon and PAH source apportionment markers in estuarine surface sediments, *Global Biogeochem. Cycles*, *22*, GB2018, doi:10.1029/2007GB002994.

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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0886-6236/08/2007GB002994$12.00

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

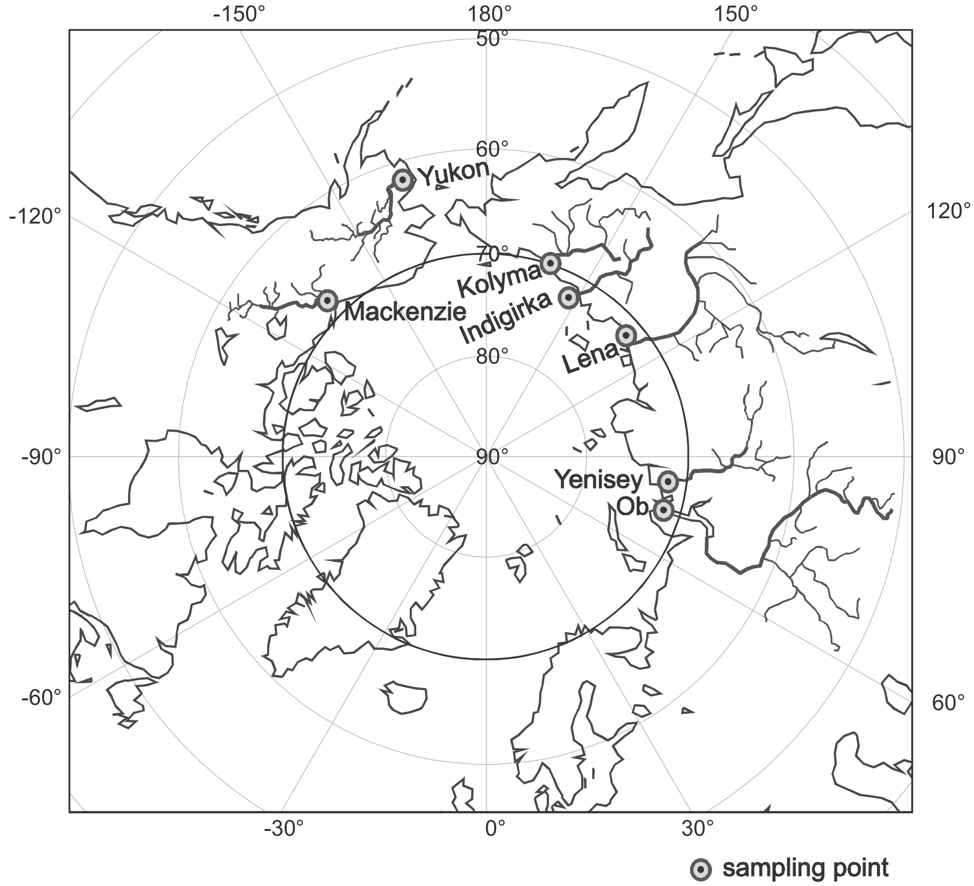

Figure 1. Map of pan-arctic sampling locations in or near the rivers Ob, Yenisey, Lena, Indigirka and Kolyma in Siberia, the Yukon in Alaska and the Mackenzie in northwestern Canada.

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.