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Characterization of organic matter in surface sediments of the Mackenzie River Basin, Canada

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ABSTRACT

The particulate organic matter in <63 μm surface sediments from the Mackenzie River and its main tributaries was studied using Rock-Eval pyrolysis and organic petrology. The organic matter in the sediments is dominated by refractory residual organic carbon (RC) of mainly terrigenous nature, as indicated by abundant inertinite, vitrinite, and type III kerogen. Sediments from the tributaries contained significantly more algal-derived organic matter than from the main channel of the river, highlighting the importance of low-energy system dynamics in the tributaries, which allows modest algal production, more accumulation, and better preservation of autochthonous organic matter. This is particularly true for tributaries fed by lacustrine systems, which showed the highest S1 and S2 fractions, and consequently higher total particulate organic carbon (POC) in the basin. Organic petrology of the sediment samples confirms abundant liptinitic materials (i.e., fat-rich structured algae, spores and pollen, cuticles, and resins). Forest fire and coal deposits are also confirmed to contribute to the basin. Assuming that suspended and fine surfacial sediments have a similar OC composition, the Mackenzie River is estimated to deliver a total POC flux of 1.1 Mt C/yr to its delta, of which 85% is residual carbon with liptinitic OC (S1 + S2) and S3 accounting for another 9% and 6%, respectively.

1. Introduction

The Mackenzie River is the largest source of suspended sediments to the Arctic Ocean, the second largest in dissolved matter, and the fourth in water discharge (Millot et al., 2003). The Mackenzie River is also a major source of terrigenous organic carbon to the Arctic Ocean, delivering a total of 2.1 Mt C/yr to its delta and 1.2 Mt C/yr to the Beaufort Sea, which accounts for more than 16% of the total terrigenous organic carbon influx to the Arctic Ocean (Macdonald et al., 1998; Stein and Macdonald, 2004). While many studies have focused on the organic carbon geochemistry in the Mackenzie delta and shelf (Macdonald et al., 1998; Goni et al., 2000, 2005; Yunker et al., 2005; O'Brien et al., 2006; Drenzek et al., 2007), few data are available on the sources, speciation, and distribution of organic carbon in the Mackenzie River Basin itself (Feinstein et al., 1988, 1991a,b).

The Mackenzie River Basin (MRB) comprises the Mackenzie River valley from Great Slave Lake to the delta, and encompasses various types of terrain including Arctic tundra, boreal forest, peatland, and mountainous cordillera (Dyke and Brooks, 2000). The tundra is virtually devoid of higher vegetation and is expected to make relatively small contribution to the total organic matter content of the MRB due to its secluded geographical location. The boreal forest is distributed along the entire length of the river with margins close to the river, mainly in the south-western part. The boreal forest is likely an important source of terrigenous organic matter of mainly higher-plant origin such as tree barks, needles, leaves, pollen, and char from the frequent forest fires (Reyes et al., 2006). This terrigenous organic matter enters the MRB through the watershed runoff and/or aerial deposition. Peatland is spread throughout much of the basin, though predominantly on the eastern side of the MRB. To the west are the Mackenzie Mountains, with elevations ranging from 700 to 2500 m a.s.l. (Larter, 2004). The mountainous regions are sparsely vegetated in most areas (Wright et al., 2003). However, the tributaries from these mountains contribute the vast majority of suspended sediment to the Mackenzie River, particularly the Liard River, which adds approximately 40% of the total sediment load of the river (Carson et al., 1998).

Diverse geological formations in the MRB include organic-rich rocks, such as shale and coal, which may provide significant input of organic matter into the MRB and the Beaufort Sea. The coal deposits are most notably located in the Brackett Basin (63–65°N; 120°–127°W) and consist of thermally immature coal, mostly lignite with some subbituminous coal (Sweet et al., 1989). These coal deposits and associated strata are exposed to the river and often subject to natural combustion as seen by frequent smoking events. The northern reaches of the river are underlain by organic-rich shale (Feinstein et al., 1988).

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Furthermore, the Mackenzie River is the drainage basin for several lakes, including the Great Slave and Great Bear Lakes, which may discharge organic matter into the MRB through their outlets.

Based on organic geochemical analysis and organic petrology, here we report the distribution, characterization, and flux of organic matter in the MRB. The distribution of organic matter in the sediments of the Mackenzie River and its tributaries may provide important information related to the carbon cycle, source identification and apportionment in the MRB and consequently in the Beaufort Sea and Arctic Ocean. The nature of organic matter in the sediments is also expected to influence the transport, cycling, speciation and bioavailability of organic and trace metal contaminants.

2. Materials and methods

Surface sediment samples were collected at intervals along the entire length (1 738 km) of the Mackenzie River in the summers of 2003 and 2004, including its main tributaries (Fig. 1). The sediment was retrieved using an Ekman or Ponar dredge onboard a river boat. The samples were collected from the top 2 cm below the sediment-water interface using a plastic spoon; the outer layer of the sediment that had contact with the dredge was removed prior to the sample collection. Samples were placed in Ziploc bags and immediately frozen at −20 °C until analysis. After freeze-drying, they were sieved to <63 μm to standardise the grain size (Horowitz and Elrick, 1988). Coal samples were collected from various locations in the Brackett Basin near the small community of Tulita (see the squared area in Fig. 1) in 1984, 1985 and 1987 and were pulverised prior to analysis.

The pulverised samples were analysed on a Rock-Eval 6 analyser (Vinci Technologies, France), with a FID detector for measuring hydrocarbon gases and an on-line infrared cell for CO and CO_2 generated during the pyrolysis (Lafargue et al., 1998). The samples were first pyrolysed in an inert atmosphere (He) from 100 to 650 °C, at a rate of 25 °C/min, to separate and determine the contents of the labile, mainly algal-derived fractions of organic matter (S1, S2; mg HC/g sample). The amounts of CO_2 (S3; mg CO_2/g sample) and CO (S3CO; mg CO/g sample) produced during pyrolysis were also measured. Samples were then automatically transferred to an oxidation oven, and were heated from 400 to 850 °C to incinerate all the residual carbon (RC; wt.%). The total particulate organic carbon (POC; in this paper "TOC" is reserved for the total organic carbon in the aquatic system which is the sum of POC and dissolved organic carbon — DOC) was calculated from the sum of the pyrolysable carbon (PC; 100–650 °C) and RC (400–850 °C). An internal shale standard (9107, Geological Survey of Canada — Calgary) was used for the QA/QC purpose.

For the imaging study, sediment samples were pelletised in 3-cm diameter Teflon moulds using a mixture of EPOTECH® epoxy-resin mixture, and after curing were sequentially polished under increasingly finer grit material (carborundum grit, 0.5 μm alumina on Pelon®, and 0.03 μm alumina on a silk lap). They were then examined under a Zeiss Axioplan II microscope in white and blue light under oil immersion. Digital images were captured using the Zeiss Axiocam® and Axiovision® software. Counting statistics were used to quantify the particles of inertinite, vitrinite (huminite) and liptinite (exinite and alginite).

The statistic analysis was done with the statistical package SPSS (version 15; SPSS Inc., Chicago, IL). Because of the relatively small sample size of the lake-fed sediment samples ($n=5$), the non-parametric Mann–Whitney Test was used to compare the differences among the three groups: sediments from the main-channel Mackenzie River, from the lake-fed tributaries, and from the other tributaries/delta. The null hypothesis (H_0) is that there is no difference between the groups. Significant difference between the groups is inferred when $p<0.05$ (the p-value is the probability of committing a Type I error, i.e., when a true H_0 is rejected).

3. Results and discussion

The results of the Rock-Eval analyses are shown in Table 1 and Fig. 2. Maceral analysis results are shown in Table 2. The POC in the sediments from the lake-fed tributaries (1.14±0.66%; mean±std) was significantly higher ($p=0.026$) than that in the main-channel Mackenzie River (0.46±0.23%). It was also higher than that from the non-lake fed tributaries (0.65±0.29), but the difference is not statistically significant ($p=0.12$).

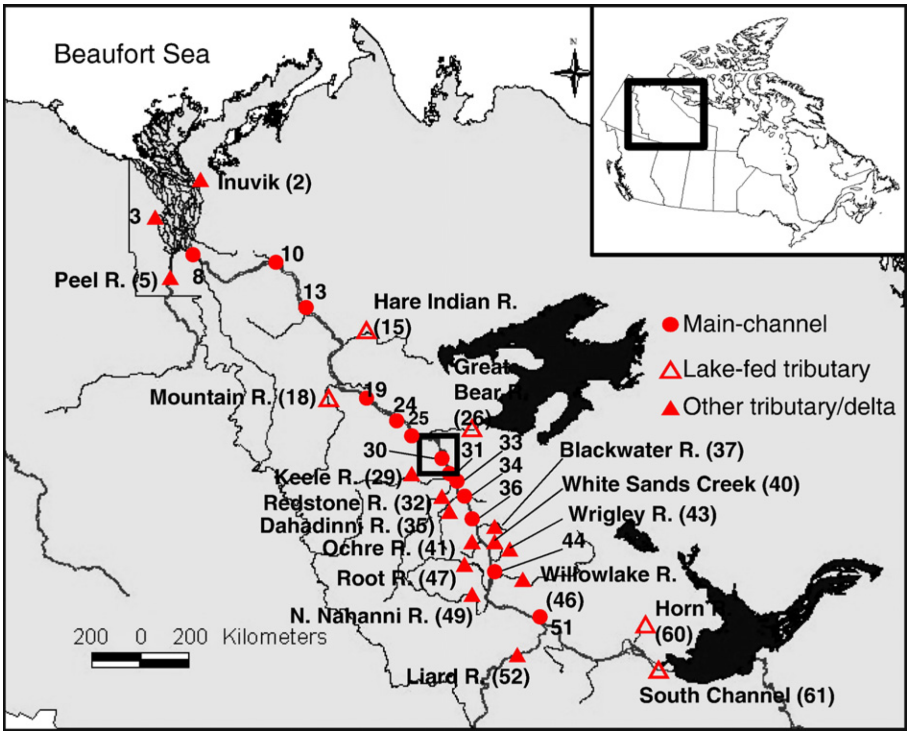

Fig. 1. Map of the Mackenzie River Basin showing the sampling locations for sediments. The square in the middle shows the sampling region for coal.