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Lipid biomarker investigation of the origin and diagenetic state of sub-arctic terrestrial organic matter presently exported into the northern Bothnian Bay

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ABSTRACT

Predicted climate warming and observed increases in river discharge in the vulnerable Arctic region can lead to alterations in the flux and composition of terrestrial organic matter (terrOM) transported into high latitude coastal waters. A benchmarking of the current sources, transport and degradation dynamics of sub-Arctic terrOM exported into the northernmost Baltic Sea was detailed with lipid biomarkers and bulk geochemical proxies along a transect extending from the unregulated Kalix River to the central Bothnian Bay. Bulk $\delta^{13}C$ and molecular biomarkers suggested a predominance of terrOM throughout both the estuary and the open bay. Terrestrial biomarkers were abundantly present in surface sediments with high molecular weight (HMW) *n*-alkanes, *n*-alkanoic acids and *n*-alkanols between 190 and 960 μg/gOC and β-sitosterol between 120 and 1500 μg/gOC, which is comparable to Russian Arctic estuaries. A relatively large contribution of the *n*-alkane C_{23} and C_{25} homologs (as shown by P_{aq} values of 0.57–0.62) indicated a high contribution of *Sphagnum*-derived OM to the surface sediments. Loss of functionality of lipid biomarkers (e.g., decreasing ratios of HMW *n*-alkanoic acids to HMW *n*-alkanes, and stanols to sterols) between surface water particles and surface sediments, and in the offshore direction for both surface water particles and surface sediments, suggested ongoing and rapid degradation of terrOM throughout the coastal system.
Comparison of terrestrial biomarker signatures (e.g., *n*-alkane carbon preference index and $C_{23}/(C_{23}+C_{29})$ values) and bulk $\delta^{13}C$ in terrOM released from Kalix River and the Russian Arctic Rivers shows that Kalix River extends the east–west trends of many molecular-level terrOM source indicators and delivers a *Sphagnum*-impacted terrestrial signal that resembles that of the River Ob.

1. Introduction

River-dominated coastal sediments are globally important for carbon burial and provide an integrated signal of land-derived organic matter export. Physical transport and degradation processes combine to determine where material is deposited and/or remineralized (e.g. Battin et al., 2008). Terrestrial organic matter (terrOM) in coastal sediments is generally considered to be more recalcitrant than marine organic matter (e.g., Hedges et al., 1997; Hedges and Oades, 1997; van Dongen et al., 2000; Burdige, 2005). In this respect, its molecular composition (i.e., the specific functional groups that differ for marine and terrestrial OM) is an important determinant as to what extent it is transported further or degraded.

The vast Arctic and sub-Arctic areas contain over a third of the global stock of soil OM (Dixon et al., 1994). Since the terrestrial Arctic is also predicted to experience among the largest climate warming (Manabe and Stouffer, 1993; Cuffey et al., 1995; Zwiers, 2002), there is a significant potential for massive remobilization of previously freeze-locked OM (e.g., Stendel and Christensen, 2002; ACIA, 2004; Guo et al., 2004; van Dongen et al., 2008). Given the heterogeneity on different scales of the pan-Arctic terrestrial mosaic, one approach is to use northern rivers to provide an integrated picture of terrOM release dynamics. Arctic rivers alone discharge 10% of global freshwater dissolved organic carbon (DOC) input to the ocean

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(Berner and Berner, 1989; Anderson et al., 1998). An increase in river discharge has already been observed for the Eurasian Arctic Shelf (e.g., Savelieva et al., 2000; Peterson et al., 2002; 2006), and has been predicted for the northern Baltic Sea (Andréasson et al., 2004). These changes could seriously alter the flux and composition of terrOM into high latitude coastal waters.

In order to observe and eventually predict changes to Arctic region terrOM release dynamics, a firm baseline of the current state needs to be established. Despite logistical challenges, there is some information available on the composition and dynamics of the terrOM export from Eurasian Arctic rivers (Peulvé et al., 1996; Zegouagh et al., 1996; 1998; Fahl and Stein, 1997; Boucsein et al., 1999; Boucsein and Stein, 2000; Fernandes and Sicre, 2000; Krishnamurthy et al., 2001; Dittmar and Kattner, 2003; Stein and Macdonald, 2004; Benner et al., 2004; Guo et al., 2004; Neff et al., 2006; Fahl and Stein, 2007; van Dongen et al., 2008). The major findings in these papers emphasize the uniqueness of the Arctic with its large shelf areas and an unusually high fluvial terrestrial input. The current picture is that terrOM is generally refractory and well-preserved in shelf sediments, whereas the marine produced components are more labile and to a much lower extent found in sediments. When considering the Russian Arctic from west to east, the terrOM exported to the shelves becomes older and less degraded. Russian Arctic studies have so far focused on the Laptev and Kara Seas, whereas the East Siberian Sea (Indigirka and Kolyma River) remains severely understudied. In the Canadian Arctic, bulk and molecular processes for terrOM on the Mackenzie shelf and the adjacent Beaufort Sea slope have been detailed (e.g., Yunker and Macdonald, 1995; Yunker et al., 1995; 2002; Macdonald et al., 1998; Goñi et al., 2000; 2005; Belicka et al., 2004; Drenzek et al., 2007). These studies show high inputs of terrOM to the smaller shelf area of the Beaufort Sea, the release of old but degraded fluvial material, with a kerogenic fraction being an important part of the Mackenzie run-off.

This study investigates the pristine Kalix River, one of the largest unregulated river systems in Europe, draining a vast (sub-) Arctic catchment that empties into the northernmost basin of the Baltic Sea. Earlier studies have suggested that the hydrogeochemistry of the Kalix River resembles the western Russian Arctic Rivers (Gustafsson et al., 2000; Guo et al., 2004; Pekka et al., 2004; Ingri et al., 2005) and it could potentially act as a valuable and easily-accessible model system. However, there is no information on the molecular-level composition and thus organic matter fractionation during the estuarine to open bay processing. Up to now, carbon budget studies in the Gulf of Bothnia (e.g., Algesten et al., 2004; 2006; Sandberg et al., 2004) have only been estimating degradation/mineralization processes indirectly by measuring CO_2 emissions. In this study, we investigate characteristics and behavior of fluvially-released terrOM by means of bulk $\delta^{13}C$ analyses and the relative distribution of a range of terrestrial lipid biomarkers along a surface sediment transect from near shore off the mouth of the Kalix River into the deeper basin of the Bothnian Bay (Fig. 1). Results from the surface sediment transect are further compared with the corresponding biomarker composition of particulate organic matter (POM) in the lower Kalix River end-member station and in the overlying freshwater plume in the estuary and offshore Bothnian Bay (van Dongen et al., submitted for publication). The dynamically varying lipid biomarker composition along the transect affords addressing the relative importance of degradation and transport of various components of the terrOM in this sub-Arctic coastal zone. Finally, to explore the potential of the Kalix River as a model system for the western Eurasian Arctic rivers, its organic geochemical characteristics are compared with the much less accessible Russian Arctic Rivers.

2. Materials and methods

2.1. Study area and sampling

The Bothnian Bay is the northernmost basin of the Baltic Sea, draining a sub-Arctic catchment of 260,675 km^2 (Fig. 1).

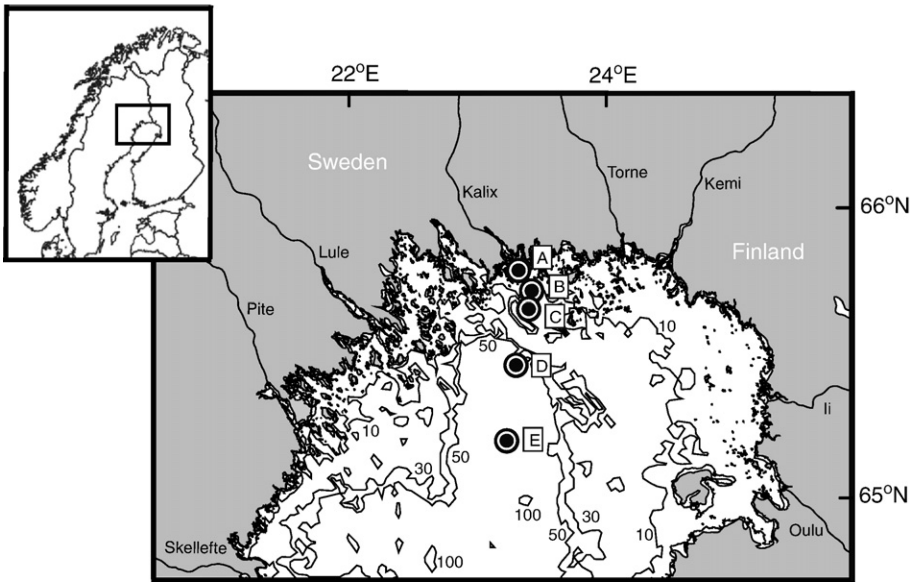

Fig. 1. Map of the northern Bothnian Bay showing the sampling stations A to E (exact positions are given in Table 2).