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Lignin biomarkers as tracers of mercury sources in lakes water column

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Abstract This study presents the role of specific terrigenous organic compounds as important vectors of mercury (Hg) transported from watersheds to lakes of the Canadian boreal forest. In order to differentiate the autochthonous from the allochthonous organic matter (OM), lignin derived biomarker signatures [Lambda, S/V, C/V, P/(V + S), 3,5-Bd/V and (Ad/Al)v] were used. Since lignin is exclusively produced by terrigenous plants, this approach can give a non equivocal picture of the watershed inputs to the lakes. Moreover, it allows a characterization of the source of OM and its state of degradation. The water column of six lakes from the Canadian Shield was sampled monthly between June and September 2005. Lake total dissolved Hg concentrations and Lambda were positively correlated, meaning that Hg and ligneous inputs are linked (dissolved OM $r^2 = 0.62$, $p < 0.0001$; particulate OM $r^2 = 0.76$, $p < 0.0001$). Ratios of P/(V + S) and 3,5-Bd/V from both dissolved OM and particulate OM of the water column suggest an inverse relationship between the progressive state of pedogenesis and maturation of the OM in soil before entering the lake, and the Hg concentrations in the water column. No relation was found between Hg levels in the lakes and the watershed flora composition—angiosperm versus gymnosperm or woody versus non-woody compounds. This study has significant implications for watershed management of ecosystems since limiting fresh terrestrial OM inputs should reduce Hg inputs to the aquatic systems. This is particularly the case for large-scale land-use impacts, such as deforestation, agriculture and urbanization, associated to large quantities of soil OM being transferred to aquatic systems.

Keywords Lignin biomarkers · Mercury · Lakes · Boreal forest · Organic matter sources · Organic matter quality

Introduction

In remote areas, high mercury (Hg) levels in natural ecosystems have frequently been attributed to the deposition of distant atmospheric emissions from natural sources—such as Hg degassing from the mantle and crust (Fitzgerald et al. 1998; Schroeder and Munthe 1998)—or from anthropogenic sources such as metal smelters, waste incinerators and coal power plants (Pacyna et al. 2006). The subsequent deposition of Hg on land and lakes since the beginning of the industrial era adds up to the Hg naturally present in these ecosystems (Lamborg et al.

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2002; Gustin et al. 2006). After more than 100 years, this anthropogenic deposition has greatly contributed to the observed increase in Hg in several compartments of boreal forest ecosystems (Lucotte et al. 1999; Hintelmann et al. 2002; Orihel et al. 2006).

In the lakes of the boreal forest domain, both direct aerial deposition of Hg on the lake surface and atmospheric inputs transiting through the watershed are to be considered in the Hg budget (Schroeder and Munthe 1998). Since these lakes have generally a very small surface area with respect to the surface area of their catchments (Kalff 2002), watersheds are recognized as playing an important role in the transfer of Hg to the aquatic biota (Hakanson 1996; St. Louis et al. 1996; Lee et al. 1998; Grigal 2002; Porvari 2003). Clear cutting or vegetation burning on lake watersheds are also related to increased levels of total Hg (THg) and methyl mercury (MeHg) in runoffs (Porvari et al. 2003) and significantly higher THg levels in predatory fish species (Garcia and Carignan 2000; Kelly et al. 2006).

Mercury concentrations in the water column have previously been linked to the presence of dissolved organic matter (DOM) (Gabriel and Williamson 2004; Lamborg et al. 2004; Ravichandran 2004). Dissolved organic matter comprises a heterogeneous mixture of lipids, carbohydrates, proteins and biochemical compounds coming from the detritus of living organisms from the lakes and their watershed (Meyers and Ishiwatari 1993). However, there is a dearth of information on differentiation between the autochthonous and allochthonous portion of DOM in lake ecosystems. This could be of negligible importance in oligotrophic lakes that mainly contain allochthonous DOM but could cause misinterpretation of the relative importance of terrigenous DOM in eutrophic lakes, where autochthonous OM occupies a significant portion of the DOM pool (Jones 1992).

Hence, despite its importance in aquatic ecosystems, organic matter (OM) is still ill characterized and its description is usually complicated by its low concentrations in most lakes or rivers. This problem can now be overcome using different methods such as portable reverse osmosis to concentrate OM. Another difficulty when trying to characterize OM is the great heterogeneity of sources (e.g. terrestrial vegetation, plankton, bacteria, fungi, etc.), accompanied by extensive transformation by biotic (microbial or fungal) and abiotic (photochemical degradation, leaching and sorption fractionation) processes that transform the collected aquatic OM. The use of stable isotopes is promising, but since the sources of both terrestrial and aquatic plants tend to overlap in aquatic systems, little source discrimination can be garnered from these tracers. (Fry and Sherr 1984; Fry 1991; Kendall et al. 2001).

Ligneous compounds are unambiguously derived from terrestrial vascular plants. Lignin is the second most abundant polymer on Earth after cellulose and constitutes a major carbon sink (Dey and Harborne 1997; Humphreys and Chapple 2002). Ligneous compounds include a group of complex and heterogeneous phenylpropane aromatic polymers connected by carbon–carbon and alkyl–aryl ether linkages (Higuchi 1997). Ligneous compounds enable vascular plants to develop upright (Dey and Harborne 1997). These aromatic compounds might be the most stable and refractory organic molecules (Kalbitz et al. 2003). Since lignin consists of large and complex molecules, the mild alkaline oxidation of their structure with cupric oxide (CuO) yields a specific signature, constituted of a series of derived phenols that can be characterized by gas chromatography coupled with a mass spectrometer (GC-MS) (Ertel and Hedges 1984; Hedges and Ertel 1985; Otto and Simpson 2006; Houel et al. 2006).

The use of lignin-derived phenols biomarkers to characterize lake water particulate organic matter (POM) and DOM is novel (Weissenberger 2007; Caron et al. 2008). The aim of this research is to assess the role of terrigenous OM, using vascular plant-derived biomarkers, on Hg loadings in lakes. The specific objectives of this investigation are: (1) to quantitatively and qualitatively describe the sources and the state of degradation of OM using lignin biomarkers, (2) to link the presence of Hg in the water column to specific terrigenous compounds.

Materials and methods

Study area and lake description

The six lakes under study, located in the Province of Québec (Canada) were sampled over a four months period (from June to September 2005). These lakes lie between 46°36′–48°23′ N and 78°22′–73°50′ W (Fig. 1). The lake surface areas vary over a wide

Fig. 1 Lakes under study

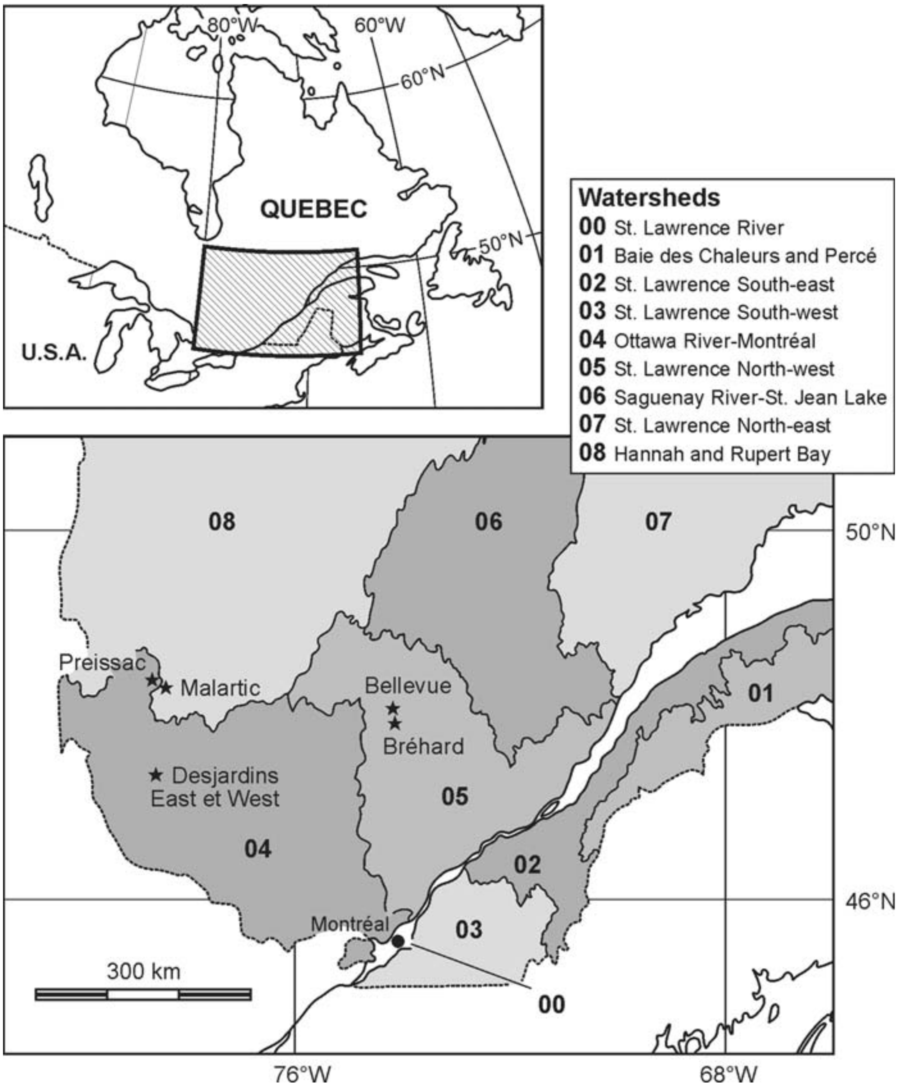


Table 1 Morphometry of studied lakes

Lake	Bellevue	Bréhard	Desjardins-East	Desjardins-West	Malartic	Preissac
Lake area (LA) (km^2)	5.99	0.81	10.12	17.40	86.64	73.80
Drainage area (DA) (km^2)	38.21	4.99	39.59	24.23	502.67	246.49
DA:LA ratio	6.38	6.16	3.91	1.39	5.80	3.34

range, from less than one square kilometer (km^2) for Lake Bréhard (0.81 km^2) to 86.64 km^2 for Lake Malartic. Lake Malartic presents the greater drainage area (501.67 km^2) while Lake Bréhard has the smallest (4.99 km^2). The ratios of drainage area versus lake area (DA/LA) are greater for the lakes Bréhard, Bellevue and Malartic. Lakes Desjardins East and Preissac have intermediate DA/LA ratios while Lake Desjardins West has the smallest one (Table 1). Lakes Malartic and Preissac are located on the clay plain formerly constituting the Ojibway-Barlow Lake in the Abitibi region. These two lakes are located less than 70 km away from the Rouyn–Noranda copper smelter—active since 1921—and are encircled by agricultural lands. Lakes Desjardins-East and Desjardins-West are linked together by a 2 m shallow arm. Logging is the principal disturbance on the watersheds of the two lakes. In contrast with the other lakes, Lake Bréhard and Lake Bellevue are headwater lakes. Lake Bellevue is impacted by a 1.5 m high wood dam at its outflow.

These lakes were selected considering their frequent use by local anglers or First Nations communities and because they cover a large range of trophic levels, DOC inputs, water color and total dissolved Hg concentrations ([TD-Hg]; Table 2). Significant differences were also observed between lakes for chlorophyll *a*, Secchi depth (Z_m), temperature, conductivity, total phosphorus (TP), total nitrogen (TN), sulphate, DOC, [TD-Hg] and DOM C/N atomic ratios. Notably, TP values were characteristic of oligo-mesotrophic status (mean value between 11 and 16 µg/L TP) for all lakes with the exception of Preissac (25.35 µg/L) being mesotrophic and Malartic (46.58 µg/L) being eutrophic. The water pH values were circumneutral, comparable in all lakes and characterized by monthly variations. The POM C/N ratios did not significantly differ between the studied lakes.

Sampling protocol

The water column was sampled monthly from June 14 to September 19, 2005. Temperature, (Z_m), conductivity, dissolved oxygen and pH profiles where measured every meter at the focal point of each lakes using a YSI 6600 multi-probe. The depth of the thermocline was calculated as the depth where the difference in water temperature was greater than 1°C for a one meter interval. Water collection was achieved using an electric pump with a maximum depth capacity of 14 m, using 210 and 64 µm pre-filters for phyto- and zooplankton collection. Integrated water column samples of 100 L were collected constantly moving sampling hose downward and upward across the water column. Total phosphorus, TN, sulphate and DOC duplicates were sub-sampled in 500 mL brown glass bottles for TP, and 4 mL glass vials for TN, SO_4 and DOC. All glass recipient were acid washed (hydrochloric acid (HCl) 10%), pre-combusted at 500°C for 3 h and capped with Teflon© liners. The water samples for [TD-Hg] were filtered on pre-burned (500°C for 3 h) GFF and GN-6 0.45 µm filters, put in pre-washed (sodium hydroxide followed by HCl 10% at 45°C) 500 mL Teflon© flasks and kept frozen until analysis.

Physico-chemical analyses

The lake water color was estimated by reading filtered samples (0.63 µm) at 250, 350 and 440 nm wavelengths, subtracted for colloids absorbance at 750 nm (Cuthbert and Del Giorgio 1992) on a TU-1800S UV–VIS spectrophotometer. The [TD-Hg] determinations were performed by cold vapour atomic fluorescence spectroscopy (CVAFS) (Bloom and Fitzgerald 1988). Triplicate chlorophyll *a* (Chl *a*) samples were kept in totally opaque bottles at 4°C and filtered on pre-combusted (500°C for 3 h) and pre-weighted Whatman GF/C (0.45 µm) filters for dry mass determination and kept frozen at −80°C until extraction with hot 90% ethanol solution. Then, the absorbance at 665 and 750 nm was measured before and after acidification (Sartory and Grobbelaar 1984). Determinations of TP, TN and sulphate concentrations were achieved using a Bran and Luebbe TRAACS (Model 800) auto-analyzer according to standard protocols. DOC samples were rapidly spiked with Hg chloride and dark- preserved at 4°C until analysis on a Shimatzu (TOC 5000A) analyser, less than 3 days after sampling was achieved.

Lignin analyses

The total OM contained in 90 L water samples was concentrated and separated into two fractions: POM—fraction between 64 and 0.45 µm and DOM—fraction under 0.45 µm. The POM fraction was isolated using a Millipore Pellicon cartridge in tangential flow filtration system. The DOM fraction was concentrated to about 8 L using a Real Soft PRO/IIS reverse osmosis system. Prior to reverse osmosis, cations were removed using a Biorad Chelex 100 resin. All samples were stored at −20°C and freeze-dried prior to analyses. The carbon and nitrogen content of these samples were determined using a N/C 2500 Carlo–Erba elemental analyser. A divergence of no more than 5% between replicates was considered acceptable. Lignin biomarkers were generated using the CuO mild oxidation protocol developed by Hedges and Ertel (1982), modified by Goñi and Montgomery (2000). The weight of OM samples

Table 2 Summary of lakes mean physical and chemical characteristics over the four months summer season

	Bellevue ($n = 4$)		Bréhard ($n = 4$)		Desjardins-East ($n = 4$)		Desjardins-West ($n = 4$)		Malartic ($n = 4$)		Preissac ($n = 4$)		ANOVA	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	*F* ratio	Prob *F*
Chl *a* μg/L	1.86^{ab}	0.84	3.42^{a}	0.86	2.29^{ab}	1.33	1.53^{b}	0.27	2.80^{ab}	0.77	2.20^{ab}	0.75	3.75	0.02
Secchi (m)	3.03^{a}	0.54	3.25^{a}	0.41	2.74^{a}	0.57	3.13^{a}	0.10	0.86^{b}	0.23	1.41^{b}	0.12	24.66	<0.0001
T (°C)	13.01^{b}	1.30	12.56^{b}	1.29	14.05^{b}	2.48	14.32^{b}	1.33	18.61^{a}	2.15	19.01^{a}	2.14	49.09	<0.0001
pH	6.43	0.58	6.80	0.44	6.41	1.47	6.33	1.10	6.44	0.94	6.66	0.69	NS	NS
Dissolved oxygen (%)	82.69	12.12	77.11	19.21	148.22	92.93	84.09	63.32	112.33	54.54	59.62	70.03	NS	NS
Conductivity (μS)	54.35^{b}	48.73	77.15^{b}	72.10	40.46^{b}	25.36	38.91^{b}	22.56	100.28^{ab}	36.69	154.51^{a}	25.00	6.99	0.002
TP (μg/L)	13.47^{c}	2.37	16.08^{c}	2.63	11.76^{c}	1.42	11.03^{c}	2.02	46.58^{a}	3.82	25.35^{b}	5.70	59.62	<0.0001
TN (μg/L)	148.45^{d}	4.77	170.40^{cd}	11.94	246.33^{b}	21.40	232.94^{cd}	21.61	380.62^{b}	53.72	539.29^{a}	82.75	63.11	<0.0001
SO_4 (mg/L)	1.08^{c}	0.29	1.21^{c}	0.15	2.84^{c}	0.32	2.57^{c}	0.38	13.99^{b}	6.83	43.22^{a}	4.07	88.72	<0.0001
DOC (mg/L)	5.15^{d}	0.42	5.13^{d}	0.38	7.33^{c}	0.83	6.51^{c}	0.54	10.44^{a}	1.33	9.26^{b}	0.72	87.1	<0.0001
TD-Hg (ng/L)	0.99^{bc}	0.09	0.70^{c}	0.09	1.54^{a}	0.29	1.10^{abc}	0.17	1.29^{ab}	0.50	0.98^{bc}	0.43	7.15	0.001
Absorption coefficient 250 nm (m^{-1})	0.14^{d}	0.03	0.14^{d}	0.04	0.22^{c}	0.03	0.18^{cd}	0.04	0.44^{a}	0.07	0.30^{b}	0.05	102.93	<0.0001
Absorption coefficient 350 nm (m^{-1})	0.36^{c}	0.04	0.37^{c}	0.05	0.55^{bc}	0.06	0.42^{c}	0.06	1.17^{a}	0.24	0.71^{b}	0.11	40.17	<0.0001
Absorption coefficient 440 nm(m^{-1})	0.07^{c}	0.01	0.07^{c}	0.01	0.11^{bc}	0.01	0.08^{c}	0.01	0.27^{a}	0.06	0.15^{b}	0.03	35.38	<0.0001
C/N DOM	54.76^{a}	5.12	49.73^{a}	15.89	40.92^{ab}	10.03	45.57^{a}	13.95	36.66^{ab}	3.68	24.16^{b}	4.80	5.91	0.003
C/N POM	35.54	8.92	27.61	1.59	36.48	10.82	33.51	2.60	32.46	5.32	25.25	3.60	NS	NS

Differences among lakes has been established using a two-way ANOVA without repetition along with Tuckey honestly significant difference

Significance threshold $p < 0.05$, *SD* standard deviation, *NS* no significance to be oxidized (about 10 mg) was precisely calculated according to the carbon content of the sample. The phenol oxidation products were derived with BSTFA and analyzed by gas chromatography-mass spectrometry using a VARIAN 3800-Saturn 2000 equipment (Houel et al. 2006). Replicate analyses were performed every 12 measurements in order to assure the reliability of the procedure. An average analytical variability of 10% was considered acceptable.

The CuO oxidation method described above enables to break down large lignin macromolecules contained in both DOM and POM and to extract their derived phenols. Lignin-derived phenols are divided into four main families: the vanillyls [V], the para-hydroxy [P], the syringyls [S] and the cinnamyls [C]. With the exception of [C] phenols, these families contain each three phenols; a carboxylic acid, a ketone and an aldehyde. The [C] phenols are not part of core lignin, they are ester-bound to lignin polysaccharides, and they are known to be more reactive compared to lignin-derived phenols (Opsahl and Benner 1995). This last family comprise only two acids, the *p*-coumaric and ferulic acids.

The sum and ratios between the different phenols are largely used in order to characterize the terrestrial OM inputs to the sediments of aquatic ecosystems (Hedges and Mann 1979b; Hedges et al. 1984; Prahl et al. 1994; Louchouarn et al. 1997; Houel et al. 2006). Lambda 8 ($\lambda 8$) is defined as the sum of [V], [S] and [C] extracted per 100 mg of organic carbon. The same sum of compounds normalized for 10 g of sample is referred as sigma 8 ($\Sigma 8$). Hence, both $\lambda 8$ and $\Sigma 8$ represent the relative amount of vascular plant derived biomarkers present in the initial sample (Houel et al. 2006). Vanillys are ubiquitous in terrestrial plants tissues while [C] are mostly found in non-woody tissues—herbaceous species, leaves and needles. Hence, the [C] versus [V] ratio (C/V) allows to distinguish between the non-woody versus woody tissues origin of OM (Hedges and Mann 1979a). Syringyls are restricted to angiosperms. The [S] versus [V] ratio (S/V) thus allows to differentiate between OM originating from fresh gymnosperm and angiosperm plants tissues. (Hedges and Mann 1979a; Goñi and Hedges 1992). The 3,5 dihydroxybenzoic acid (3,5-Bd) is another product of the CuO mild oxidation. This compounds is thought to derive in part from tannins and tend to accumulate in decaying plant cells (Ugolini et al. 1981; Prahl et al. 1994) or inorganic soil horizons (Houel et al. 2006). The P/(V + S) and 3,5-Bd/V ratios respectively increase with increasing pedogenesis and humification in soils, or diagenesis in sediments (Prahl et al. 1994; Goñi and Hedges 1995; Dittmar and Lara 2001; Dickens et al. 2007). Finally, side chain oxidation of lignin phenols occurring during the OM degradation process converts aldehydes to acids during lignin degradation, hence increasing the ratio between the vanillic acid versus vanillin ((Ad/Al)v) contents in the oxidation by-products (Bianchi et al. 1999). Increase in (Ad/Al)v ratios thus reflects a greater pedogenetic state of OM.

Statistical analysis

Two-way ANOVA tests were used to establish statistical differences between lakes and between sampling periods. The lack of degrees of freedom rendered testing for interactions between lakes and months impossible. Tukey's Honestly Significant Difference (HSD) was used to segregate between lakes with a significance threshold of $p < 0.05$. Assumption for normality of residuals and homogeneity of variance was tested prior to analysis. Least square mean regression ($\alpha < 0.05$) were applied to determine the strength of the relation between [TD-Hg] and the lignin biomarkers and/or their summation and/or ratios. All statistical analyses were conducted using the JMP 5.1 software (SAS).

Results

Temporal variation of lignin biomarkers

The lignin CuO oxidation products derived from land vascular plants were detected in all samples. Taking into account all lakes, a decrease in vascular plant-derived biomarkers inputs is observed from June to September in both the DOM ($\lambda 8$: prob *F*: 0.001, $\Sigma 8$: prob *F*: 0.0004) and the POM fractions ($\lambda 8$: prob *F*: <0.0001, $\Sigma 8$: prob *F*: <0.0001) (Table 3). Taken individually, all lignin derived biomarkers ([S], [V], [C] and [P]) present the same decreasing trend over the four months sampling period. This trend suggest that while in area without snow accumulation, concentration of lignin phenols tends to be higher

Table 3 Average inter-month variability lignin biomarkers in the dissolved (DOM) and particulate organic matter (POM) for the six lakes

Lignin biomarker	June ($n = 6$)		July ($n = 6$)		August ($n = 6$)		September ($n = 6$)		ANOVA	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	*F ratio*	*Prob F*
DOM $\lambda 8$	0.59^{a}	0.33	0.50^{ab}	0.13	0.33^{bc}	0.07	0.22^{c}	0.08	9.004	0.001
DOM $\Sigma 8$	8.19^{a}	5.50	7.63^{a}	3.48	3.10^{b}	1.45	1.84^{b}	1.47	11.13	0.0004
DOM S	0.142^{a}	0.118	0.081^{ab}	0.022	0.057^{ab}	0.019	0.042^{b}	0.014	3.83	0.03
DOM V	0.44^{a}	0.22	0.41^{a}	0.10	0.26^{b}	0.06	0.17^{b}	0.07	12.26	0.0003
DOM C	0.011^{a}	0.006	0.009^{ab}	0.003	0.007^{ab}	0.001	0.006^{b}	0.002	5.54	0.009
DOM P	0.27^{a}	0.13	0.26^{a}	0.06	0.19^{ab}	0.04	0.16^{b}	0.05	6.90	0.004
DOM S/V	0.31	0.17	0.20	0.02	0.22	0.08	0.25	0.03	NS	NS
DOM C/V	0.026^{b}	0.004	0.022^{b}	0.006	0.029^{ab}	0.005	0.036^{a}	0.008	5.51	0.009
DOM P/(V + S)	0.49^{c}	0.07	0.52^{bc}	0.04	0.61^{b}	0.04	0.77^{a}	0.13	30.75	<0.0001
DOM 3,5-Bd/V	0.59^{b}	0.06	0.59^{b}	0.05	0.66^{ab}	0.10	0.76^{a}	0.13	5.16	0.01
DOM (Ad/Al)v	1.02	0.18	1.07	0.20	1.02	0.16	0.93	0.13	NS	NS
POM $\lambda 8$	1.16^{a}	0.24	0.89^{b}	0.22	0.83^{c}	0.16	0.63^{c}	0.11	20.91	<0.0001
POM $\Sigma 8$	29.70^{a}	6.34	21.57^{b}	8.47	20.93^{b}	7.01	16.10^{b}	7.04	15.85	<0.0001
POM S	0.31^{a}	0.11	0.21^{ab}	0.11	0.17^{b}	0.07	0.13^{b}	0.03	6.08	0.0064
POM V	0.83^{a}	0.18	0.66^{b}	0.16	0.64^{b}	0.12	0.49^{c}	0.10	24.33	<0.0001
POM C	0.025^{a}	0.015	0.020^{ab}	0.012	0.019^{ab}	0.011	0.013^{b}	0.009	4.76	0.02
POM P	0.38^{a}	0.06	0.34^{b}	0.05	0.34^{b}	0.05	0.33^{b}	0.04	11.31	0.0004
POM S/V	0.39	0.17	0.34	0.22	0.27	0.10	0.28	0.08	NS	NS
POM C/V	0.029	0.012	0.030	0.018	0.031	0.016	0.025	0.012	NS	NS
POM P/(V + S)	0.34^{c}	0.03	0.40^{bc}	0.05	0.43^{b}	0.06	0.54^{a}	0.08	18.29	<0.0001
POM 3,5-Bd/V	0.36	0.04	0.42	0.08	0.41	0.06	0.43	0.05	NS	NS
POM (Ad/Al)v	1.29	0.19	1.30	0.15	1.35	0.27	1.21	0.20	NS	NS

Differences among lakes have been established using two-way ANOVA along with Tuckey honestly significant difference (values for $\lambda 8$ are mg/100 mg OC and values for other lignin biomarker and 3,5-Bd are mg/g)

Significance threshold $p < 0.05$, *NS* no significance

in wet and rainy months (Kaiser et al. 2001), in area of snow accumulation and snow melt, such as the boreal ecosystem, concentration of lignin phenols tends to be highest in spring runoff. However, the [S], [V], [C] and [P] signatures are not necessarily directly related to temporal changes in the nature of terrestrial OM inputs since diagenetic transformation and dilution of the bulk OM by autochthonous lignin-free OM can modify the obtained values (Ertel and Hedges 1984). No temporal variation is observed for the compositional indicator S/V of both DOM and POM, possibly indicating fairly constant relative inputs of angiosperms and gymnosperms species over time (Hedges and Mann 1979a). Presence of lignin derived biomarkers indicative of herbaceous and vascular plants soft tissues increases over the summer period in the DOM fraction (C/V of 0.022 to 0.036 from June to September, prob. *F*: 0.004) but not in the POM fraction (prob. *F*: >0.05). Indication of increasing diagenetic activity through the summer months is seen for both DOM (prob. *F*: <0.0001) and POM (prob. *F*: <0.0001) using P/(V + S) ratios. Similarly, the 3,5-Bd/V ratio increases significantly throughout summer in the DOM fraction (prob *F*: 0.01) but presents a non-significant trend in the POM fraction (prob. *F*: >0.05). This difference between the two fractions could be attributed to the greater lability of DOM versus POM in the watershed soils, prior to entrance of both fractions in the lake water column. Finally, the (Ad/Al)v ratios in both fractions are fairly high compared to sediment values published elsewhere—0.93–1.07 for DOM; 1.21–1.35 in the POM (Table 3) compared to 0.38–0.51 in sediments; see Prahl et al. 1994; Goñi and Montgomery 2000;

Louchouarn et al. 2000; Houel et al. 2006—yielding values similar to observations in boreal reservoirs reported by Weissenberger (2007). Vanillic acid to vanillin remained constant during the study period, suggesting steady aerobic degradation of the lignin polymers (Hedges et al. 1988).

Spatial variation of lignin biomarkers

Lignin derived biomarkers and their ratios for each lake have been estimated using mean values obtained during the 4-months study period. These averages indicate that dissolved and particulate vascular plant-derived biomarkers vary significantly between the six lakes (Table 4). There is a two-fold difference between the highest and the lowest DOM $\lambda 8$ value—respectively Lake Malartic 0.69 ± 0.43 and Lake Bréhard 0.30 ± 0.16. High inter-lake CuO oxidation products variability is observed for the [V], [C] and [P] families in both the DOM and POM fractions. However, in neither fractions [S] yields varies significantly. In the dissolved fraction, S/V and C/V ratios remain relatively similar between lakes. However, the POM S/V (prob. F: 0.03) and C/V (prob. F: 0.004) ratios are statistically different between lakes. The indicators of pedogenetic activity also differs between lakes but only for the DOM P/(V + S) ratios (prob. F: 0.005) and the POM (Ad/Al)v ratios (prob. F: 0.0006). In contrast, the DOM and POM 3,5-Bd/V ratios and the POM P/(V + S) ratio are similar for all lakes.

Lignin biomarkers and mercury

Figure 2 presents scatter plots for relationships between $\lambda 8$, $\Sigma 8$, P/(V + S) and 3,5-Bd/V versus [TD-Hg]. For both the DOM and POM fractions, $\lambda 8$ is positively related to [TD-Hg] (respectively r^2: 0.52; $p < 0.0001$ and r^2: 0.63; $p < 0.0001$.) when taking into account all the data gathered in this study. There is also a positive but weaker relationship between $\Sigma 8$ and [TD-Hg] both for DOM (r^2: 0.39; $p = 0.001$) and POM (r^2: 0.51; $p < 0.0001$). Indicators of OM degradation and soil maturation present a negative correlation with [TD-Hg] in both the DOM (P/(V + S): r^2: 0.49; $p < 0.0001$; 3,5-Bd/V: r^2: 0.42; $p = 0.0007$) and the POM fractions ((P/(V + S): r^2: 0.54; $p < 0.0001$; 3,5-Bd/V: r^2: 0.56; $p < 0.0001$). Most of these regressions with [TD-Hg] are stronger when involving the POM fraction rather than the DOM fraction. No significant relationships between S/V or C/V and [TD-Hg] were observed.

Discussion

OM characterization: sources

Efforts to characterize terrestrial OM using vascular plant-derived biomarkers has evolved, from relating environmental mixtures to pure plant endmembers (Hedges and Mann 1979a; Hedges et al. 1984; Hedges et al. 1986; Hedges et al. 1988), to those of degraded sources of soil OM as more integrated and authentic endmembers (Opsahl and Benner 1995; Louchouarn et al. 1999; Dittmar and Lara 2001; Farella et al. 2001; Houel et al. 2006; Otto and Simpson 2006; Hernes et al. 2007). Additionally, much work has been done on dissolved OM as an important vector of terrigenous OM transport from watershed throughout the water column of the oceans (Bianchi et al. 1997; Opsahl and Benner 1997; Benner et al. 2005; Hernes and Benner 2006; Tesi et al. 2007) and river ecosystems (Hedges et al. 1994; Hedges et al. 2000; Benner and Opsahl 2001). The characterisation of OM in the water column of lakes using lignin-derived phenols only received limited attention although it constitutes the main intermediate between soils of the watershed and lake sediments. Organic matter issuing from angiosperms yields both [S] and [V] compounds while gymnosperms only produce [V] derivatives (Hedges and Mann 1979a; Hedges and Ertel 1982). Our results for values of C/V versus S/V (Fig. 3) are lower than those from pure plant sources cited in the literature (Hedges and Mann 1979a; Goñi and Hedges 1992).

The S/V values we report are in accordance with those observed in soil layers by Otto and Simspon (2006). The DOM and POM S/V ratios with values greater than 0.4 we observed are likely associated with angiosperms or peatland soil signatures (Teisserenc, personal communication). Although, no significant differences appear between months, higher S/V ratios are mainly observed in June. Lower S/V ratios could be resulting from greater gymnosperms contribution, pedogenetic processes (Otto and Simpson 2006) or selective dissolution/sorption processes in soil, prior to the introduction of the terrestrial OM

Table 4 Average summer values of lignin biomarkers in the dissolved (DOM) and particulate organic matter (POM), sampled in June, July, August and September, of six boreal forest lakes

Lignin biomarker	Bellevue ($n = 4$)		Bréhard ($n = 4$)		Desjardins-East ($n = 4$)		Desjardins-West ($n = 4$)		Malartic ($n = 4$)		Preissac ($n = 4$)		ANOVA	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	*F ratio*	Prob *F*
DOM $\lambda 8$	0.35^{b}	0.09	0.30^{b}	0.16	0.45^{ab}	0.12	0.31^{b}	0.11	0.69^{a}	0.43	0.37^{b}	0.14	4.51	0.01
DOM $\Sigma 8$	4.14^{b}	2.92	4.53^{b}	3.13	5.90^{ab}	3.73	3.42^{b}	3.00	10.37^{a}	6.73	2.78^{b}	1.40	5.51	0.005
DOM S S	0.051	0.006	0.058	0.027	0.102	0.047	0.067	0.044	0.149	0.147	0.056	0.017	NS	NS
DOM S V	0.29^{b}	0.08	0.24^{b}	0.13	0.34^{ab}	0.09	0.24^{b}	0.09	0.52^{a}	0.28	0.31^{b}	0.12	5.81	0.004
DOM S C	0.0069^{b}	0.0014	0.0055^{b}	0.0022	0.0093^{ab}	0.0016	0.0070^{b}	0.0022	0.0141^{a}	0.0065	0.0086^{b}	0.0019	6.46	0.02
DOM S P	0.17^{b}	0.02	0.18^{b}	0.07	0.22^{b}	0.03	0.18^{b}	0.05	0.35^{a}	0.14	0.21^{b}	0.04	7.31	0.001
DOM S/V	0.18	0.03	0.26	0.07	0.30	0.11	0.29	0.16	0.25	0.11	0.19	0.03	NS	NS
DOM C/V	0.024	0.002	0.030	0.017	0.028	0.004	0.030	0.004	0.029	0.007	0.030	0.007	NS	NS
DOM P/(V+S)	0.53^{b}	0.07	0.69^{a}	0.18	0.52^{b}	0.10	0.61^{ab}	0.09	0.59^{ab}	0.18	0.63^{ab}	0.14	5.30	0.005
DOM 3,5-Bd/V	0.62	0.03	0.71	0.13	0.59	0.06	0.61	0.06	0.66	0.21	0.71	0.09	NS	NS
DOM (Ad/Al)v	1.00	0.19	0.98	0.12	0.99	0.15	1.05	0.25	1.10	0.23	0.95	0.06	NS	NS
POM $\lambda 8$	0.81^{b}	0.13	0.76^{b}	0.25	0.98^{ab}	0.23	0.77^{b}	0.15	1.16^{a}	0.34	0.78^{b}	0.30	7.32	0.001
POM $\Sigma 8$	22.83^{b}	4.43	20.97^{b}	6.20	31.87^{a}	6.84	24.33^{ab}	4.37	21.04^{b}	9.55	11.39^{c}	5.98	14.50	<0.0001
POM S S	0.16	0.07	0.27	0.14	0.22	0.08	0.16	0.03	0.27	0.12	0.16	0.13	NS	NS
POM S V	0.64^{b}	0.07	0.48^{c}	0.12	0.75^{ab}	0.17	0.60^{bc}	0.14	0.85^{a}	0.22	0.60^{bc}	0.18	14.09	<0.0001
POM S C	0.011^{b}	0.002	0.018^{b}	0.006	0.014^{b}	0.003	0.013^{b}	0.008	0.040^{a}	0.008	0.020^{b}	0.012	14.04	<0.0001
POM S P	0.31^{c}	0.01	0.34^{bc}	0.04	0.35^{b}	0.01	0.31^{bc}	0.02	0.45^{a}	0.04	0.34^{bc}	0.03	35.36	<0.0001
POM S/V	0.24^{b}	0.09	0.54^{a}	0.20	0.29^{ab}	0.09	0.29^{ab}	0.07	0.30^{ab}	0.10	0.25^{b}	0.14	3.54	0.03
POM C/V	0.016^{b}	0.002	0.038^{ab}	0.017	0.019^{b}	0.003	0.022^{b}	0.008	0.047^{a}	0.002	0.031^{ab}	0.013	5.76	0.004
POM P/(V+S)	0.39^{a}	0.05	0.48^{a}	0.10	0.38^{a}	0.08	0.42^{a}	0.06	0.42^{a}	0.11	0.48^{a}	0.13	3.40	0.03
POM 3,5-Bd/V	0.39	0.02	0.47	0.08	0.35	0.02	0.40	0.05	0.41	0.08	0.41	0.05	NS	NS
POM (Ad/Al)v	1.46^{a}	0.18	1.31^{abc}	0.07	1.47^{a}	0.11	1.35^{ab}	0.15	1.05^{c}	0.11	1.10^{bc}	0.11	7.88	0.0006

Differences among lakes has been established using a two-way ANOVA without repetition along with Tuckey honestly significant difference (values for $\lambda 8$ are mg/100 mg OC and values for other lignin biomarker and 3,5-Bd are mg/g)

Significance threshold $p < 0.05$, *NS* no significance

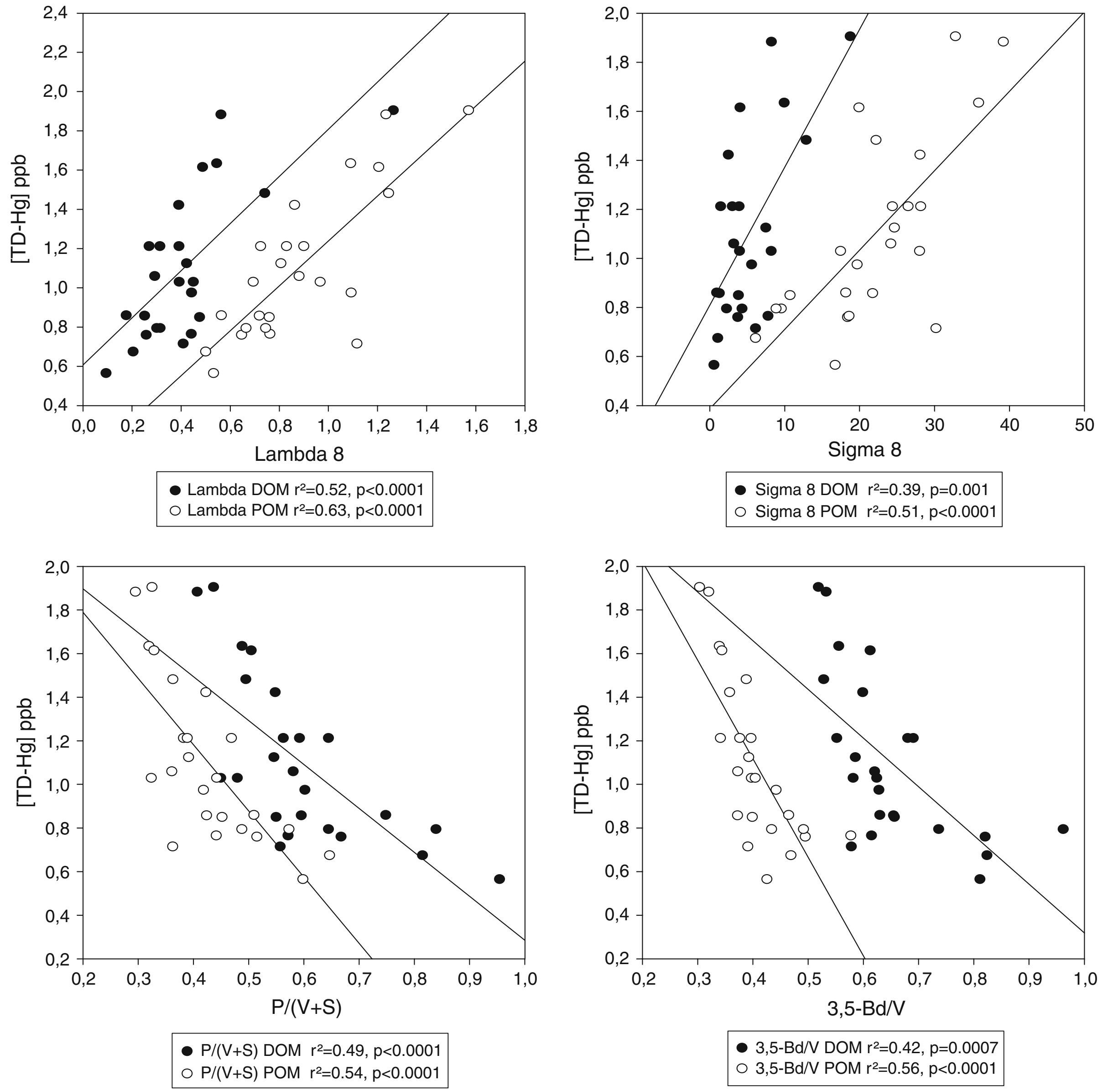


Fig. 2 Relationships between [TD-Hg] and lignin derivatives biomarkers Lambda (λ8), Σ8, P/(V + S) and 3,5-Bd/V for DOM (*squares* and *full line*) and POM (*circles* and *dotted line*) for all six lakes of the boreal forest sampled in June, July, August and September 2005

in the water column (Kaiser et al. 2001; Rumpel et al. 2002; Houel et al. 2006; Hernes et al. 2007). The degradation of lignin through fungal, microbial and fractionation, during leaching and sorption in soil, has been reported to modify signatures in soils horizons from pure sources signals (Hedges et al. 1988; Opsahl and Benner 1995; Klap et al. 1999; Hernes et al. 2007). This degradation of lignin has been associated with changes in S/V and C/V ratios (Hedges et al. 1988; Opsahl and Benner 1995; Dittmar and Lara 2001). Hence, lower S/V ratios in the months of July, August and September (Table 3) could be the result of the predominantly warmer and humid conditions occurring during summer, favouring microbial-mediated lignin decomposition in soils (Kaiser et al. 2001). An alternative explanation could be related to

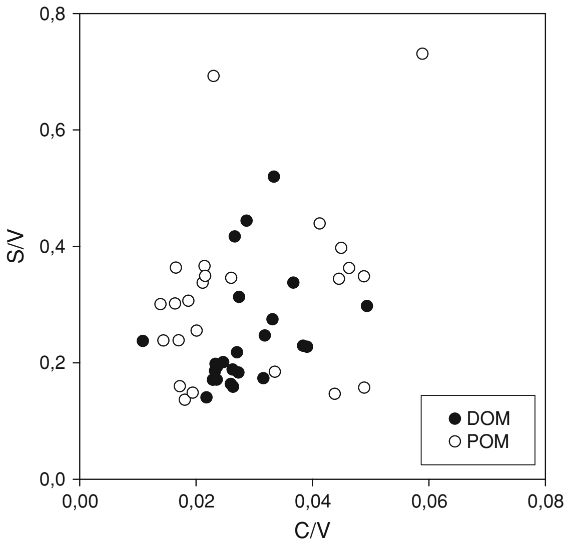


Fig. 3 Scatter plot of OM characteristics from six boreal forest lakes sampled in the month of June, July, August and September. DOM, dissolved organic matter; POM, particulate organic matter; C/V, cinnamyl/vanillyl phenols, S/V, syringyl/vanillyl phenols

lignin photo-oxidation processes having course in the water column. Photo-oxidation has been accounted to explain a two-fold decrease in the abundance of dissolved [S] compared to [V] contents in riverine and ocean waters (Opsahl and Benner 1998; Benner and Opsahl 2001; Hernes and Benner 2003). However, if photo-oxidation was that substantial, then acid/aldehyde ratio of [V] ((Ad/al)v) would be expected to increase as observed by Opsahl and Benner (1997, 1998). In the absence of a significant change in (Ad/Al)v ratio during the studied period, photo-oxidation appears to play a minor role in the shift observed in the S/V ratio.

The studied lakes appear to receive plant tissues impoverished in [C] phenols. Substantial inputs from vascular plant woody tissues could account for the very low C/V ratios (<0.06) (Fig. 3). Only herbaceous species, conifers needles and leaves of both angiosperms and gymnosperms contain [C] (Hedges and Mann 1979a) while lignin molecules from woody structures do not. An alternative and more likely explanation for the low observed C/V values could be the loss of [C], through sorption, in deeper soil horizon prior to the entry of DOM and POM in the lakes (Rumpel et al. 2002; Kaiser et al. 2004; Hernes et al. 2007). Some authors reported that C/V ratios remain pretty constant between pure vegetal sources, leaf litter and the upper soil horizon (Otto and Simpson 2006). However, a significant increase in C/V ratios has been observed in the deeper inorganic soil horizon with respect to the organic soil horizon (Houel et al. 2006). That is, [C] tend to be leached disproportionately, compared to [V] phenols upon early degradation processes (Opsahl and Benner 1995; Klap et al. 1999; Dittmar and Lara 2001). The mobility of [C] in soil environments could occur not only horizontally—erosion toward lakes—but also vertically (Kaiser et al. 2001; Rumpel et al. 2002). This migration would result in the preferential storage of certain lignin degradation products in the deep mineral horizons (Rumpel et al. 2002). Although one laboratory study reported higher resistance of the [C] phenols to photo-oxidation compared to the [V] phenols (Opsahl and Benner 1998), the absence of shifts in the (Ad/Al)v makes unlikely the influence of photo-oxidative processes a viable explanation for changes in C/V ratios. Hence, the increasing C/V ratios in the DOM fraction (prob. *F*: 0.0009) throughout the sampling period could be the result of a selective leaching of cinnamyls, and ester-bound acids (Opsahl and Benner 1995; Klap et al. 1999). Besides, decreases of the C/V ratios were solely reported to occur during the pedogenetic or diagenetic OM degradation (Opsahl and Benner 1995; Klap et al. 1999; Louchouarn et al. 1999). In temperate regions, increased leaching of litter OM has been reported to occur towards the end of summer seasons (Huang and Schoenau 1996; Kaiser et al. 2001). However, as presented in Table 3, a decrease in [S], [C] and [V] lignin biomarkers would rather reflect a greater influence of spring runoff from snowmelt in a boreal region.

OM characterization: state of degradation according to lignin biomarkers ratios

P/(V + S) ratios

Dittmar and Lara (2001) proposed, when certain conditions are met, that the P/(V + S) indices can be used as an unequivocal indicator of terrestrial aerobic OM degradation, since demethylation by brown-rot fungi affects exclusively the [V] and [S] contents. Phenols [V] and [S] families are exclusively derived from ligneous OM (Hedges et al. 1988). However, [P] phenols are not restricted to terrestrial OM CuO oxidation derivatives. Brown macroalgae and plankton-derived amino acids have presented [P] phenol fingerprints affecting the P/(V + S) ratios (Goñi and Hedges 1995). Hence, although [P] compounds are not exclusive to terrestrial plants, in oligotrophic lakes the contribution of the autochthonous freshwater OM can be negligible. In a wide spectrum of lake trophic state, [P] signature can be largely influenced by autochthonous (lacustrine) inputs. Nevertheless, since *p*-hydroxyacetophenone (Pn) is exclusively derived from lignin constituents (Hedges et al. 1988) a constant ratio or a correlation between Pn and [P] supports the use of [P] as a compound predominantly terrestrially derived (Houel et al. 2006). The strong correlation we observed between P and Pn ($r^2 = 0.90$) indicates that *p*-hydroxyphenols are indeed mostly related to ligneous compounds (Fig. 4). In our study, the variations of the P/(V + S) ratios over the summer months for all lakes are characterized by a clear increase in both the dissolved and particulate fractions ($p < 0.0001$) (Fig. 5a). This observation suggests a progressive increase of the state of degradation of the terrestrial OM entering the lakes from early to late summer.

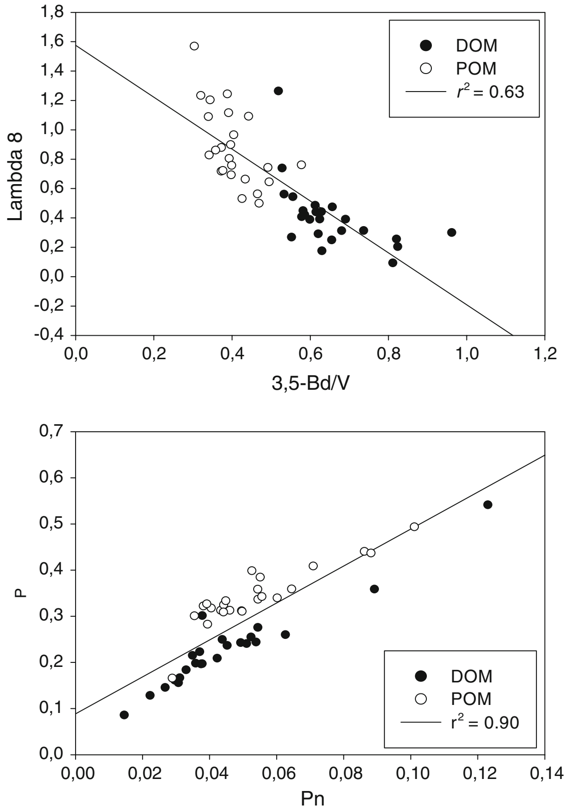


Fig. 4 Relationship between lignin derivatives biomarkers 3,5-Bd/V and lambda 8 and relationship between the sum of *p*-hydroxy phenols (P) and *p*-OH acetophenone (Pn) for all six lakes of the boreal forest sampled in June, July, August and September 2005

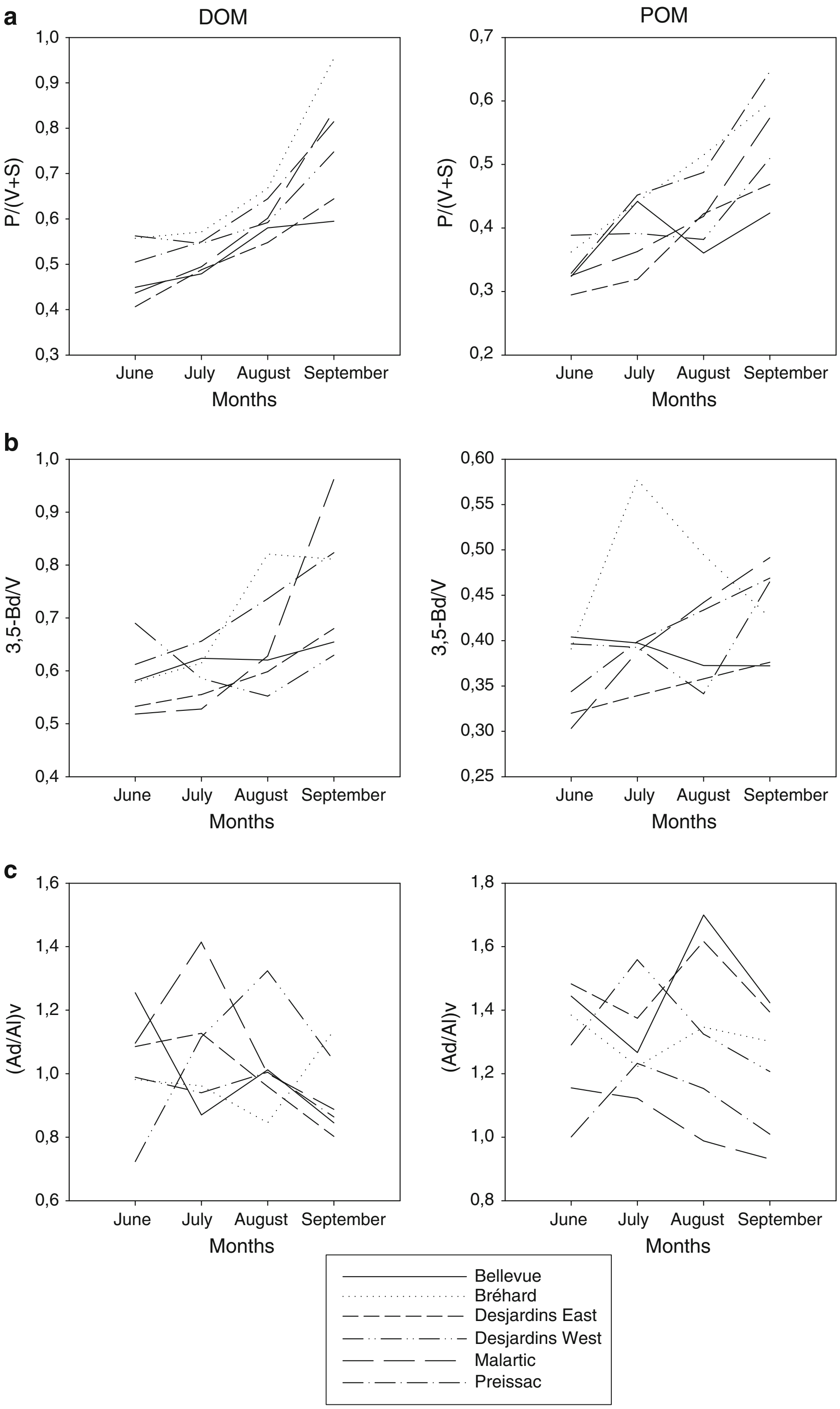
3,5-Bd/V ratios

The 3,5-Bd is not a lignin derived compound *per se* but rather derives from tannins and flavonoids (Goñi and Hedges 1995). Hence it has been proposed as an indicator of soil humification processes (Prahl et al. 1994; Farella et al. 2001; Houel et al. 2006). Like [P] compounds, the 3,5-Bd can also origin from autochthonous brown-macroalgae (Goñi and Hedges 1995) but once again, this has negligible effect in freshwater ecosystems (Houel et al. 2006). Figure 5b shows that the DOM 3,5-Bd/V ratios present a progressive maturation through the summer season ($p = 0.01$). However, no clear and significant temporal trend is observed in the POM fraction. The 3,5-Bd/V values we observed for both DOM and POM were all over 0.3. Meanwhile, Prahl et al. (1994) and Louchouarn et al. (1999) reported sedimentary 3,5-Bd/V values mainly under 0.3. In boreal forest soils, Houel et al. (2006) also observed 3,5-Bd/V ratios mostly all under 0.3 for organic soil horizons, while inorganic soil horizon had values that ranged between 0.2 and 1.5 on average, soils under gymnosperms cover presenting higher values. To explain the high 3,5-Bd/V ratios found in the water column OM, it could be suggested that OM from inorganic soil horizons could largely contribute to allochthonous OM inputs or, as suggested by Houel et al. (2006), vertical maturation in soil could reflect maturation processes occurring during lateral transport of OM from the watershed to the water column. The good correlation observed between $\lambda 8$ and 3,5-Bd/V ($r^2 = 0.63$) is indeed suggesting that 3,5-Bd is a biomarker of TOM (Fig. 4). The distinction between DOM and POM on the graph also confirms that distinct diagenetic transformations occur in the water column between POM and DOM.

(Ad/Al)v ratios

Increasing (Ad/Al)v ratios reflect greater progress of pedogenetic processes by white-rot and soft-rot fungi

Fig. 5 Monthly summer variations of lignin derived indicators of organic matter degradation. **a** P/(V + S), **b** 3,5-Bd/V and **c** (Ad/Al)v



(Hedges et al. 1988; Goñi et al. 1993; Nelson et al. 1995) or microbial degradation in the water column (Opsahl and Benner 1995). Here, the measured temporal variations of either the POM or DOM (Ad/Al)v ratios do not allow for any clear-cut interpretation (Fig. 5c). The quick monthly shifts of

(Ad/Al)v values could simply illustrate seasonal changes in the watershed flora composition, since [V] are produced by all terrestrial plants in varying amounts. For example, in boreal region, black spruce (*Picea mariana*) dominates the cover of many watersheds and fresh pollen have presented high (Ad/Al)v values (Hu et al. 1999).

Lignin biomarkers as tracers of mercury

The role of OM as a ligand, a transport vector or a speciation factor influencing both Hg mobility and bioavailability has been addressed by several authors (Montgomery et al. 2000; Haitzer et al. 2002; Porvari et al. 2003; Ravichandran 2004; Chadwick et al. 2006). Conventional indicators of terrestrial OM inputs, such as lake water color, DOC or C:N ratios were used with some of predictive power when comparing oligotrophic lakes (Ravichandran 2004) but are weak predictors of the [TD-Hg] when comparing lakes of differing trophic status.

Taking into account temporal and spatial variations reflecting terrestrial inputs, lignin OC-normalized yields ($\lambda 8$), present a fair predictive power to determine [TD-Hg] in the water column in both POM (r^2, 0.63; $p < 0.0001$) and DOM (r^2, 0.52; $p < 0.0001$). Although, both DOM and POM slopes are similar when using $\lambda 8$ to predict [TD-Hg] (Fig. 2), DOM appears to be of greater importance than POM in [TD-Hg] transport, since lower $\lambda 8$ values of DOM are associated with higher [TD-Hg] than POM. These positive relationships illustrate the importance of both POM and DOM as vectors of Hg from the watershed, underlying the importance of terrestrial OM as a vector of transport of Hg to the water column. Similarly, lignin concentration ($\Sigma 8$) is positively related to [TD-Hg], DOM being once again of greater influence for the transport of [TD-Hg]. These results are in accordance with work on atmospheric Hg deposition in the boreal forest done by Hintelmann et al. (2002). Within a few months following deposition of enriched stable isotopes of Hg, the authors observed that only 1% of the newly deposited Hg appeared in runoff, 8% was volatized in the atmosphere, and 66% was associated with ground vegetation while the rest was added to soils. They concluded that senescence and decomposition of the vegetation in the litterfall was the main pathway of Hg incorporation in the soil pool. Hence, Hg bound to decaying plants into the soils, forming the OM pool, are largely responsible for Hg found in the water column.

Plant foliage accumulates atmospheric Hg as a function of time of exposure to Hg-bearing air (Frescholtz et al. 2003). A ten fold increase in Hg concentrations from spring bud break to autumn litterfall has been observed (Rea et al. 2002). Stomata and physiologically active mesophyll cells appear to be the site of sequestration for foliar Hg (Hanson et al. 1995). In turn, 80% of total Hg in the aboveground biomass is found in leaves (Ericksen et al. 2003), leading some authors to conclude that deciduous species are playing a more active role in Hg cycling than evergreen species. Consequently, deciduous angiosperms should be greater contributor of Hg inputs to the water column than evergreen gymnosperms. However, no pattern of influence from the flora composition of the watershed could be observed with respect to [TD-Hg]. Scatter plot of the contribution of angiosperms and gymnosperms (S/V) in the OM does not predict [TD-Hg] in the water column ($p > 0.05$) (Table 2). Non-woody tissues present the highest Hg concentrations in plant shoot. Hence, contribution of leaves, needles and herbaceous tissues to Hg exports should be greater compared to woody tissues. However, the C/V ratios do not correlate with [TD-Hg]. Pedogenetic processes in the soils could be influencing S/V and C/V ratios. Dittmar and Lara (2001) used these ratios as indicators of diagenetic degradation, since [V] reactivity is lower that of [S] and [C] compounds (Hedges et al. 1988 Opsahl and Benner 1995). However, Houel (2002) identified potential biases when using the S/V and C/V ratios as indicators of degradation since differences in values could be attributable to changes in floral composition such as the contribution of pollen (Hu et al. 1999).

As previously mentioned, [P] which are not exclusively derived from lignin, are less likely degraded than compounds of the [V] and [S] families (Goñi and Hedges 1995). Hence, the P/(V + S) ratios indicate the state of degradation of the OM. In both DOM and POM a greater state of degradation is associated with a lesser [TD-Hg] in the water column—e.g. inverse relationship between P/(V + S) and [TD-Hg] (Fig. 2). Consequently, the fresher the OM entering the lake water, the more Hg it appears to carry to the aquatic ecosystem.

Similarly to P/(V + S) ratios, 3,5-Bd ratios are negatively correlated to [TD-Hg] (Fig. 2). Elevated 3,5-Bd concentrations are related to the accumulation of humified OM due to cell senescence during humification processes. These results suggest that most of the mercury transported by the OM entering the lakes is coming from the upper soil horizon or with fresher material. These results reinforce previous work done in Sweden which reported that Hg transport is predominantly taking place in the upper layer of soil and that 80% of Hg atmospheric deposition is located in the mor layer (Aastrup et al. 1991).

Conclusion

Lignin biomarkers, taken as indicators of the sources and the state of degradation of terrigenous POM and DOM inputs, are powerful tools when comparing lakes of differing trophic status and allow to follow the role of terrestrial OM in the transport of pollutants like Hg to boreal lakes. In the observed set of lakes from the boreal forest, lignin-derived phenols in the dissolved and particulate OM fractions revealed the great spatial and temporal variability of terrestrial inputs. The $\lambda 8$ and $\Sigma 8$ lignin indicators were higher in June and decreased to reach their lowest values in September. The spatial and temporal variation of $\lambda 8$ and $\Sigma 8$ were significantly related to [TD-Hg] concentrations in the water column. Source descriptors of OM varied temporally only in the DOM, but selective leaching of cinnamyls through dissolution and sorption processes are suspected to play a major role in the shift of C/V ratios. The POM C/V ratios remained constant throughout the season. The relative contribution to the bulk DOM-TOM from angiosperms versus gymnosperms sources (S/V) did not vary during the summer season. No relationship was found between the source indicators of the terrestrial OM and [TD-Hg]. However, the indicators of OM degradation and maturation showed a clear negative correlation with [TD-Hg], suggesting that fresh plant materials are important Hg vectors to the water column. These indicators also suggested a progressive degradation of terrestrial OM inputs to lakes along the summer season. Inversely, OM that has undergone extensive pedogenesis or humification in the soils carries less Hg to the aquatic ecosystem. The surface layer of soils appears to be the main vector of terrigenous Hg toward lake water columns. Thus, this study stresses the importance of properly managing watersheds in the sense of limiting massive remobilization of fresh soil organic matter after logging or agriculture practices in order to limit terrigenous mercury inputs to boreal lakes.

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