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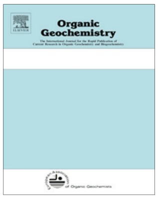

Variations in lignin-derived phenols in sediments of Japanese lakes over the last century and their relation to watershed vegetation

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ABSTRACT

Lignins have been used as a biomarker to explore changes in terrestrial organic matter input into lakes and to investigate past watershed vegetation. Burial of organic carbon (OC) in lake sediments, an important component of the global C cycle, is likely associated with the terrestrial OC input. However, few studies have explored changes in terrestrial C input into lakes in the last century. Furthermore, the relationship between lignin phenol compositions and watershed vegetation remains poorly examined. In this study, we examined changes in OC concentrations, OC mass accumulation rates (MAR), and lignin phenol compositions over the last century in sediments from six lakes in Japan that differ in watershed land-use and vegetation. The sediments were dated using ^{210}Pb and ^{137}Cs, and showed increased OC concentrations and MARs in three lowland lakes over the last century. This pattern was not found in three mountain lakes. In one of the lowland lakes, lignin phenol concentrations normalized to OC did not change during the periods with high OC concentrations and MARs. This indicates that not only eutrophication but also enhanced terrestrial OC input could lead to greater burial of OC. The lignin phenol compositions did not show clear trends over the last century in most of the lakes examined. The ratios of syringyl to vanillyl phenols and the lignin phenol vegetation index had significant relationships with proportions of angiosperms in watershed vegetation. These results demonstrate that lignin phenols are useful in inferring recent as well as past changes in lake watershed environments.

1. Introduction

Lignins are polymers of phenols synthesized by higher (vascular) plants to support their vascular systems (Weng and Chapple, 2010; Novo-Uzal et al., 2012). The types of phenols yielded by alkaline copper oxide (CuO) oxidation differ among plant taxa and among tissue types. Vanillyl phenols are present in all higher plant tissues, whereas syringyl phenols are synthesized only by angiosperms, and cinnamyl phenols are only abundant in non-woody tissues. Therefore, lignin phenol compositions can indicate taxonomic groups of higher plants (gymnosperms and angiosperms) and tissue types (woody tissue and non-woody tissue) of land-derived organic matter (Hedges and Mann, 1979; Jex et al., 2014). Most terrestrial plants produce lignins, which are recalcitrant toward microbial degradation (Meyers, 1997). As such, lignins found in sediments have often been used to explore historical changes in terrestrial organic matter input in aquatic ecosystems and terrestrial vegetation (Hedges et al., 1982; Meyers and Ishiwatari, 1993; Jex et al., 2014).

Recent studies have shown that organic carbon (OC) accumulation rates in inland freshwater sediments (e.g., lakes) are comparable to, or much higher than, those in marine sediments and terrestrial soils, indicating the importance of organic C burial in lake ecosystems in the global C cycle (Cole et al., 2007; Tranvik et al.,

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2009; Hanson et al., 2014). The high burial efficiency of OC in lake sediments is likely related to the preservation of terrestrially derived organic C in sediments on a millennial timescale (Cole et al., 2007; Sobek et al., 2009). The C accumulation rates are also known to be higher in lakes exposed to greater anthropogenic influences, such as eutrophication (Schelske and Hodell, 1991; Meyers, 2006; Downing et al., 2008; Anderson et al., 2013), logging, urbanization (Moingt et al., 2014), and impoundment (Teisserenc et al., 2014). Despite such recent changes in C input into lake ecosystems, few studies have explored the relative contribution of terrestrial organic matter to C deposits over the last century (Hyodo et al., 2008; Moingt et al., 2014; Chmiel et al., 2015).

Earlier studies used lignin phenols in lake sediments to reconstruct past vegetation types in watersheds, such as gymnosperms versus angiosperms or woody versus herbaceous species, by referring to the phenol compositions of plant tissues of these taxonomic groups (Hedges et al., 1982; Ishiwatari and Uzaki, 1987; Moingt et al., 2014). Further, abiotic (e.g., photo-oxidation) and microbial degradation prior to sedimentation can alter lignin phenol compositions (Hedges et al., 1988; Opsahl and Benner, 1995; Hernes and Benner, 2003). Teisserenc et al. (2010) confirmed that lignin-derived phenols reflect the vegetation in the watershed in a boreal region. However, it is still unclear whether this relationship could hold in temperate regions where angiosperms often dominate over gymnosperms.

In this study, we explored historical changes in the OC concentrations, OC mass accumulation rates (MAR), and lignin phenol compositions in the sediments of three lowland and three mountain lakes in Japan. We dated the sediments using ^{210}Pb and ^{137}Cs and focused on the last century, when the anthropogenic influence became globally significant. Watersheds of the lowland lakes currently include both urban and agricultural lands, whereas those of the mountain lakes appear to be unaffected by direct human activity. Therefore, it was expected that eutrophication and land-use change altered OC MARs and lignin phenol compositions in the lowland lakes over the last century. However, such patterns were not expected to emerge in the mountain lakes. Further, these lakes include watershed vegetation in a temperate region that differ in proportions of angiosperms and gymnosperms as well as life forms such as trees and grasses. These differences allowed us to assess the environmental factors that affect lignin phenol compositions through a comparison of the lakes. We investigated the relationship between lignin phenol compositions and the watershed vegetation, which was estimated using a geographic information system (GIS). For the analysis, we added the results of a previous analysis of Lake Biwa, the largest lake in Japan (Hyodo et al., 2008). Our results showed that the patterns in OC inputs into lakes and the relative contribution of terrestrial OC to them varied across the different lakes examined, and that lignin phenols could certainly reflect the watershed vegetation.

2. Materials and methods

2.1. Study sites

We sampled the lake sediments of six lakes: lakes Akan, Oshima-Ohnuma, Kizaki, Rausu, Niseko-Ohnuma and Mikuri-ga-ike (Fig. 1 and Table 1). Three of these lakes (Akan, Oshima-Ohnuma and Kizaki) are situated on plains where the watersheds include urban and agricultural areas. The other three lakes (Rausu, Niseko-Ohnuma and Mikuri-ga-ike) are located in mountainous regions with no urban or agricultural areas in the watershed (Fig. 1). We used previously published data on Lake Biwa to compare lignin phenol compositions across lake sediments (Hyodo et al., 2008).

2.2. Sediment sampling

Sediment samples of lakes Rausu and Niseko-Ohnuma and those of lakes Mikuri-ga-ike and Kizaki were collected in July 2010 and August 2011, respectively. Sediments of Lake Akan were collected in July 2010 and July 2012, because the sediment core (Ak2) obtained by the first sampling in 2010 (30 cm) was not long enough to represent the last century (see Results). The core collected in 2012 (AKE) was used for OC and lignin phenol analyses. Samples of lakes Rausu, Niseko-Ohnuma, Mikuri-ga-ike and Akan (Ak2) were collected using a gravity corer fitted with an acrylic tube (11 cm i.d. and a length of 50 cm; model HR, RIGO Co., Ltd., Saitama, Japan). Cores from Lake Oshima-Ohnuma were collected in February 2011 using a 1 m long gravity corer (model HRL, RIGO Co., Ltd.). The samples from lakes Kizaki and Akan (AKE) were collected by professional divers using the acrylic tubes. Several undisturbed cores were collected from each lake. One core from each lake was selected for this study and was sectioned at 1 cm intervals immediately after collection. The only exception was that for Lake Mikuri-ga-ike which was sectioned at 0.5 cm intervals. The samples were placed into plastic bags and were stored in freezers. They were later freeze-dried and homogenized using a mortar and pestle for the following analyses.

2.3. Determination of the age and accumulation rates of the core sediments

The core chronology was determined by the constant rate of supply (CRS) method of ^{210}Pb dating (Appleby and Oldfield, 1978) and was checked by the ^{137}Cs peak traced in 1962–1963 (Appleby, 2001). The age of a given sample mass depth was calculated using the $^{210}\mathrm{Pb}_{\mathrm{excess}}$ inventory, which was obtained by the numerical integration of the radioactivity of $^{210}\mathrm{Pb}_{\mathrm{excess}}$ versus the mass depth profile using the following equations (Appleby, 2001):

$$A = \int_m^\infty \mathrm{C}(m)dm \tag{1}$$

and

$$A(0) = \int_0^\infty \mathrm{C}(m)dm, \tag{2}$$

where m denotes the depth of the sediment layer of age t, $\mathrm{C}(m)$ is the radioactivity of $^{210}\mathrm{Pb}_{\mathrm{excess}}$ at the depth m, and A and $A(0)$ are $^{210}\mathrm{Pb}_{\mathrm{excess}}$ inventories below m and the total inventories, respectively. From the values calculated above, the age t of sediments at depth m were calculated by

$$t = 1/\lambda \ln(A(0)/A), \tag{3}$$

where λ is the ^{210}Pb radioactivity decay constant.

Accumulation rate (r) at a given sample mass depth m was determined from the equation (Appleby, 2001)

$$r = \lambda A/\mathrm{C}(m), \tag{4}$$

where λ is the ^{210}Pb radioactivity decay constant, A is the total inventory below the mass depth, and $\mathrm{C}(m)$ is the radioactivity of $^{210}\mathrm{Pb}_{\mathrm{excess}}$ at the depth m.

^{210}Pb, ^{214}Pb, and ^{137}Cs activities were determined by the γ-spectroscopy analysis of the dried sediment. The dried samples were sealed in standard holders for one month to allow ^{222}Rn and its short-lived daughters to equilibrate. Radioactivities for the cores Mk6 from Lake Mikuri-ga-ike and Ra1 from Lake Rausu were determined with a Ge-detector (GWL–90-15–S, EG & G ORTEC, USA) equipped with a multichannel analyzer (MCA7700,