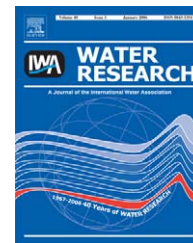


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Biogenic phosphorus in oligotrophic mountain lake sediments: Differences in composition measured with NMR spectroscopy

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ABSTRACT

Phosphorus (P) composition in alkaline sediment extracts from three Swedish oligotrophic mountain lakes was investigated using ³¹P-NMR spectroscopy. Surface sediments from one natural lake and two mature reservoirs, one of which has received nutrient additions over the last 3 years, were compared with respect to biogenic P composition. The results show significant differences in the occurrence of labile and biogenic P species in the sediments of the different systems. The P compound groups that varied most between these three systems were pyrophosphate and polyphosphates, compound groups known to play an important role in sediment P recycling. The content of these compound groups was lowest in the reservoirs and may indicate a coupling between anthropogenic disturbances (i.e., impoundment) to a water system and the availability of labile P species in the sediment. A statistical study was also conducted to determine the accuracy and reliability of using ³¹P-NMR spectroscopy for quantification of sediment P forms.

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1. Introduction

Most Scandinavian river systems are impounded and regulated in order to provide a source of hydroelectric power. Mountain reservoirs typically fill during summer and autumn, and water is then released during winter and early spring. This often results in yearly water level fluctuations greater than 10 m. In the years following impoundment, increased leaching of nutrients from inundated soil and vegetation increases the biological production within the reservoir. This has been termed the “inundation effect” and has been observed in mountain reservoirs in the Canadian Shield (Grimard and Jones, 1982) and in Scandinavia (Rodhe, 1964).

During post-impoundment years, however, the littoral zone is typically eroded by wave action and ice due to winter drawdown, eliminating it as a major food source for fish (Nilsson, 1964). Thus, after the initial increase in production due to the inundation effect, these systems seem to become less productive than prior to impoundment, resulting in declining fish populations (Runnström, 1955; Aass et al., 2004). Phosphorus (P) is a key nutrient, especially in oligotrophic mountain lakes and reservoirs. Primary production is dependent on external sources of P as well as the turnover and release of orthophosphate (ortho-P) from particulate P in the water column and available, labile P in the surface sediment. The extent of this mobilization is largely depen-

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dent on the character of particulate P. Because the dominant form of P load to sediment generally is biogenic P (see below) (Pettersson, 2001; Turner et al., 2005), the amount available for mineralization and subsequent release will impact the overall productivity.

Although there have been some publications dealing with P retention in reservoirs (e.g., Straskraba et al., 1995), most of the literature focuses on the inundation effect (Grimard and Jones, 1982; Hambright et al., 2004). A few studies have focused on nutrients in the sediments (e.g., Hellsten et al., 1993) but have yielded limited knowledge on how sediment P composition is affected by ongoing water level regulation in oligotrophic mountain reservoirs. Auer et al. (1998) used a P fractionation scheme to differentiate between sediment P species but it was inadequate in terms of providing detailed information about organic P species. These species are generally known to comprise the majority of potentially mobile P in sediments (Rydin, 2000; Reitzel et al., 2003; Ahlgren et al., 2005; Reitzel et al., 2005), and thus have great importance in the overall P turnover.

An efficient way of assessing the P composition in extracts of solid matrices, such as sediments and soils, is through the use of ^{31}P -NMR (nuclear magnetic resonance) spectroscopy. This method of analysis differentiates between P compound groups by using their specific resonance frequencies and can indicate the presence of ortho-P, pyrophosphate (pyro-P) and polyphosphate (poly-P), or organic-bound P (e.g., monoesters, diesters and phosphonates). While quantification of these compound groups in natural samples with ^{31}P -NMR have been performed previously, there has (to our knowledge) never been an attempt to statistically evaluate the accuracy of this procedure.

Of the various P compound groups identified by ^{31}P -NMR, the only one not considered organic or of entirely organic

origin is ortho-P, even if some of the detected ortho-P might be decomposition products from organic compounds. Both pyro-P and poly-P are inorganic compounds that result from biological transformations. Hence, the term biogenic P is used to denote all organic P compound groups, as well as pyro-P and poly-P (Ahlgren et al., 2005). Ortho-P is thus not included in this pool.

In this study, ^{31}P -NMR spectroscopy is used to determine the biogenic P composition in surface sediments from two mature mountain reservoirs and one mountain lake situated in Sweden. One of the reservoirs was subjected to P and nitrogen (N) nutrient addition over a period of three years in order to evaluate the trophic web response. The aim of this study was to statistically evaluate ^{31}P -NMR quantification and to detect possible differences in sediment P composition between natural lakes, reservoirs, and fertilized reservoirs.

2. Materials and methods

2.1. Lake and reservoir description

The reservoirs and the lake (Table 1, Fig. 1) are part of the Indalsälven river system in the province of Jämtland, Sweden. Lake Stor-Burvattnet (hereafter Lake Burvattnet) is the uppermost reservoir in the catchment and Lake Stor-Mjölkvattnet (hereafter Lake Mjölkvattnet) is a reservoir situated 1 km downstream of Lake Burvattnet. The drainage areas of these reservoirs are unpopulated and include mostly bare mountain regions above the tree-line, with forest and mires covering less than 15%. The reservoirs do not stratify during summer and ice cover usually occurs from late November to May or June. Water level fluctuates between 6 and 9 m

Table 1 – Lake and reservoir characteristics

	Lake Burvattnet	Lake Mjölkvattnet	Lake Ånnsjön
Catchment (km ²)	106	246	2900
Lake area (km ²)	13.2	13.6	65
Mean depth (m)	42	31	15
Max. depth (m)	139	97	40
Water retention time (year)	3.9	1.1	1.2
Sampling position	63°59'26 N, 13°20'46 E	63°52'57 N, 13°21'28 E	63°16'24 N, 12°36'43 E
Water level (above sea level) (m)	559–566	543–554	525
Dam construction (year)	1942	1942	—
Water column total P (µg/l)	4	7 ^a (4)	4
pH	6.8	6.8	7.3
Al (mg/g DW)	16	30	24
Ca (mg/g DW)	6	7	10
Mn (mg/g DW)	—	56	48
Fe (mg/g DW)	17	35	54
C (mg/g DW)	86	84	46
N (mg/g DW)	5	5	4
C/N (molar)	13	13	13

Metals, C, and N concentrations from surface (0–1 cm) sediment.

^a Indicates total phosphorus concentration after nutrient addition.

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