Mobility of Pb in Sphagnum-derived peat

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Abstract. One important assumption in applying 210Pb-dating is that atmospherically deposited 210Pb is immobilized in the peat or sediment column. This assumption has been challenged widely, but has never been evaluated experimentally. We evaluated Pb mobility and the chemical forms in which Pb is stabilized in peat profiles by adding either soluble or particulate Pb to intact peat cores that were maintained under different water level regimes (permanently high, permanently low, fluctuating between high and low) and were subjected to simulated precipitation over a five month period. By analyzing the behavior of stable Pb we made inferences about the expected behavior of 210Pb. Results indicate that added soluble Pb2+ was retained in the peat through physiochemical binding to organic matter, and as such Pb2+ was largely immobile in peat even under conditions of a fluctuating water table. Added particulate Pb was largely (most likely by physical entrapment), but not completely, immobilized in peat. In none of the water table treatments was there evidence to support mobility of Pb by alternating formation and oxidation of sulfides, or by any other mechanism. The binding of Pb2+ with organic matter at the peat surface, and the absence of Pb mobility lend credence to 210Pb-dating of Sphagnum-dominated peat deposits, which are over 90% organic matter throughout, and have high cation exchange capacities.

Introduction

Sphagnum-dominated peatlands have been used extensively for geochemical monitoring (e.g., Oldfield et al. 1978; Madsen 1981; Schell 1987; Cole et al. 1990; Vile et al. 1995). Sphagnum mosses grow apically from compact structures called capitula while dying at the base. The dead remains accumulate when the rate of organic matter production exceeds the rate of organic matter decomposition, resulting in a vertically accreting organic deposit that undergoes progressive chemical and structural alteration during long-term decomposition (Clymo & Hayward 1982). Sphagnum moss contains substantial amounts of unesterified polyuronic acids in their cell walls, accounting...
for 99% of it's cation exchange capacity (CEC). Decomposition of Sphagnum further contributes to Sphagnum's CEC by creating organics containing a greater number of negatively charged functional groups, which sorb positively charged metals (Clymo 1983). If left undisturbed, peat deposits are capable of recording historical environmental and anthropogenic changes.

\(^{210}\text{Pb}\)-dating is a popular tool used in reconstructing past environmental conditions in peat (Appleby & Oldfield 1978). Two implicit assumptions of using \(^{210}\text{Pb}\)-dating to derive age as a function of depth within a peat or sediment profile are: (1) there is a constant flux of \(^{210}\text{Pb}\) from the atmosphere to the surface of a peat or sediment deposit, and (2) atmospherically deposited \(^{210}\text{Pb}\) is immobilized in the vertically accreting peat or sediment column. The first assumption generally is regarded as valid, but the second assumption has been challenged widely.

The assumption of Pb immobility has been questioned based on interpretations of depth profiles of Pb concentration in peat. For example, in a study of metal distributions in Swedish raised mires, Damman (1978) found peaks in Pb concentration in adjacent hummock and hollow peat profiles that corresponded to the position of the water table within each profile measured on the day of sampling. Damman (1978) suggested that within the zone of water table fluctuation, Pb is immobilized as PbS when the peat is saturated. When the water table drops, oxidation to slightly soluble PbSO\(_4\) can allow for Pb mobility. Therefore, Damman (1978) attributed peaks in Pb concentration to the remobilization with subsequent accumulation of Pb within the zone of water table fluctuation. In light of this phenomenon, Clymo and Hayward (1982) suggested that the most important process responsible for heavy metal (including Pb) redistribution in peat may be the fluctuation in redox potential associated with water table movements creating aerobic-anaerobic boundaries, which in turn affect metal solubility and mobility. Other descriptive studies also have interpreted patterns in vertical distribution as indicative of at least partial mobility of Pb in peat (e.g., Pakarinen et al. 1983; Pakarinen & Gorham 1983).

The question of Pb immobility in peat or sediment profiles never has been evaluated experimentally, which seems surprising given the centrality of the Pb immobility assumption involved in the application of \(^{210}\text{Pb}\) dating. Therefore, we evaluated Pb mobility and the chemical forms in which Pb is stabilized in peat profiles by adding either soluble or particulate Pb to intact peat cores that were maintained under different water level regimes in the laboratory, and were subjected to simulated precipitation over a five month period.