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Deposition and migration of atmospheric Pb in soils from a forested silicate catchment today and in the past (Strengbach case): Evidence from ^{210}Pb activities and Pb isotope ratios

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ABSTRACT

^{210}Pb activities, Pb isotope ratios and elemental abundances of leachates from soils were determined to identify the origin of atmospheric Pb and characterize its migration in mineralogically and chemically different soil systems of a forested silicate catchment. Leaching experiments were performed to separate the leachable, mobile reservoir of the soil system – mainly containing atmosphere derived Pb – from that of the residual bedrock reservoir. Pb isotope data allow recognition of an evolution in the soil leachates with increasing depth pointing to at least two major Pb sources. Surface samples collected in 2001 show a Pb isotopic signature which is comparable with that of particulate matter (PM) collected in 1995 and 2005/2006 in an urban environment close to the catchment and hence corresponds to a very recent isotopic signature of the atmosphere. The more radiogenic Pb isotopic signature in soil leachates from 30 to 40 cm depth corresponds to older airborne Pb probably derived from historical mining and smelting close to the catchment (<5 km). ^{210}Pb inventories confirm trace element data and indicate that the soils are important sinks of atmospheric Pb in the uppermost part (40 cm) of the soil profile. The migration speeds derived from these inventories for the different depths (0.5 cm y^{-1}, 0.2 cm y^{-1}, 1.6 cm y^{-1}) suggest that the atmospheric Pb needs less than 150 years to reach the depth of 40 cm. Thus, the Pb enrichments above this depth might be related to a period of local mining activities which ceased in the mid-20th century. The soil solutions are not in isotopic equilibrium with the corresponding soil leachates. Soil solutions from 5 to 60 cm depth have Pb isotopic compositions similar to those of stream and spring waters and soil leachates from 10 to 20 cm depth. They carry a Pb with current atmospheric Pb isotopic compositions. The presence of anthropogenic Pb in spring waters might suggest that some of it migrated rather quickly through the soils.

1. Introduction

Anthropogenic Pb emitted from a great variety of sources into the atmosphere can be carried by submicrometer aerosols over long distances before its deposition under dry and/or wet conditions (Véron et al., 1994; Hamelin et al., 1997; Bollhöfer and Rosman, 2001; Haack et al., 2004; Grousset and Biscaye, 2005; Le Roux et al., 2008). Aerosol deposition is strongly controlled by parameters such as topography, wind direction, precipitation and vegetation (Pourcelot et al., 2003; 2008; Le Roux et al., 2008). The observed trace element enrichments in surface soils of remote areas provide clear evidence of long range transport of anthropogenic pollutants from urbanized regions (Boutron and Patterson, 1987; Berg et al., 1994; Halstead et al., 2000).

It has been shown that anthropogenic Pb is still dominating the input despite a decrease in Pb flux due to the ban of leaded gasoline in Europe in 2000 as discussed by Michelutti et al. (2009). These authors report Pb isotopic compositions, ^{210}Pb activities and elemental abundances of lake sediments from Baffin Island (arctic region in Canada) indicating a lack of decrease in the input of anthropogenic Pb. Diaz-Somoano et al. (2009) suggest that with the phasing out of leaded gasoline the influence of coal combustion becomes globally important. The current Pb flux is at least 100 times greater in rural environments than the natural pre-anthropogenic flux (Le Roux et al., 2005). Thus, anthropogenic Pb is even present and enriched in remote areas (Ng and Patterson, 1981; Boutron and Patterson, 1987; Erel et al., 1990) and might create together with other trace metals a specific risk for ecosystems. This is especially the case for ecosystems at higher altitudes. These are highly sensitive because the environmental conditions are extreme, growing seasons are short and most of them suffer from the deposition of atmospheric acid pollutants causing acidification of the soils and their depletion in nutrient basic cations (Probst et al., 1992; 2000). Thus, the observation and tracing

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of atmosphere derived pollutants deposited on soils and migrating through soil solutions to groundwater and/or spring waters remains an important task in environmental geochemistry especially for ecosystems at higher altitudes.

Many studies have already shown that Pb isotope ratios provide a very useful and effective method of monitoring and tracing past and present anthropogenic atmospheric pollution (Walraven et al., 1997; Lahd Geagea et al., 2008 and cit. therein). ^{210}Pb has been successfully determined in peat bogs, which are useful archives of Pb deposition, in order to date past atmospheric inputs (Novak et al., 2003; Le Roux et al., 2005; Shotyk et al. 2005; Michelutti et al., 2009). Atmospheric ^{210}Pb was primarily formed from the decay of gaseous ^{222}Rn in the atmosphere then sorbed onto the surface of aerosols before deposition. Therefore, this radionuclide can be used to trace the contribution of atmospheric particulates; similarly atmospheric ^{210}Pb soil inventories were used to estimate long term (>75 yr) deposition of submicron aerosols (Le Roux et al., 2007). Similarly, ^{210}Pb has successfully been used to trace the migration of non native Pb in soils and to discuss forest floor response times and depositional models of Pb for forested ecosystems (Kaste et al., 2003).

The aim of the present study is to quantify Pb impact on the small mainly spruce forested silicate catchment of the Strengbach streamlet in the Vosges mountains (France), to trace and quantify Pb migration in the soil and spring waters of the ecosystem, and to determine the rate of Pb migration by using Pb isotope ratios and soil inventories of ^{210}Pb. This catchment is particularly well suited for such a study because its isotopic (Sr, Nd, U, Ca, B, Li) and rare earth element characteristics have already been extensively studied and many processes occurring at the atmosphere–soil–water–vegetation interfaces have already been observed and described (Amiotte-Suchet et al., 1999; Aubert et al., 2001; 2002a; 2004; Schmitt et al., 2003; Schmitt and Stille, 2005; Stille et al., 2006; 2009; Cenki-Tok et al., 2009; Cividini et al., 2010; Lemarchand et al., 2010). The combined use of ^{210}Pb activity values and of frequently used Pb isotope ratios such as ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb is a particularly powerful approach for the quantification of the Pb impact in the different soil and water compartments as demonstrated recently in a study on lake sediments (Michelutti et al., 2009).

2. The setting of the forested Strengbach catchment

The forested Strengbach catchment is located in the eastern part of the Vosges mountains (NE of France). It covers an 80 ha area at altitudes ranging from 883 m at the outlet to 1146 m at the top (Fig. 1). This catchment has been transformed into a completely equipped environmental observatory with permanent sampling and measuring stations (http://ohge.u-strasbg.fr). The forest covers 90% of the area and is composed of about 80% spruce (mainly *Picea abies* L.) and 20% beech (*Fagus sylvatica*). The prevailing wind direction is west. The wet precipitation (rain and snow) is more abundant on the southern slope (HP plot; 1500 mm y^{-1}) than on the northern slope (PP plot; 1200 mm y^{-1}) (http://ohge.u-strasbg.fr). Hydrological and hydrochemical processes within the catchment have been studied extensively (Viville et al., 1993; Lu et al., 1995; Idir et al., 1999; Riotte and Chabaux, 1999; Tricca et al., 1999; Ladouche et al., 2001; Aubert et al., 2002b; Viville et al. 2006). The bedrock of the catchment is a fractured, hydrothermally altered Hercynian granite.

The northern slope bedrock was subjected to stronger hydrothermal alteration, which caused disappearance of albite and biotite and decreased K-feldspar abundances but an increase of quartz, clays and white mica contents and the occurrence of hematite (El Gh'Mari, 1995; Fichter, 1997). Three representative forested experimental

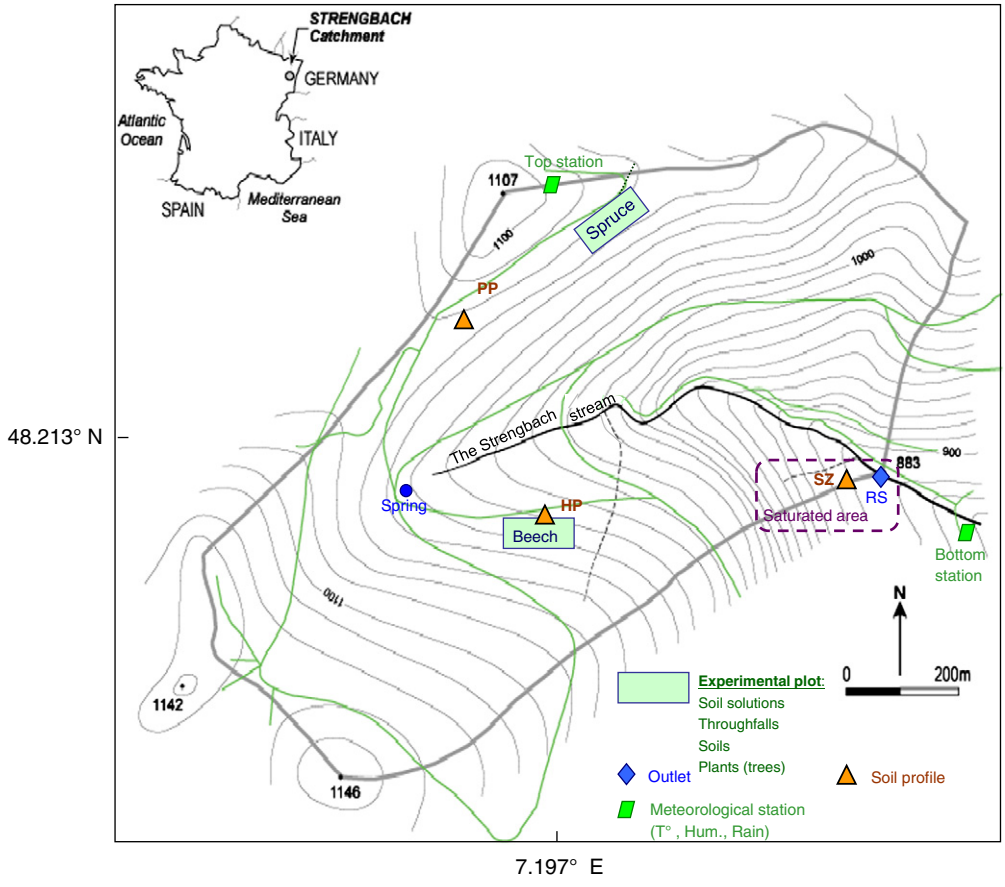

Fig. 1. Uppermost Strengbach catchment with sampling sites HP, PP and SZ. HP soil profile below beech and PP soil profiles below spruce. SZ: soil profile in the water saturated zone close to the catchment outlet.