DEPOSITION HISTORY OF TRACE METALS AND FALLOUT RADIONUCLIDES IN WETLAND ECOSYSTEMS USING ^{210}Pb CHRONOLOGY

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Abstract. A comparative study has been made of the history of lead and other trace metals that have been deposited on wetlands. A series of sediment cores from the USA, Ireland and the Czech Republic were measured for ^{210}Pb , Pb, other trace metals and the radionuclides ^{137}Cs, ^{90}Sr and ^{239,240}Pu. The ^{210}Pb chronology of the core profiles was established using the CRS method of Appleby and Oldfield and the minimum variance method of Tobin and Schell, i.e., the CRS-MV method. Using the minimum variance of the least-squares fit of the line representing the total core data and propagating the errors, the apparent time error ranges from 2 to 10 years. Cores were taken from Hudson River wetlands, a mountain top bog in the USA, blanket bogs in western and eastern Ireland, and bogs in a highly polluted and a "pristine" zone in the Czech Republic and provided profiles. At the most westward European station in Ireland, the Pb deposition history appears to exceed background levels at dates similar to those in eastern USA, whereas the profiles near Dublin exceed background values at approximately the same date but have maximum deposition values significantly later. Such initiation of the Pb deposition in Ireland could be due to long-range transport across the Atlantic Ocean. In the Czech Republic, the initiation of metal deposition occurs before that in Ireland and the USA, reflecting the earlier development of industrialization and release of metals.

1. Introduction

The role of atmospheric-introduced pollutants in ecosystems is of global concern. Studies have identified that aluminum and pollutant trace metals may cause damage to the biological functions of plants both from deposition on the leaves and by root uptake (Meyer, 1983). The rate of migration of trace elements through the upper soil layers is variable and plant uptake of these elements may be a problem in the future. To estimate element deposition and the migration rates over time in bog and forest ecosystems, radioactive tracers that have known input functions may be utilized. Input times for the tracers are from the atmospheric nuclear weapons testing period and the "instantaneous" input from the Chernobyl NPP and Kyshtym accidents in Ukraine and Russia, respectively that contaminated much of the Northern Hemisphere. The deposition of fallout radionuclides has been well documented for the northeastern USA by the Department of Energy - Environmental Measurements Laboratory in New York City, and in Europe by the Swedish Defense Ministry and the UK Atomic Energy Authority, Harwell (Krey and Krajewsky, 1970). These fallout tracers provide timing fluxes that can be used to estimate the trace metals deposition, provided a suitable geochemical repository is found. Such repositories for certain elements may be lakes as well as marshlands, bogs, forests and other organic-rich ecosystems. Biological activity in a bog decomposes plant matter that becomes humified at increasing depths.

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When organic matter decomposes, inorganic sediments of clay like material may remain to further retard migration (Schell *et al.*, 1989). Little or no mixing of many elements occurs below the active root zone where anoxic conditions exist, except by diffusion and advection due to water transport.

The development of a chronology for regional deposition of chemicals introduced into the environment from anthropogenic and natural sources provides information on quantitative measurement of pollutants in ecosystems. The main goal of this paper is to compare the chronology and intensity of atmospheric metal deposition (Pb, Cu, Cd, Ni, Zn) using peat cores from bogs in the northeastern USA, Ireland, and the Czech Republic.

2. Materials and Methods

2.1. SAMPLE SITES

The sampling sites selected are near sources of pollutants at a mountain top (ombrotrophic/mineratrophic) bog near Pittsburgh, PA, at a marshland on the Hudson River, New York, at blanket bogs in Ireland near both the west coast and Dublin, and in the Czech Republic at a relatively pristine site in southern Bohemia, Jezerni slat, and at one of the most polluted regions of Europe, Bozi Dar in northern Bohemia. These sites were selected because they record the pollutant input primarily from atmospheric deposition processes.

The Spruce Flats Bog, PA sampling site, 40°7 'N, 79°11' W, is located at 823 m elevation and is only 30 m below the peak of the Laurel Mountains of the western Allegheny Mountain system (Schell, 1987). The bog is east of the Great Plains and on the first mountain range where 1350 mm/y orographic precipitation occurs and where pollutants are deposited from local and long-range sources. The local sources have been heavy industries located in Pittsburgh and the Mid-West, including steel mills and coal mines that now produce only a small fraction of their peak. The Tivoli Bays core, 42°2'4" N, 73°55'57" W was taken at mile 120 of a back water Hudson River marshland shielded from the main river by a railroad landfill. One of the sites sampled in Ireland near the far western shore on the Atlantic Ocean, Bellacorick Bog, 54°6' N, 9°34' W with 1400 mm/y precipitation, was expected to be the least contaminated blanket bog in Europe. At the other Irish sites, Clara Bog, 53°20' N, 7°38' W and Kippure Bog, 53°10' N, 6°18' W near Dublin, heavy industries and domestic coal burning have developed nearby. The Czech Republic site Jezerni slat, is a bog with 1 m thick floating mat on top of a lake (Novak, 1990), located in the relatively pristine Sumava Mountains of southern Bohemia at an elevation of 1070 m with 760 mm/y precipitation. Bozi Dar Bog, 50°24' N, 12°54' E, is located in the Krusne hory Mountains of northern Bohemia near the center of the heavy industries of central Europe and has precipitation of 850 mm/y. The peat deposit reaches 5.5 m depth and consists of *Sphagnum*-derived material that has had little growth in recent years (Vile *et al.*, 1995).

2.2. SAMPLE COLLECTION AND ANALYSIS

Sediment cores were taken by driving a 10-cm diameter sharpened polyvinyl chloride tube vertically into a site away from tree roots and hummocks. The cores were sectioned into 1 or 2 cm thick layers, often in the field, weighed, dried at 70°C or freeze dried, and homogenized upon arrival in the laboratory. Particular care was taken to avoid contamination by using double plastic bags in field collections and by minimizing sample exposure to the laboratory environment. The first work on a core was to determine if the ^{210}Pb decay profile was continuous. Extensive radiochemical and element analyses were then initiated on the suitable cores.

The distribution of the natural radionuclide, ^{210}Pb, with a half-life of 22.3 years, in a sediment or bog core provides the time scale for atmospheric chemical input over the past 200 years. After dissolution with aqua regia, each layer was spiked with ^{208}Po, as a chemical yield tracer, and the solution electroplated onto silver discs for the analysis of the ^{210}Pb by measuring the ^{208}Po and ^{210}Po content. Aliquots were then taken for the various radiochemical and elemental analyses. Standard radiochemical techniques were used to analyze for the radionuclides ^{210}Pb, ^{137}Cs, ^{90}Sr, and $^{239,240}Pu$ (Volchok and de Planque, 1983; Schell and Barnes, 1986). Additional aliquots of each layer were taken for ICP-MS and ICP-AES analysis where up to 60 elements can be analyzed simultaneously. Analysis for specific elements were made with graphite furnace AAS. Duplicate samples were taken, where possible, and quality control procedures used to validate the analytical results. The ^{210}Pb data, used to construct the chronology for the sediment layers, applied the constant rate of supply (CRS) interpretation (Appleby and Oldfield, 1978) with the minimum variance treatment, the CRS/MV model (Tobin and Schell, 1988; Schell and Tobin, 1994). The ^{137}Cs, ^{90}Sr, and $^{239,240}Pu$ are global fallout radionuclides and have been deposited at well defined periods of weapons testing (Hardy *et al.*, 1968) and following the Chernobyl NPP accident in 1986.

3. Results and Discussion

3.1. LEAD DEPOSITION IN THE USA AND EUROPE

A comparative study of contaminated and pristine areas shows the global nature and timing of pollutant input to ecosystems. It also establishes methods to determine the inputs of heavy metals and their consequent exposure to man and to ecosystems over the past 200 years. The cores were: (a) dated using the ^{210}Pb technique to determine if they were suitable for further evaluation, (b) analyzed for Pb, Cd, Cu, Ni, Zn and other trace metals, and (c) compared with other geochemical and biological information to provide validation of the dating technique (Wieder *et al.*, 1994). Nuclear weapons test fallout radionuclides ^{137}Cs, ^{90}Sr, and $^{239,240}Pu$ were also measured on the same cores.

Examples of the concentration and deposition of Pb and ^{210}Pb found in the eastern USA, Ireland and the Czech Republic are shown in Figure 1. The Bellacorick Bog location is at the far west of Ireland where the nearest westerly land is the American continent, 3700 km away. This sampling location should have the lowest flux of heavy metals in Europe because it is influenced by precipitation from the eastern Atlantic with minimal contamination from the UK and the Continent. In contrast, the Clara Bog and the Kippure Bog cores show Pb increasing at the same time as Bellacorick but also show the influence of urban and industrial Pb sources, with Kippure Bog, near Dublin, giving a maximum flux in 1948 and Clara Bog, a maximum in 1978 (Mitchell *et al.*, 1992). The Czech Republic bog cores indicate that pollution from industrialization occurred earlier, namely from coal burning for heavy industries that must have been initiated about 1680. Bozi Dar Bog shows a rapid increase of several metals especially Pb in the early 1700's at the major industrial zone near the border with Germany. In contrast, the Jezerni slat Bog near the Austrian border is a relatively pristine area showing a more gradual increase in Pb deposition (Novak *et al.*, 1994; Schell *et al.*, 1993). The Pb deposition rate

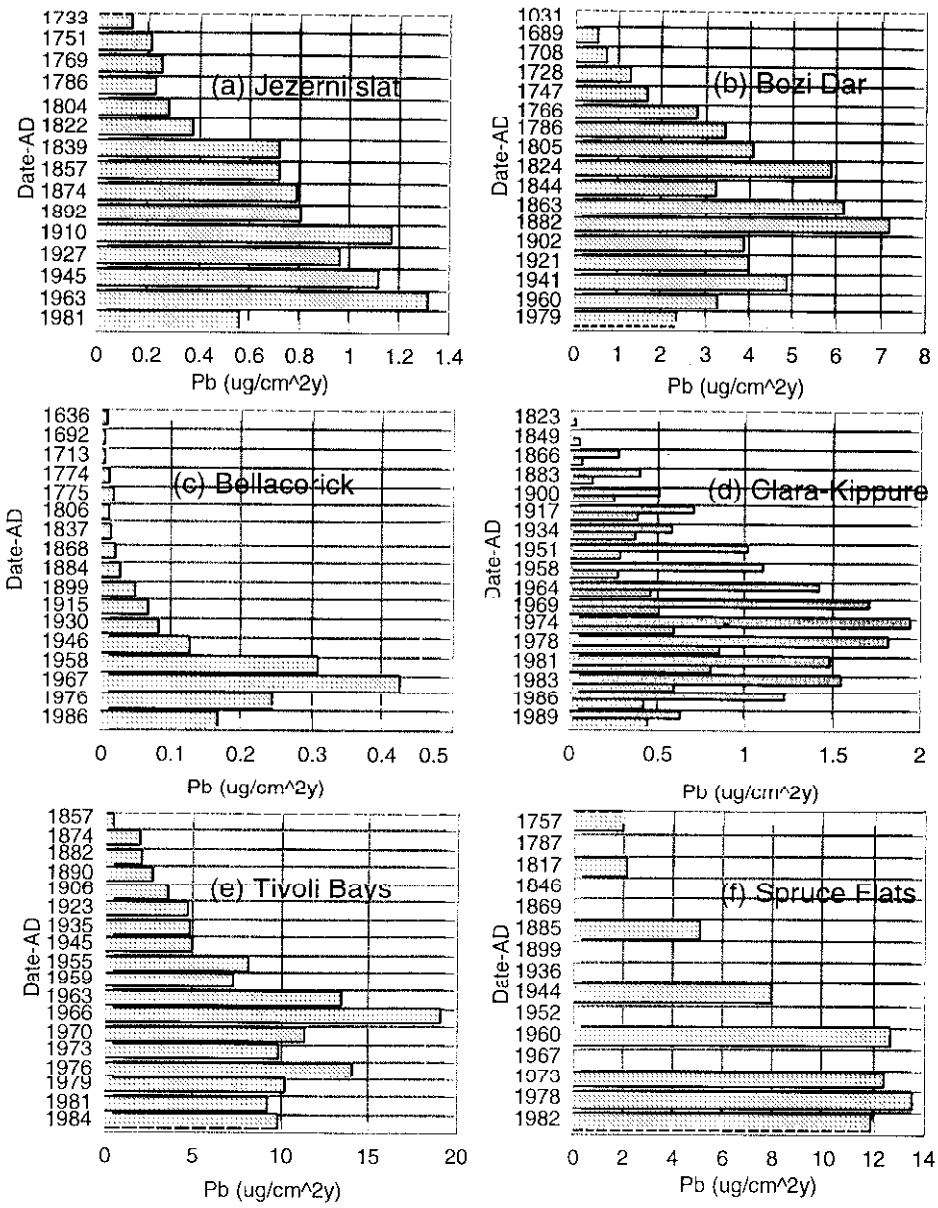

Fig. 1. Lead deposition and chronology for bog cores in Europe, Ireland and USA: Czech Republic (a) Jezerni slat, (b) Bozi Dar; Ireland (c) Bellacorick, (d) Clara and Kippure; USA (e) Tivoli, and (f) Spruce Flats.

continues to be 3-6 times higher at Bozi Dar than at Jezerni slat. Also shown for comparison is Pb deposition measured near Pittsburgh, demonstrating the excessive industrial pollution in the eastern USA. The pollution increased to levels above background in the USA and Ireland about 120 years later than in the Czech Republic.

The lead deposition at both the Ireland and USA bog sites shows peaks at about the same time, the 1970's, with an initial increase over background levels starting about 1860. The range of the deposition rates shows the comparatively low pollution in western Ireland which was about 40 times less than that at the continental sites. The Clara and Kippure Bog profiles reflect the industrial combustion of coal nearby until the 1920's. Subsequently the Pb increase was due to consumption of gasoline containing tetraethyl Pb to a maximum in the 1970's when pollution controls were initiated. The Tivoli Bays site may have a component of Pb supplied from the Hudson River as it is a marshland susceptible to flooding, though far from the river channel. The Spruce Flats Bog sampling location reflects the local coal and wood burning activities for heavy industries in the late 19th and early 20th Century in the eastern part of the American continent.

3.2. GLOBAL TRANSPORT OF TRACE METALS

The Tivoli Bays and Spruce Flats sampling sites are repositories of pollutants from heavy industry sources originating in several eastern USA states. The Irish sampling stations show that the relatively pristine area on the west coast of Ireland has the lowest values for Pb deposition, compared to rates about 5 times greater near Dublin. The Clara Bog sampling station shows that there may have been a change in input of Pb between 1920 and 1950, presumably due to some local industry but this has not been observed at the Bellacorick site. The similarity in the chronologies of atmospheric Pb deposition in western Ireland and the northeastern USA suggests that long-range transport of Pb from America may be the main source of pollutant Pb in western Ireland. The size of Pb particles are small and can move large distances with the prevailing wind currents and thus are international contaminants similar to ^{131}I from the Chernobyl NPP accident fallout in 1986. Long-range transport of lead was demonstrated at a remote subalpine pond in the Sierra Madre Mountains of California (Shirahata *et al.*, 1980) and at Greenland glaciers (Hong *et al.*, 1994; Hong *et al.*, 1996). Such airborne combustion products can often be deposited on forests, agricultural lands and the population over time periods of decades before their critical effects are observed.

3.3 TRACE METAL DEPOSITION IN BOHEMIA

In the Czech Republic, the levels of Pb at the "pristine" site, Jezerni slat, are much lower than those at the heavily contaminated site, Bozi Dar, where the highest deposition is near the surface. In contrast, the Pb deposition profile at the Bozi Dar site shows the highest Pb levels from 1820-1900 (Figure 1). The rapid increase of the several metals at both sites began about 1720 and the Bozi Dar site is 5-10 times greater than at the Jezerni slat site (Figure 2). The Czech cores show that the environment was being contaminated by coal burning and associated heavy industries about 120 years before the Industrial Revolution began in western Europe. The concentration and deposition of these metals can be compared with the Pb values shown in Figure 1. The structure of the two bogs is quite different yet both a lake mat bog and a land bog can be used to measure the history of metals pollution. The Jezerni slat site represents long-range transport of pollutants released downwind from the bog since no major heavy industries are located nearby.

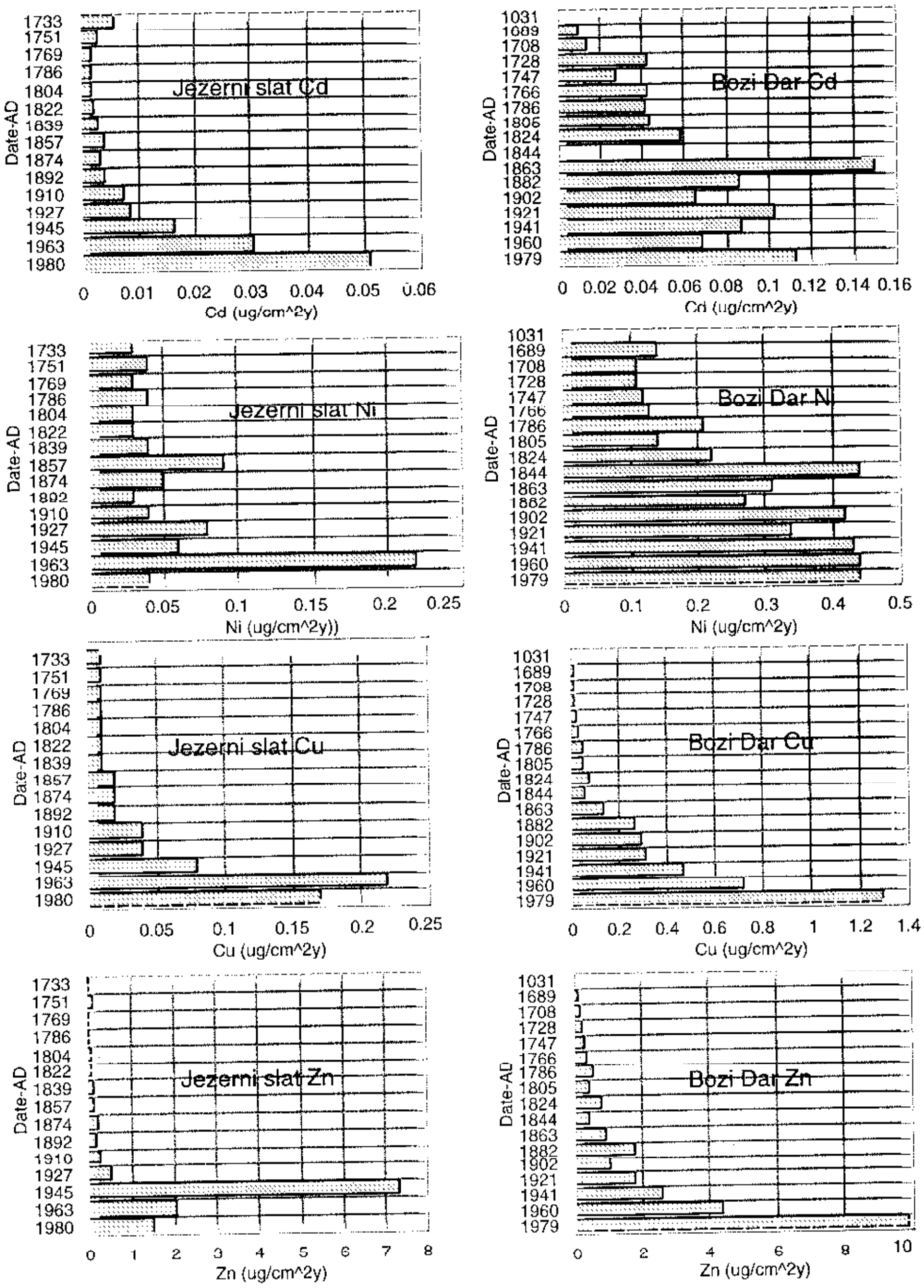

Fig. 2. Deposition and comparative chronology of trace metals input to bog ecosystems in the Czech Republic: (a) Jezerni slat, (b) Bozi Dar.

4. Conclusions

These results show that the deposition history of pollutants can be reconstructed using age-dated core profiles. The history of element deposition in the northeastern USA and in Europe are used as examples. Results may be used to validate models for predicting transport and dispersion of metals and to suggest remediation methods for contaminated lands. Long-range transport of radioactive fallout and other pollutants was demonstrated conclusively from the nuclear weapons tests and the Chernobyl NPP accident. The historical information presented here can help in setting local metals emission limits, give credence to the regulations already written, and document past pollution practices. The data provide additional information that man and the global ecosystem have been exposed to Pb and other elements from the input of industrial wastes continuously since 1700 and longer.

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