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Lithologically inherited variation in Pb isotope ratios in sedimentary soils in The Netherlands

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ABSTRACT

Knowledge on the lithologically inherited variation in present day Pb isotope ratios in soils is remarkably limited. Such information is essential to determine the anthropogenic Pb fraction and anthropogenic Pb sources in Pb-polluted soils. This study presents results of a survey of subsoil samples from approximately 350 rural locations covering the entire Netherlands, for which the bulk geochemical and Pb isotope composition was determined. The sample density was approximately 1 site per 70 km^2. The aim was to establish a geochemical reference for the lithologically inherited variation in Pb isotope ratios in Dutch soils based on the subsoil samples, with which to compare the topsoils (companion paper in this journal issue).

The lithologically inherited variation in Pb isotope ratios of the subsoils in The Netherlands is established at 1.175–1.221, 2.441–2.494 and 0.478–0.492 for $^{206}Pb/^{207}Pb$, $^{207}Pb/^{208}Pb$ and $^{206}Pb/^{208}Pb$ respectively. The four main lithologies distinguished, sand, clay, peat and loess, have distinct Pb isotope signatures. No significant difference in isotope signature was found between marine and fluviatile clays. Multiple regression analysis established that the observed variation can be primarily explained by the textural and mineralogical variation within Dutch subsoils, with Al and Zr content representing useful predictors for the observed Pb isotope variability. Clay soils are characterised by a radiogenic Pb isotope signature that is notably low in ^{207}Pb. Soils with a high Zr content are especially high in ^{206}Pb. Although the vast majority (~90%) of the Pb isotope variation in the subsoils appears to be controlled by lithological inheritance, some subsoils (mainly peats) are suspected of containing a component of non-lithologically derived Pb.

1. Introduction

Lead has an average crustal abundance of 17 mg/kg (Wedepohl, 1995). Because of the malleability of the pure metal and its specific chemical and physical properties, Pb ores have been mined since 5000 B.C. (Patterson et al., 1970; Heskel, 1983). As a result of the production (including mining and smelting) and the use of the metal (batteries, pigments, ceramics, plastics, etc.), combustion of coal and leaded gasoline, and the recycling and disposal of Pb and Pb containing products, anthropogenic Pb has entered the environment on a worldwide basis. It is estimated that in the environment, anthropogenic Pb emissions are at least 1–2 orders of magnitude greater than from natural sources (Komárek et al., 2008).

The World Health Organisation lists Pb as a neurotoxin with no known biological benefit to humans. It is a cumulative poison that affects the development and functioning of the brain, especially in young children. It can further damage other organs, such as the reproductive system and kidneys, and can cause high blood pressure and anaemia. At very high levels, Pb may lead to convulsions, coma and death. Because of its toxicity, the use of Pb has been discouraged over the years. However, despite current caution, Pb in the environment still poses a serious problem. In The Netherlands alone, several thousand sites, including back yards of family homes, are estimated to be polluted with Pb (Hagens et al., 2009; Compendium, 2011).

Information on the occurrence, behaviour and fate of the various anthropogenic Pb sources in the environment is considered to be crucial in understanding and abating the Pb problem (e.g. Steele et al., 1990; Ruby et al., 1999; Rieuwerts et al., 2000; Hagens

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et al., 2009). This includes distinguishing historic from recent pollution, as the former of course cannot be prevented; identifying the source-related chemical form of environmental Pb, as this may influence its toxicity; and the need sometimes to identify the origin of Pb pollution for legal reasons.

Based on measurements of Pb content alone, it is often difficult, if not impossible, to determine the cause of the elevated Pb content and to distinguish between natural and anthropogenic origins and among specific anthropogenic Pb sources. Chow and Johnston (1965) were some of the first researchers to show that clues on Pb provenance could be obtained through the study of the four stable Pb isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Of these, ^{204}Pb is non-radiogenic and ^{206}Pb, ^{207}Pb and ^{208}Pb are formed by the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. Lead ores, and the products derived from them, have characteristic Pb isotope signatures, depending on the initial U/Pb and Th/Pb ratios of the source rocks and the geological age at which Pb, as the daughter, separated from the melt (mother) during ore formation. In their use as geochemical tracers, Pb isotopes are commonly utilised as ratios; with the ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and ^{206}Pb/^{208}Pb ratios often used in environmental studies as they can be determined rapidly and precisely with ICP-MS and generally exhibit sufficient variability between different sources (Komárek et al., 2008). Sangster et al. (2000) calculated that 86% of the discriminative power of Pb isotope signatures is due to the ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes.

In many environmental studies, Pb isotope analysis has proved to be a powerful tool. However, Pb isotope measurements can only be used to trace anthropogenic Pb sources in polluted soils and sediments if:

1. the Pb isotope composition of anthropogenic Pb differs from that of lithologically inherited Pb and
2. the content and isotopic composition of lithologically inherited Pb are known, to allow correction for its presence.

Polluted soils always contain lithologically inherited as well as anthropogenic Pb. If the ratio of anthropogenic Pb versus lithologically inherited Pb is high, the influence of the latter on the Pb isotope composition is negligible. Conversely, if this ratio is small, the presence of lithologically inherited Pb dominates the Pb isotope composition of the total sample. For this reason, knowledge of the lithologically inherited variability and spatial distribution of the Pb content and the Pb isotope composition of sediments and soils is indispensable in environmental tracer studies involving Pb.

To the authors' knowledge, there are few extensive studies on the spatial distribution of the Pb isotope composition of soils. Notable exceptions are Reimann et al. (2011, 2012), who determined Pb contents and Pb isotope ratios in topsoils collected (1) along an east–west transect across the USA at 40 km resolution and (2) in Ap horizons of agricultural areas in Europe at an average density of 1 site/2500 km^2. All other studies of Pb in mineral soils are local in nature and based on a limited number of selected profiles that are sampled at various depths, to distinguish the hypothesised anthropogenic Pb isotope signature in the upper (and generally more organic rich) part of the soil from the lithologically inherited signature at depth (Chow, 1970; Gulson et al., 1981; Walraven et al., 1997; Hansmann and Köppel, 2000; Cloquet et al., 2006). Although Reimann et al. (2011, 2012) determined the spatial distribution of the Pb isotope composition in soils, they did not distinguish lithologically inherited from anthropogenic Pb. Their Pb isotope maps consequently represent a mixture of lithologically inherited and anthropogenic Pb in topsoils.

In this study, results are presented of a survey of subsoil samples of approximately 350 rural locations covering the entire Netherlands, of which the bulk geochemical (Pb content) and Pb isotope compositions were determined. The aim of this study is to determine the lithologically inherited variation in Pb isotope ratios in subsoils in The Netherlands. A proper understanding and adequate description of this variation will serve as a base for the analysis of spatial patterns of anthropogenic Pb isotope signatures in the topsoils in a companion article in this issue (Walraven et al., 2013).

2. Background information

2.1. General geology of The Netherlands

The Netherlands is located in north-western Europe and is bordered by Germany, Belgium and the North Sea (Fig. 1). It is part of the subsiding North Sea Basin that is enclosed by the Brabant Massif in the South and the Rhenisch Massif in the East. As a result of extensive subsidence and sedimentary infill of the North Sea Basin during the Cenozoic, the subsurface of The Netherlands largely consists of a 200–500 m thick layer of unconsolidated sediments that are of Pleistocene age in the eastern and southern part and of Holocene age in the northern and western part. (see e.g., Zagwijn and Van Staalduinen, 1975; Westerhoff et al., 2003).

The Pleistocene sediments are made up of coarse river deposits and various glaciogenic deposits, which are overlain by a substantial layer of aeolian cover sand. The coarse river deposits have both a southern provenance (drainage basins of Rhine, Meuse and Scheldt) as well as a partly eastern provenance (drainage basin of Baltic rivers). The glaciogenic deposits, which are confined to the northern part of The Netherlands, are largely derived from Scandinavian massifs. As a result, the overlying Pleistocene aeolian sands have a diverse origin in terms of sediment provenance. Yet, lithological and mineralogical differences within the aeolian deposits are small. Other Pleistocene aeolian sediments include loess deposits, which are locally found in the south-eastern parts of The Netherlands.

The Holocene sediments consist of more silty to clayey marine and fluviatile sediments alternating with extensive peat layers. Apart from these locally formed peat layers, the provenance of the Holocene deposits is restricted to the drainage basins of the Rhine, Meuse and Scheldt.

2.2. General pedology of The Netherlands

For classification purposes, soil in The Netherlands is arbitrarily defined as the first 120 cm of the profile below the litter layer (Locher and de Bakker, 1987). The depth of actual soil formation, if even present, is often much less. Due to intensive sediment deposition, soil profiles often contain various sediment layers with different lithological characteristics (Van der Veer, 2006). Lead mineralisation and soil formation on hard bedrock (only in the Winterswijk area and most southern part of Limburg) does not occur in The Netherlands.

The different types of parent material in The Netherlands are classically grouped into five districts: sand, loess, peat, fluviatile and marine clay. Whereas the largely Pleistocene sand and loess districts are mainly found in the elevated northern, eastern and southern parts of The Netherlands, the Holocene clay deposits are mainly confined to the low lying coastal areas in the SW, west and north (Fig. 1). Peat is found in various areas in The Netherlands, but a substantial fraction has been excavated for fuel over the last centuries (Bazelmans et al., 2011).

Time is an important soil forming factor. Soil formation in The Netherlands started only after ice receded. Therefore, soils in The Netherlands are relatively young: 12 ka for loess to <50 a for marine clay (for details see Van der Veer, 2006). As a result of the restricted age of the parent material and a temperate climate, soils in The Netherlands are poorly developed compared to those in