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Factors controlling the oral bioaccessibility of anthropogenic Pb in polluted soils

N. Walraven [a,*], M. Bakker [b], B.J.H. van Os [c], G.Th. Klaver [d], J.J. Middelburg [e], G.R. Davies [f]

[a] GeoConnect, Meester Dekkerstraat 4, 1901 PV Castricum, The Netherlands
[b] Rijksinstituut voor Volksgezondheid en Milieu (RIVM), P.O. Box 1, 3720 BA Bilthoven, The Netherlands
[c] Rijksdienst voor Archeologie, Cultuurlandschap en Monumenten, P.O. Box 1600, 3800 BP Amersfoort, The Netherlands
[d] BRGM, 3 avenue Claude-Guillemin, BP 36009, 45060 Orléans Cedex 2, France
[e] University Utrecht, Faculty of Geosciences, P.O. Box 80021, 3508 TA Utrecht, The Netherlands
[f] VU University Amsterdam, Faculty of Earth and Life Sciences, Petrology, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands

HIGHLIGHTS

- Ingestion of soil is considered a major route of toxic Pb exposure.
- The oral bioaccessibility of soils polluted with various Pb sources was determined.
- The oral bioaccessibility was determined with an in-vitro test.
- Factors controlling the oral bioaccessibility were determined.
- Factors include pollution characteristics and soil composition.

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ABSTRACT

In human risk assessment, ingestion of soil is considered a major route of toxic Pb exposure. A large body of research has focussed on the measurement of the 'total' Pb contents in sediment, soil and dust as a measure for the exposure to lead. We report that Pb bioaccessibility (i.e. the maximum bioavailability), determined with an *in vitro* test, does not necessarily depend on the total Pb content. In contrast, the Pb bioaccessibility is initially controlled by the chemical form and particle size of the Pb source, which in turn determine its solubility. Furthermore, when anthropogenic Pb resides within the soil, it may form new, more stable, minerals and/or binds to organic matter, clay, reactive iron or other reactive phases, changing its bioaccessibility.

The bioaccessible Pb fraction of 28 soils, polluted with various Pb sources (including residues of Pb bullets and pellets, car battery Pb, city waste and diffuse Pb), was determined with an *in vitro*-test and varied from 0.5% to 79.0% of total Pb. The highest Pb bioaccessibility (60.7% to 79.0%) was measured in soils polluted with residues of Pb bullets and pellets (shooting range), while the lowest Pb bioaccessibility (0.5%–8.3%) was measured in soils polluted with city waste (including remnants of Pb glazed potsherds and rooftiles, Pb based paint flakes, and Pb sheets). Bioaccessibility of Pb was correlated with pH, organic matter and reactive Fe. These results indicate that soil characteristics play an important role in the oral bioaccessibility of lead in polluted soils. Instead of basing human risk assessment solely on total Pb contents we propose to incorporate *in vitro* bioaccessibility tests, taking factors such as soil pH, organic matter content and reactive iron content into account. This approach will result in a better insight into the actual risks of Pb polluted soils to children.

1. Introduction

Egyptian, Greek and Roman Physicians were aware of the toxicity of lead (Pb) (Gilfillan, 1965). Despite this widely known information, it was not until the 1970s that governments started taking legislative measures to reduce the input of Pb and related heavy metals into the environment. The use of leaded gasoline has been reduced significantly wordwide, Pb in paints is officially banned in a large number of countries and active public information campaigns have been carried out to encourage the replacement of Pb water pipes. This raises the question; is the environmental Pb problem now solved? In general, the main problems have been addressed in most developed countries. Many sites in the world are, however, (still) heavily polluted with Pb. Should such soils be used for agriculture or residential building, they may pose a threat to human health.

* Corresponding author.
E-mail addresses: n.walraven@geoconnect.nl (N. Walraven), martine.bakker@rivm.nl (M. Bakker), B.van.Os@cultureelerfgoed.nl (B.J.H. van Os), g.klaver@brgm.nl (G.T. Klaver), j.b.m.middelburg@uu.nl (J.J. Middelburg), g.r.davies@vu.nl (G.R. Davies).

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Children are particularly sensitive to the toxic effects of Pb, and environmental exposure may cause chronic health effects, such as disturbances to cognitive development and damage to the central nervous system (Elhelu et al., 1995). Due to the frequent hand-to-mouth behaviour of young children, soil ingestion is an important exposure route for Pb (Duggan and Inskip, 1985; Davis and Waller, 1990; Calabrese et al., 1997). In addition, children absorb higher percentages of metals through the digestive system into the blood stream than adults, which may leave them more susceptible to adverse health effects (Hamel et al., 1998 and references therein). Since for children ingestion of soil is considered a major exposure route for Pb, absorption and toxicity of ingested Pb has been studied extensively (Oomen, 2000 and references therein). It appears that less adsorption and toxicity is observed in animal tests when Pb is ingested with soil compared with Pb that is ingested with food, suspensions and liquids (Freeman et al., 1992; Dieter et al., 1993; Oomen, 2000 and references therein). This difference can, among others, be caused by variations in, 1) the chemical composition of the anthropogenic Pb source and its solubility (Steele et al., 1990; Cotter-Howells and Thornton, 1991; Davis et al., 1993; Ruby et al., 1992, 1996, 1999; Rieuwerts et al., 2000; Hettiarachchi and Pierzynski, 2004), 2) the specific reactive surface of Pb in soils (Steele et al., 1990; Ruby et al., 1992, 1999) and 3) the soil type, i.e., soil composition and properties, and capacity to form secondary Pb phases (Yang et al., 2003; Ruby et al., 1999; Davis et al., 1993; Casteel et al., 1997; Rieuwerts et al., 1998a,b, 2000; Hettiarachchi and Pierzynski, 2004; Selinius, 2005; Cave et al., 2011; Farmer et al., 2011). Current risk limits for Pb in soil are based on the measurements of oral bioavailability of Pb in food, suspension and liquids, consequently the oral bioavailabilitiy for Pb in soils can be substantially overestimated (Oomen et al., 2003).

Determination of the oral bioaccessibility of Pb (F_B) in soils using *in vitro* tests is an indication for the maximum oral bioavailability of Pb in soils. Although there is evidence that oral bioavailability of Pb in soils depends on soil matrix and type, particle size and chemical composition of the Pb source (e.g., Steele et al., 1990; Cotter-Howells and Thornton, 1991; Davis et al., 1993; Ruby et al., 1992, 1996, 1999; Rieuwerts et al., 2000; Hettiarachchi and Pierzynski, 2004; Selinius, 2005; Cave et al., 2011; Farmer et al., 2011), relatively little research has been performed to quantify these factors. The main aims of the current study are to determine: 1) the bioaccessibility of soils polluted with various Pb sources and 2) if Pb pollution characteristics (chemical composition and particle size of the anthropogenic Pb fraction) and soil characteristics (pH, total Pb, organic matter, clay, calcium carbonate, and reactive iron content) influence oral bioaccessibility. Lead polluted soils from The Netherlands were chosen for this study, because The Netherlands is one of the most densely populated countries in the world, with many lead polluted sites. In addition, the regional distribution of Pb in the environment has already been well studied by Walraven et al. (1997, 2013b, 2014a, submitted for publication).

For this study, 28 Pb polluted soils were selected and Pb isotope analysis was used to distinguish natural Pb and various anthropogenic lead sources. Electron microscopic images of selected samples were made to study the chemical composition and particle size of the anthropogenic Pb fraction. The soil composition and mineralogy were quantified using X-ray Fluorescence (XRF) and Thermal Gravimetric Analysis (TGA). Oral bioaccessibility of Pb in the selected polluted soils was determined with an *in vitro* digestion model developed and tested by Oomen et al. (2003). This method is reproducible, easy to perform and allows simultaneous determination of large numbers of samples (Oomen et al., 2003).

2. Background information

Geographical characteristics, general geology and general pedology of The Netherlands are described in detail in Van der Veer (2006) and Walraven et al. (2013a,b). The natural Pb content of soils (excluding peat) in The Netherlands varies from 3 to 53 mg/kg (Van der Veer, 2006). Natural Pb shows a strong correlation with Al due to its joint occurrence in aluminosilicates (e.g., Huisman, 1998; Van der Veer, 2006; Mol et al., 2012; Walraven et al., 2013a). In The Netherlands soils can be polluted with various Pb sources, in which diffuse and local sources can be distinguished. Diffuse Pb sources in The Netherlands include gasoline Pb, incinerator ashes, fertilisers and animal manure (Walraven et al., 2013b). Local Pb sources include residues of Pb bullets and pellets (henceforth referred to as Pb bullets and pellets), car battery Pb, made grounds and city waste (Walraven et al., 1997). Lead bullets and pellets are used for hunting, sports and military activities and can end up in soils after use. Car batteries often contain Pb. At car battery repair facilities, Pb entered the environment due to accidents, ignorance or indifference. Made grounds in The Netherlands were mainly formed between the 15th and the 19th century. In this period peat was extensively mined in The Netherlands. Boats that transported peat to the city, brought back city waste, manure, sludge to fill up the peat holes, and to raise and fertilize the land. These layers are called made grounds and have thicknesses typically between 15 and 50 cm (Bosveld and De Poorte, 1999). Due to the presence of among others paint flakes, remnants of Pb glazed potsherd, glass and Pb sheets in city waste, the Pb content in made grounds can be greater than the Dutch Intervention Value of Pb for standard soils (530 mg/kg). City waste was not only dumped in peat holes and in subsiding areas but it also ended up in city soils. Soils in Dutch cities and villages with a long habitation history often contain elevated contents of heavy metals, and Pb in particular (Walraven et al., submitted for publication). Lead contents in such soils can reach values of several thousand mg/kg Pb (Walraven et al., 1997).

Several researchers have demonstrated that Pb isotope analysis can be used to distinguish natural from anthropogenic Pb, but also to identify the anthropogenic Pb source in the environment (see review by Komárek et al., 2008 and references therein). In The Netherlands the Pb isotope composition of anthropogenic Pb sources differs clearly from natural Pb and various anthropogenic Pb sources have characteristic Pb isotope ratios (e.g., Walraven et al., 2013a,b, 2014a,b, submitted for publication). The principles of stable lead isotope analysis are described in detail in Faure (1986). In the present study we aim to use Pb isotope ratios to determine the specific anthropogenic Pb sources in soil samples.

3. Materials and methods

3.1. Sample selection

The selected 28 soil samples were collected in the framework of other studies (see Groot and van Swinderen, 1993; Oomen and Hagens, 2006; Van der Veer, 2006; Walraven et al., 2013b, submitted for publication). These samples were selected because they contain anthropogenic Pb from various (inferred) Pb sources (Pb bullets and pellets, car battery Pb, Gasoline Pb, diffuse Pb, made ground and city waste) and the characteristics of the soils (pH, total Pb, organic matter, clay, calcium carbonate, and reactive iron content) vary considerably. The sample locations are shown in Fig. 1. Description of the sample sites and sample depths are given in Table 1.

To determine if different anthropogenic Pb sources have different bioaccessibilities, only samples inferred to be polluted with one dominant anthropogenic Pb source were selected: Pb bullets and pellets ($n = 2$), car battery Pb ($n = 2$), gasoline Pb ($n = 6$), diffuse Pb ($n = 5$), made grounds ($n = 7$) and 'old' city waste ($n = 6$) containing various Pb-based artefacts (e.g. Pb glazed potsherds, Pb sheets and Pb-based paint flakes). These Pb sources were selected based on their difference in chemical composition and particle size.

To determine if bioaccessibility of Pb depends on soil characteristics, Pb polluted soil samples from the following soil types were selected: 1) aeolian sands ($n = 12$), 2) (peat-bearing) marine clays ($n = 9$) and 3) fluviatile clays ($n = 7$). These soil types were selected because they cover ~75% of the soils present in The Netherlands.