Chapter 1

General introduction

Lead is abbreviated with the symbol Pb, originating from the Latin word *plumbum* meaning liquid silver (Webelements, 2014). It is a bluish-white lustrous metal which is very soft, highly malleable, ductile, corrosion-resistant and a relatively poor conductor of electricity (Webelements, 2014). Because of the malleability of the pure metal and its specific chemical and physical properties, Pb ores have been mined since ~6400 B.C. (Patterson et al., 1970; Heskel, 1983). The main source for Pb is from sulphide ores (galena), but today just under half of the annual Pb production of near 8 million tons is from recycling (Smith, 2004). Lead or its oxide, have been used extensively in piping, building material (Fig. 1.1), ceramics, pewter, paint and Pb glazes since Roman times. In the 20th century, tetraethyl Pb was widely used as an anti-knock additive to petrol. Current commercial uses of Pb include among others building material, cable sheathing, car batteries, Pb crystal glass, ammunition, radiation protection and solders.

Fig. 1.1. Lead containing building materials used in The Netherlands. (P = Pb-based paint on wood; S= Pb sheet; CP = Pb-glazed chimney pot; RT = Pb-glazed roof tile).

1.1 Lead in the environment

Lead occurs naturally in all soils and sediments. Its terrestrial abundance ranges from 1 to 200 mg/kg with most values in the range of 5 to 25 mg/kg (Swaine, 1955; USGS, 1976). Several researchers determined baseline levels for Pb in The Netherlands by sampling subsoils in rural areas at depths generally > 0.5 m below surface (Huisman, 1998; Lamé et al., 2004; Spijker, 2005; Van der Veer, 2006). According to these studies the natural Pb content of Dutch soils ranges from <0.05 to 55 mg/kg. The dominant mineral groups in Dutch soils and sediments are quartz, feldspars, micas, chlorites, clay minerals, heavy minerals and secondary minerals. All minerals contain ‘natural’ trace contents of Pb. The Pb content in these minerals can vary from 0-5 mg/kg in quartz to 2-1000 mg/kg, 5-2000 mg/kg and 0.9-
10,000 mg/kg in pyrites, apatites and K-feldspars respectively (Wedepohl and Doe, 1974). Feldspars and apatites can contain high amounts of Pb, because Pb\(^{2+}\) (1.18-1.32 Å) can replace potassium (1.33 Å) in potassium feldspars, and calcium (0.99-1.06 Å) and strontium (1.12-1.27 Å) in apatites (Nriagu, 1978). Lead can also replace barium (1.34-1.43 Å) and even sodium (0.95-1.0 Å) in mineral lattices. The high lead content in base metal sulfides, like pyrites, are due to the entrapment of fine-grained galena in these mineral phases. In addition, lead has a high affinity for iron and manganese oxides. In the clay fraction, soil contain the residual lead of weathered rocks from which they formed.

Due to the production, use, combustion, recycling, disposal of Pb and Pb containing products, (so-called) anthropogenic Pb entered, and still enters, the environment worldwide. Pollution of soils with heavy metals, including Pb, started with the domestication of fire (Nriagu, 1996). The remnants of burnt firewood are rich in heavy metals and alter the metal content of the topsoil near the fireplace. The first contamination of the atmosphere is estimated to be ~5000 years old when smelting technologies were introduced in south-western Asia (processing of sulphides containing Pb-Ag alloys) (Komárek et al., 2008) (Fig. 1.2). The world Pb production at that time was estimated to be ~200 t per year (Komárek et al., 2008) (Fig. 1.2). The annual average Pb production increased to ~80,000 t per year during the era of the Roman Empire (Fig. 1.2). The Romans used Pb in numerous ways. One of the most important historical uses was in the manufacture of aqueducts and water pipes (Nriagu, 1978). The Romans also used Pb in cooking and cooking utensils. The bronze pots of the Romans were lined with Pb to prevent food spoilage as well as to sweeten the foods (e.g., wines and sapa) (Nriagu, 1978). This pervasive domestic use of Pb in the Roman culture probably lead to contamination of their food and drink, and the theory has been advanced that the fall of the Roman Empire was largely due to endemic Pb poisoning (Gilfillan, 1965; Nriagu, 1978). A further increase in annual worldwide Pb production (~ 4\times10^6 t per year in 1975 A.D.) occurred due to emerging industrial activities and the introduction of leaded gasoline (Komárek et al., 2008) (Fig. 1.2). The accumulated total world Pb production since ancient times is estimated to be 300 Mt (Reimann et al., 2012).

The environmental effects of the production and use of Pb remain measurable all over the globe. The highest Pb contents are found in Pb mining areas (e.g., Moffat, 1989; Gulson et al., 1994), near Pb smelters (Rieuwerts et al., 1999; Etter et al., 2004), in roadside soils (e.g., Chow, 1970; Erel, 1998) and in villages and cities with a long habitation history (e.g., Walraven et al., 1997; Hansmann and Köppel, 2000). But even far from the actual sources, elevated Pb contents are measured. For example, Boutron et al. (1991) and Rosman et al. (1994) measured elevated Pb concentrations in Greenland snow. Even in the remote ice cap of Antarctica researchers have demonstrated that the Pb content in ice samples increased during the years 1960-1980 due to extensive leaded gasoline combustion (e.g., Barbante et al., 1997 and Vallie\-longa et al., 2002).

Due to the toxicity of Pb, governments started taking legislative measures in the 1970s to reduce the input of anthropogenic Pb to the environment (see Section 1.3). The use of leaded gasoline has been reduced significantly worldwide, 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. However, many sites in the world are (still) heavily polluted with Pb. In The Netherlands alone, several thousand sites, including back yards of family homes, are estimated to be polluted with Pb.
(e.g., Hagens et al., 2009; Compendium, 2011). Should such Pb polluted soils be used for agriculture or residential building they may pose a threat to human health and, if they remain unattended, Pb and related heavy metals may become available and leach to the groundwater.

Fig. 1.2. Historical production and consumption of lead (after Patterson et al., 1970; Nriagu, 1978).

1.2 Toxicity of Pb

Egyptian, Greek and Roman physicians were already aware of the toxicity of Pb (Gilfillan, 1965). In 370 B.C., for example, Hippocrates described a severe attack of colic in a man extracting metals, and Pliny reported cases of Pb poisoning between 23 and 79 A.D. (Gilfillan, 1965). Even the fall of the Roman Empire has been attributed to chronic Pb poisoning (Healy and Aslam, 1981). In more recent history, Thackrah in 1831 A.D. directly associated Pb poisoning with the 'miners' sickness, first described by Paracelsus in the sixteenth century and supported later by a contemporary study of the ill-health of miners in Derbyshire in 1857 A.D. (Gilfillan, 1965). In 1923 A.D., between 13 and 15 known deaths occurred, due to acute Pb poisoning at various tetraethyl production plants and over 300 men became psychotic (Needleman, 1998).

Currently, the World Health Organisation lists Pb as a neurotoxin with no known biological benefit to humans. There is currently no conclusive proof that Pb is carcinogenic to humans (ATSDR, 2007). However, kidney tumours have developed in rats and mice that had been given large doses of Pb compounds (ATSDR, 2007). Lead poisoning commonly occurs
after prolonged exposure to Pb or its compounds. The groups most at risk for the adverse effects of Pb are pregnant women, breast-feeding women and young children. Even at low exposure levels, the effects of Pb on children include impairment of normal neurological development leading to learning and reasoning difficulties, retardation of physical development, hearing loss, hyperactivity, and reduced attention span (Von Storch et al., 2003). The USA Centers for Disease Control and Prevention use a reference value for Pb in blood of 5 µg/dL to identify children who have been exposed to Pb and who require case management (CDC, 2014a). 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). Effects in adults include damage to the reproductive system and kidneys, elevated blood pressure and hypertension - resulting in increased risk of cardiovascular diseases - and renal deficiencies. At very high levels (oral dose of ~ 450 mg of Pb per kg of body weight; air Pb concentrations of 100 mg/m³), Pb may lead to convulsions, coma and death (CDC, 2014b; WHO, 2014).

Exposure to Pb can be minimised if people know about the Pb sources and if education is carried out on ways to actively avoid exposure to Pb. Old homes that have been constructed and painted with Pb-based products (e.g., paint, gutters and glazed roof tiles) and/or contain leaden water pipes can cause risks of exposure to Pb and are therefore a particular problem. Demolition and/or renovation of such homes (e.g., using heat to peel the paint) may cause exposure to high levels of Pb (ATSDR, 2007). Residing and/or recreation in areas where Pb has been mined, processed and or used in large quantities (e.g., Pb mines, Pb smelters and shooting ranges) should be avoided. Discouraging young children from eating soil and other hand-to-mouth activity will significantly reduce the risk of exposure to Pb.

1.3 Policy / critical limits

Health concerns led to a series of worldwide measures to reduce the input of anthropogenic Pb to the environment. In the 1970s lead-based paint and the usage of Pb solder in water pipes and food cans was prohibited in developed countries worldwide (Von Storch et al., 2003). In the Netherlands house owners were financially supported by the government to remove leaden water pipes from their water distribution system (Schepers et al., 2007). Gasoline Pb, added for its antiknock properties, and the largest source of anthropogenic Pb in the atmosphere in the 1970s to 1990s (Nriagu, 1990; Von Storch et al., 2003; Denier van der Gon and Appelman, 2009), was a target for worldwide regulations between 1970 and 2005 A.D.. Japan was the first country to market lead-free gasoline, which became available in 1972 A.D. (Nriagu, 1990). In 1980s the European countries took active measures to reduce the usage of leaded gasoline. The Netherlands, for example, reduced the maximum allowed Pb concentration in gasoline from 0.4 g/l by January 1978 A.D. to 0.15 g/l by October 1986 A.D. (Janus et al., 1999) In addition in 1986 A.D. fiscal measures were taken by the Dutch government to promote the use of unleaded gasoline (Janus et al., 1999). The 1998 Aarhus Treaty stipulated the exclusive usage of unleaded gasoline in Europe by the year 2005 A.D. Other measures to reduce the emission of Pb to the environment include a ban on the use of metallic Pb in shot cartridges for hunting, reduction of Pb as a stabilizer in PVC and the introduction of quality criteria for the allowable (permissible) amount of inorganic Pb in soil, groundwater, surface water and air (Janus et al., 1999).
In 1999 A.D. the European Council Directive 1999/30/EC came into force. This Directive describes the numerical limits and thresholds required to assess and manage air quality for pollutants including Pb. The limit value for the yearly average Pb air concentration was set at 500 ng/m³. Limit or threshold values for Pb were also established for other environmental compartments (e.g., soil and groundwater). In The Netherlands the critical limits are called intervention values. The Dutch intervention value for Pb is 530 mg/kg for standard soils (25% clay and 10% organic matter) (Staatscourant, 2013). Soils with a higher Pb content than the intervention value are classified as ‘seriously’ polluted (Swartjes, 1999). In case of a serious soil pollution, the polluted site has, in principle, to be remediated. However, the need for remediation is decided on the basis of actual risk to humans and ecosystems and the actual risk due to migration of the contamination. Dutch risk assessment for Pb is based on criteria laid down by FAO/WHO (1993) and IPCS (1995). It is recommended to avoid Pb blood levels above 50 μg/l. Limit values were also established for groundwater. In the Netherlands, the intervention value for Pb in groundwater is set at 75 μg/l (Staatscourant, 2013).

1.4 Research questions

Although numerous Pb polluted sites have been remediated and various measures have been taken to reduce the input of Pb to the environment (see Section 1.3), thousands of sites worldwide are still polluted with Pb. In addition, Pb products are still manufactured and used (e.g., building material (sheeting and gutter material), cable sheathing, car batteries, Pb crystal glass, ammunition, radiation protection and solders) and can enter the environment after use. The goals of this thesis are to map Pb distribution in rural and urban soils in The Netherlands, to unravel Pb sources and to obtain information about the mobility and bioavailability of anthropogenic Pb in the Dutch environment. The main research questions are:

1) What is the lithological inherited variation (background) in Pb isotope composition in soils in The Netherlands?
2) What is the extent of soil Pb pollution and what are the anthropogenic Pb sources in rural and urban (top)soils in The Netherlands?
3) What is the extent and what are the anthropogenic sources of historical atmospheric Pb deposition in The Netherlands?
4) What is the mobility of anthropogenic Pb in (roadside) soils in The Netherlands?
5) What is the oral bioaccessibility of Dutch soils polluted with various anthropogenic Pb sources?

1.5 Research area, The Netherlands

This study is carried out in The Netherlands, because it is one of the most densely populated countries in the world (498 persons/km² in 2013; CBS, 2014) with several thousand registered Pb polluted sites (e.g., Hagens et al., 2009; Compendium, 2011). In several parts of The Netherlands exposure to Pb, especially in soil, remains a serious risk (mainly in cities and villages with a long habitation history). The Netherlands has a maritime-climate resulting in moderate summers and winters. The average daily temperatures range from 2 ºC in January to 16 ºC in July (Huisman et al., 1998). Average annual rainfall is 750 mm. Mean annual evaporation is in the order of 550 mm, resulting in an average annual precipitation excess of 200 mm (Van der Veer, 2006).
The Netherlands is located in north-western Europe where it is bordered by Germany, Belgium and the North Sea (Fig. 2.1). The Netherlands has a total area of 41,526 km² of which 33,939 km² is land surface and some 6,500 km² is reclaimed land, or polder. 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. The older, often consolidated sediments sparsely crop out in the east and south-eastern parts of The Netherlands (Fig. 1.3). Most sediments close to or at the surface in The Netherlands were deposited during the Quaternary period, and are of Pleistocene or Holocene age (Fig 1.3). The Pleistocene sediments are made up of coarse river deposits and various glacial deposits, which are overlain by a substantial layer of locally reworked aeolian 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 glacial deposits, which are confined to the northern part of The Netherlands, are derived largely from the 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 sediments include the 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 alternated 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. The interlayered marine deposits also consist of locally reworked Pleistocene material.

![Fig. 1.3. Geological map of The Netherlands (after Berendsen, 2004). Lithostratigraphy after De Mulder et al. (2003). Source: Utrecht University (2014).](image_url)
Soil parent materials in The Netherlands are classically grouped into five categories: sand, loess, peat, marine clay and fluviatile clay (Fig. 2.1). 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 southwest, west and north (Fig. 2.1). Peat is found in various areas in The Netherlands, but a substantial fraction has been excavated for fuel during the last centuries (Fig. 2.1). For more details see Van der Veer (2006).

Time is an important soil forming factor. Soil formation in The Netherlands started essentially after the last glacial period (Weichselian) when the temperature rose and vegetation started to stabilize the unconsolidated sediments. The oldest soils, 12,000 to 10,000 years old, are found in the loess district in the southern part of The Netherlands and the youngest soils are only a few 100’s years old. As a result of the restricted age of the parent material and a temperate maritime-climate, soils in The Netherlands are generally poorly developed compared with those in many other parts of the world. Soil formation is often restricted to the first 20 cm. For more details see Van der Veer (2006).

1.6 Use of Pb isotopes in environmental research

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 among of the first researchers to show that clues on the Pb provenance could be obtained through the study of four stable Pb isotopes with the following approximate abundances: \(^{204}\text{Pb}\) (2%), \(^{206}\text{Pb}\) (25%), \(^{207}\text{Pb}\) (21%) and \(^{208}\text{Pb}\) (52%). Of these, \(^{204}\text{Pb}\) is non-radiogenic and \(^{206}\text{Pb}, \(^{207}\text{Pb}\) and \(^{208}\text{Pb}\) are formed by the radioactive decay of \(^{238}\text{U}, \(^{235}\text{U}\) and \(^{232}\text{Th}\) respectively with half-lives of \(4.468\times10^9\), \(0.7038\times10^9\) and \(14.010\times10^9\) years, respectively (Faure, 1986). Lead ores, used to manufacture Pb-based products, have characteristic Pb isotope ratios. These ratios mainly depend on the initial U/Pb and Th/Pb ratios and geological age of the source rocks from which Pb was derived during ore formation. As Pb isotopes do no fractionate measurably during ore processing (e.g., mining and smelting), the Pb isotope ratios of the Pb containing products (anthropogenic Pb) are similar to the isotopic ratios of the ores from which they are made. In their use as geochemical tracers, Pb isotopes are commonly utilized as ratios; with the \(^{206}\text{Pb}/^{207}\text{Pb}, \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) ratios often used in environmental studies as they can be determined fast 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}\text{Pb}, \(^{207}\text{Pb}\) and \(^{208}\text{Pb}\) isotopes. In general it can be stated that the older the Pb ore, the less radiogenic the isotopic composition and the lower the \(^{206}\text{Pb}/^{207}\text{Pb}, \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) ratios.

1.7 Thesis outline

Lead isotope analysis can be a powerful tool to study the origin and behaviour of anthropogenic Pb in the environment (e.g., Komárek et al., 2008 and references therein). However, Pb isotope measurements can only be used to trace anthropogenic Pb sources in polluted soils and sediments if:
General introduction

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

Polluted soils always contain natural, i.e. lithologically inherited, as well as anthropogenic Pb. If the ratio of anthropogenic to 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. In chapter 2 the lithologically inherited variation in Pb content and Pb isotope composition was determined based on a survey of 342 rural subsoils covering The Netherlands. This is a sample density of approximately 1 site per 70 km². The studied subsoils included sand, loess, peat, marine clay and fluviatile clay. The established lithologically inherited variation served as a base to determine the Pb content and Pb isotope composition of the anthropogenic Pb fraction in rural and urban Pb polluted soils in The Netherlands.

In addition to subsoils, the overlying topsoils were also sampled during the nationwide soil survey. To study the effect of land use, these soils were sampled from rural sites used for agricultural (arable land and grassland) and semi-natural (forest, open nature and moor) purposes excluding the potentially contaminated soils in urbanized and industrialized areas. Based on bulk geochemical and Pb isotope analysis, the anthropogenic Pb sources in the topsoils were determined (chapter 3). The spatial distribution of anthropogenic Pb was examined in terms of different land use and pollution sources.

In chapter 3 it is shown that one of the main anthropogenic Pb sources in rural Dutch topsoils is atmospheric Pb (e.g., gasoline Pb and incinerator ash). Although various measures have been taken to improve air quality and reduce atmospheric Pb deposition (e.g., phase out of leaded gasoline and use of filter systems in incinerators), detailed information about the effect of these measures was not available yet for The Netherlands. Various studies have shown that natural archives, such as mires, lake sediments and ice cores can be used to reconstruct historical atmospheric Pb deposition (Komárek et al., 2008 and references therein). In chapter 4 historical anthropogenic Pb deposition has been reconstructed based on 137Cs dated sediments from 2 urban lakes. Anthropogenic Pb sources in the lake sediments were identified using Pb isotope analysis. Lake sediment data were compared with national air monitoring data and conclusions were drawn on the effectiveness of the measures taken to improve the air quality with respect to Pb.

Although atmospheric Pb deposition rates decreased sharply after the ban on leaded gasoline (see chapter 4), roadside soils still contain high anthropogenic Pb contents due to the combustion of leaded gasoline in the past. It is thought that topsoils are in general permanent sinks for anthropogenic Pb. Since gasoline Pb is not emitted to roadside soils anymore, this offers an unique possibility to study the mobility of gasoline Pb in these soils. In chapter 5 the Pb sources and transport rates of anthropogenic Pb in roadside soils over a period of 12 year was determined. In addition, the groundwater composition was studied to establish if anthropogenic Pb already reached groundwater.

In chapter 2 to 5 diffuse anthropogenic Pb sources were studied. Point sources can also cause elevated Pb contents in soils. For example, topsoils in cities and villages with a long habitation history are known for their high Pb content due to the presence of Pb containing household and construction artefacts (e.g., Walraven et al., 1997). Although, these artefacts
only cause a very localised Pb pollution, it poses a serious threat to human health because they often end up in the topsoil of gardens where people grow vegetables and children play. In Chapter 6 anthropogenic Pb sources, mainly related to domestic activities, were traced in Pb polluted soils in two villages and two cities in The Netherlands with a habitation history dating back to Roman times.

Lead can enter the human body after oral ingestion of vegetables and soil, either accidentally via hand-to-mouth behaviour or deliberately (Duggan and Inskip, 1985; Davis and Waller, 1990; Calabrese et al., 1997). Children are especially sensitive to Pb poisoning (Elhelu et al., 1995). Even at low exposure levels (see Section 1.3), Pb causes impairment of normal neurological development in children leading to learning and reasoning difficulties, retardation of physical development, hearing loss, hyperactivity, and reduced attention span (Von Storch et al., 2003). The risk of a Pb polluted soil for children is often expressed as the oral bioaccessibility of Pb in a polluted soil. Chapter 7 examines the oral bioaccessibility of soils polluted with various Pb sources (e.g., gasoline Pb, Pb bullets and pellets and car battery Pb). In addition, the influence of the 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) on oral bioaccessibility was studied. Lead polluted soils from The Netherlands were chosen for this study, because it is one of the most densely populated countries in the world, with many Pb polluted sites (see Section 1.5).

References
General introduction


