Chapter 3

Tracing diffuse anthropogenic Pb sources in rural soils by means of Pb isotope analysis


Abstract

Knowledge of the cause and source of Pb pollution is important to abate environmental Pb pollution by taking source-related actions. Pb isotope analysis is a potentially powerful tool to identify anthropogenic Pb and its sources in the environment. Spatial information about the variation in anthropogenic Pb content and anthropogenic Pb sources in rural topsoils is remarkably limited. This study presents results of a survey of approximately 350 topsoil samples from rural locations covering the entire Netherlands, for which the bulk geochemical and Pb isotope compositions were determined. The specific aim of this study is to determine the anthropogenic Pb sources in the topsoils from rural areas in The Netherlands. The spatial distribution of anthropogenic Pb in soils in The Netherlands will be explained in terms of land use and pollution sources.

Nearly all studied topsoils display Pb contents that exceed the amount expected based on the soil lithology. The range in Pb isotope ratios of the additional Pb fraction in rural Dutch topsoils is established at 1.056- 1.199, 2.336-2.486 and 0.452-0.490 for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ respectively. Five land use types are distinguished (forest, open nature, moor, arable land and grassland) with distinct isotopic compositions for the added Pb. Additional Pb in soils of natural areas (forest, open nature and moor) has on average lower $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios than the agricultural soils (arable land and grassland). Additional Pb in both natural area soils and agricultural soils is interpreted to be of anthropogenic origin: most likely a mixture of coal/galena, incinerator ashes and gasoline Pb. The dominant sources of additional Pb in the topsoil of open nature areas are most likely incinerator ash and gasoline Pb. In contrast, the on average higher $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios of additional Pb in agricultural soils are most likely caused by the presence of animal manure and N-P fertilisers.

Several areas are observed with notably high additional Pb contents (26-211 mg/kg on an organic matter-free basis) in the topsoil. The largest area is the Randstad area, which has the highest population and traffic density, and hosts a considerable fraction of the Dutch chemical industry. Two other areas with high additional Pb contents in the topsoil are located near the Dutch borders and are most likely influenced by German and Belgian chemical industries. The topsoils in the coastal dunes and southern, central and northern forests are characterized by relatively low additional Pb contents (<10 mg/kg on an organic matter-free basis). The
population, traffic and chemical industry density is low in these areas and no fertilisers are applied.

3.1 Introduction

Although no archaeological time period has been named after it, the use of the metal lead (Pb) has been long lived (since the early bronze age, ~6400BC; (Heskel, 1983)). Lead is among the most ductile of metals. In addition to widespread use as piping and building material, Pb or its oxide, have been used extensively in 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 still include building material (sheeting and gutter material), cable sheathing, car batteries, Pb crystal glass, ammunition, radiation protection and solders. The main source for Pb is from sulphide ores (galena), although today just under half of the total annual Pb production of near 8 million tons is from recycled Pb (Smith, 2004).

In a biological (human) context, Pb is a non-essential and toxic metal, that ranks second in the list of prioritised hazardous substances issued by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR, 2007). It can affect almost every organ and system in the human body. The most sensitive is the central nervous system, particularly in young and unborn children. Unborn children can be exposed to lead through their mothers. Harmful effects include premature births, smaller babies, reduced mental ability in the infant, learning difficulties, and reduced growth in young children. In adults, exposure to Pb may decrease reaction time, cause weakness in fingers, wrists, or ankles, and possibly affect the memory. Lead may also cause anaemia and abortion and damage the male reproductive system.

Due to production, use, combustion, recycling, and disposal of Pb and Pb containing products (incl. gasoline Pb, coal and fertilisers), anthropogenic Pb entered, and still enters, the environment worldwide. It is detected in urban and rural soils in many countries (see review of Komárek et al., 2008), and even in very remote areas, like Greenland snow (e.g., Boutron et al., 1991; Rosman et al., 1993, 1994) and Antarctic ice (e.g., Valleslonga et al., 2002). In The Netherlands, for example, it is often claimed that soils without anthropogenic influence no longer exist (e.g., Van der Meent et al., 1990). It is believed that over time almost all topsoils (0-20 cm) have been subjected to human activities in one form or another. The presence of anthropogenic Pb in nearly all Dutch topsoils confirms this conclusion (Van der Veer, 2006). The highest Pb contents in topsoils in The Netherlands – up to 0.5 wt.% of dry matter – are in general measured in urban areas (Walraven et al., 1997; Walraven et al., 2001a,b), but nearly all topsoils in rural areas also show elevated Pb contents (Huisman, 1998; Walraven et al., 2000; Lamé et al., 2004; Van der Veer, 2006). According to Groot and van Swinderen (1993) and Walraven et al. (2000) the main Pb sources in rural areas in The Netherlands are linked to atmospheric deposition and fertilization of the land with animal manure and artificial fertiliser, whereas the major anthropogenic Pb sources in urban areas are remnants of Pb containing products (paint, ceramics, Pb sheets, etc.).

Based on measurements of Pb content alone, it is difficult, if not impossible, to determine the provenance of the elevated Pb content (natural enrichment or human impact), or to determine the anthropogenic Pb source when pertinent. Knowledge about the cause and source of Pb pollution is important to abate environmental Pb pollution by taking source-related actions. Pb isotope analysis has proved to be a powerful tool to distinguish anthropogenic Pb from other sources and to attribute the anthropogenic Pb retained in soils to
Pb consists of four stable isotopes with the following approximate abundances: $^{204}\text{Pb}$ (2%), $^{206}\text{Pb}$ (25%), $^{207}\text{Pb}$ (21%) and $^{208}\text{Pb}$ (52%). $^{204}\text{Pb}$ 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-lifetimes of $4.468 \times 10^9$, $0.7038 \times 10^9$ and $14.010 \times 10^9$ years respectively (Faure, 1986). Pb ores, used to manufacture Pb-based products, have characteristic Pb isotope ratios (e.g., $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ are the most used Pb isotope ratios in environmental studies). These ratios mainly depend on the U/Pb and Th/Pb ratios and geological age of the source rocks from which Pb was derived during ore formation. Because different Pb-based products originate from various Pb ore deposits, Pb isotope ratios of these products are similar to the isotopic ratios of the ores (Faure, 1997). In general it can be stated that the older the Pb ore, the less radiogenic the isotope 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.

Although various studies have been performed to determine anthropogenic Pb sources in soils, these studies are generally based on a limited number of selected soil profiles that are sampled at various depths (e.g., Chow, 1970; Gulson et al., 1981; Walraven et al., 1997; Hansmann and Köppel, 2000; Bränvall et al., 2001; Cloquet et al., 2006b). Studies of a regional or even national level of Pb isotopes in soils, however, are remarkable limited. To our knowledge only Reimann et al. (2011, 2012) determined Pb concentrations and Pb isotope ratios in leaches derived from soils on a national and continental level. They determined Pb and Pb isotopes in 7 N HNO$_3$ leaches from soil samples along an east-west transect across the United States and in agricultural soils of Europe. The sample density in these studies was limited, every 40 km in the USA and at an average density of 1 site/2500 km$^2$ in Europe.

In this study, the bulk geochemical (among others Pb content) and Pb isotope composition of approximately 700 topsoils and subsoils from rural areas, covering the entire Netherlands, were analysed. The subsoil (BC, or C horizon, 100-120 cm by default) samples were used to determine the lithologically inherited variation of the Pb isotope composition in Dutch soils and to estimate the isotopic composition of this Pb in the topsoils. The results of the subsoils are presented in Walraven et al. (2013). The aim of this present study is to unravel the anthropogenic Pb sources in the topsoils of rural areas in The Netherlands. In addition, the spatial distribution of anthropogenic Pb in soils in The Netherlands will be examined in terms of different land use and pollution sources.

### 3.2 Background information

#### 3.2.1 General geology and land use of The Netherlands

The general geology of The Netherlands is described in Walraven et al. (2013). As many deltaic areas, The Netherlands with its ~16.7 million inhabitants is densely populated (average density of ~500 inhabitants/km$^2$). About one third of the population lives in the three major cities in the Midwest of The Netherlands: Amsterdam, Rotterdam and The Hague (collectively known as the “Randstad”). About 17% of the total available land surface in The Netherlands can be classed as built-up areas, such as cities, industrialized areas, roads and roadsides (Van der Veer, 2006). Most of the Dutch land surface (~70%) is used as agricultural land and the remaining 13% is used as production woods and natural areas (Van der Veer, 2006). The latter includes heath lands, small forests and various types of wetlands. Fig. 3.1 gives a spatial overview of the distribution of the various basic land use types (agricultural
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land, production forest and nature reserve) in The Netherlands. In the present study five land use types are distinguished: grassland, arable land, forest, open nature and moor (data from Statistics Netherlands (CBS, 2012)). Grassland and arable land are assigned as agricultural land in Fig. 3.1; open nature and moor are part of the nature reserve; forest and production forest are grouped under the same land use.

![Overview map showing the basic land use types in The Netherlands](image)

Fig. 3.1. Overview map showing the basic land use types in The Netherlands (source: Van der Veer, 2006; with permission; data from CBS, 2012).

3.2.2 General pedology of The Netherlands

A concise description of the pedology of the subsoil can be found in Walraven et al. (2013). Relevant topsoil pedology is briefly described here. Time is an important (top)soil forming factor. As a result of the restricted age of the parent material (from 12,000 years for loess to <50 years for marine clay) – most of the Holocene sediments were covered with peat until 100 A.D. – and a temperate climate, (top)soils in The Netherlands are poorly developed compared with those in other parts of the world. As a consequence, soil formation did not have a strong effect on the distribution of major and trace elements in the topsoil layers (Van
der Veer, 2006). For the very young Holocene soils, which only experienced ripening and soil organic matter accumulation, this is obvious. Pleistocene soils, however, often show both organic matter accumulation as well as some podzolization. Podzolization will have slightly altered the composition of the topsoil layer, because it involves eluviation/illuviation of clay particles, iron and related elements. On a bulk chemical/mineralogical scale, however, this effect seems rather marginal as no strong depletions of the mobile elements are observed (Van der Veer, 2006).

3.2.3 Geochemical soil survey of The Netherlands

The topsoil samples collected by Van der Veer (2006) for an extensive geochemical soil survey of The Netherlands are used in this study. One of the aims of the study of Van der Veer (2006) was to quantify enrichment/depletion of elements in the topsoil (0-20 cm). Elemental enrichment/depletion can be determined by directly comparing the content of an element in the topsoil with the content in the parent material (subsoil). However, to exclude differences caused by different lithology/mineralogy between both the topsoils and subsoil layer, as well as within the different lithologies, Van der Veer (2006) performed a correction based on the linear regression of elemental compositions with respect to Al. Such Al-based correction has been used previously by many others (e.g., Huisman, 1998; Spijker, 2005) and is based on the joint occurrence of most trace metals (including Pb) in aluminosilicates.

Aluminosilicates (clays, micas, chlorite and feldspars) represent the dominant host minerals for the majority of the elements in the soil parent material in The Netherlands. Only a few elements are partly, or mainly, contained in other phases, which include Si (quartz), Ca (calcite), S (organic matter or sulphide/sulphates) and Zr and Hf (zircon). Since the soil parent material in The Netherlands consists of eolian sands, loess, sandy to clayey fluviatile and marine deposits and peat layers, the elements that are contained in, or associated with, the aluminosilicates show increasing abundance from sandy lithologies (low Al content) to more silt and clay rich lithologies (higher Al contents). An alternative way to describe this variation is that quartz (i.e., sand) acts as a diluter to elemental abundances in soils.

Van der Veer (2006) observed a more or less linear relationship between the contents of Al and various trace elements, including Pb, in the soil parent material (subsoils) in The Netherlands. To determine enrichment/depletion factors for the topsoil layers, Van der Veer (2006) assumed that this subsoil derived relation is representative of the parent material and the pristine condition of the topsoil layer (i.e. before soil formation and possible anthropogenic imprint). The effects of possible anthropogenic dispersion of trace elements are expected to be independent of the Al concentrations as there is no major anthropogenic Al source. As such, the potential enrichment (or depletion) of elements is quantified as the absolute difference between the content expected on the basis of the Al content (derived from the relation in the soil parent material) and the actual content in the topsoil. It implies that effects of soil formation on Al content – that are not directly related to textural changes – are assumed negligible. Only if Al is removed (depleted) and Pb is not, there would be a natural enrichment of Pb due to soil formation. This, however, was not observed by Van der Veer (2006).

The relation between the Al and Pb content in Dutch subsoils and topsoils, as established by Van der Veer (2006), is illustrated in Fig. 3.2. Fig. 3.2a shows an increasing Pb content with an increasing Al content in the subsoils. This relation is also visible in the topsoils, however, they contain additional Pb. This relative Pb enrichment in the topsoils is shown per
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lithology in Fig. 3.2b. Apart from Pb, the topsoils in The Netherlands are also enriched in P, Cd, Cu, Hg and Zn (Van der Veer, 2006). Compared with the prevailing contents in the parent material, average enrichment factors of around two or three are observed. This is clear evidence for an additional source/supply of these trace elements on the scale of The Netherlands (Van der Veer, 2006). The enrichment observed for the topsoil layer in The Netherlands is likely to be largely of an anthropogenic origin.

![Graph](image)

**Fig. 3.2.** (a) Pb (mg/kg) versus Al (wt.%) in subsoils and topsoils of The Netherlands (data from Van der Veer, 2006). (b) Pb (mg/kg) enrichment/depletion in topsoils in The Netherlands (data from Van der Veer, 2006). Enrichment/depletion is calculated according to: 
\[ \text{Pb}_{\text{t}(\text{enrichment/depletion})} = \text{Pb}_t - (\text{Al}_t \times 3.4 + 2.7), \]  
where Pb\(_t\)(enrichment/depletion) is calculated enrichment/depletion of Pb (in mg/kg) in topsoil, Pb\(_t\) and Al\(_t\) are measured Pb (in mg/kg) and Al (in wt.% content in topsoil (after Van der Veer, 2006).

3.3 Methods

3.3.1 Soil sampling

During an extensive soil sampling campaign in The Netherlands, 358 locations were sampled by Van der Veer (2006). At each sample location, a soil sample was taken from the soil parent material (BC, or C horizon, 100-120 cm by default) as well as the topsoil (A-horizon, 0-20 cm). Sampling details are given in Walraven et al. (2013), where the overall procedures and the results of the subsoil samples are addressed. In this study we will discuss the results of the 336 topsoil samples – in relation to those of the subsoils – that were analysed for Pb isotopes as well as major and trace element composition.

3.3.2 Sampling of anthropogenic Pb sources

The dominant anthropogenic Pb sources in rural soils in The Netherlands are atmospheric deposition (among others coal Pb, gasoline Pb, incinerator Pb) and fertilisers (Groot et al.,
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1998). Ten natural Dutch coal samples were obtained from the former geological Survey of The Netherlands. The samples originate from coal mines in Limburg, a province in the southern part of The Netherlands. Unless otherwise stated, these samples were handled the same way as the topsoil samples. Gasoline Pb and incinerator Pb were not sampled or analysed in this study, but relevant data are reported elsewhere (Komárek et al., 2008; Walraven et al., 2014).

Twenty-two commonly used animal manures and N-P fertilisers were obtained from the National Institute of Public Health and the Environment. These comprise manure from pigs (PM), dairy cattle (DCM) and poultry (CM), and diammonium phosphate (DAP), nitrogen phosphate (NP) and triple superphosphate (TSP). Unless stated otherwise, these samples were also handled the same way as the topsoil samples.

3.3.3 Sample preparation

Prior to analysis, soil samples were dried at 40 °C to a constant weight, disaggregated and sieved (<2 mm). To create a representative subsample for laboratory analysis as well as a sample archive, the material was split into 20-30 g aliquots using a mechanical splitter. At this stage of the processing, sample duplicates and a standard sample were inserted for quality evaluation purposes. The subsamples for analysis were thereafter ground using an automated tungsten-carbide mill (Herzog HSM-HTP). The grinding procedure ensured homogeneous samples, of which representative subsamples could be taken for each analytical method (for details see Van der Veer, 2006).

Prior to analysis, fertiliser and coal samples were dried at 60 °C and 105 °C respectively to a constant weight and ground using an automated tungsten-carbide mill (Herzog HSM-HTP). The grinding procedure ensured homogeneous samples, of which representative subsamples could be taken for each analytical method.

3.3.4 Soil sample analysis

The soil samples were analysed for major and trace elements using X-ray Fluorescence (XRF) spectrometry. XRF analysis was conducted on pressed powder tablets using an ARL9400 spectrometer with a Rh-tube and a full matrix correction for the major elements and a Compton scatter method for trace elements. In addition, the organic matter (OM) contents were established by Thermo-Gravimetric Analysis (LECO TGA601). All contents are either expressed as wt.% or as mg/kg, all based on 40 °C dry sample weight. For the elements considered in this study – Pb, Al, Zr, OM-content – the relative precision ranges from 3.2% to 9.6%; 2 times relative standard deviation (RSD) (based on sample duplicates with values >3× limit of quantification (LOQ)). The accuracy for Pb, Al, Zr, OM-content – as determined by soil standard ISE 921 – is 1.9%, 14%, 4.2% and 0.2% respectively (relative bias). Precision and accuracy are based on the entire analytical procedure starting with the sample splits. See Van der Veer (2006) for details.

Lead isotope analysis was performed after HF-based sample destruction. Details of the HF-based sample destruction procedure can be found in Van der Veer (2006). After destruction, samples were measured for Pb isotopes using an Agilent 7500 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with a low uptake nebulizer. Lead contents were also determined by ICP-MS to validate that Pb was totally dissolved with the HF-based destruction procedure. Lead contents measured by ICP-MS match the Pb contents determined with the XRF (logPbicp-ms = 1.01 × logPbref - 0.005; n = 336; R² = 0.94) establishing that Pb is
totally dissolved. Lead content data determined by XRF is henceforth used in this study. To properly determine the Pb isotope ratios using a quadrupole based ICP-MS, a method similar to that described by Krachler et al. (2004) was used. To diminish mass bias in relation to concentration differences, the HF destruction solutions obtained for trace element analysis were diluted with 1 M HNO₃ to a Pb concentration of about 50 µg/kg in solution prior to introduction to the mass spectrometer. Data were taken in the peak jumping mode with three data points acquired across each peak at masses m/z 206, 207 and 208; dwell time for these masses was 20 ms/channel. Ten runs were measured for each sample and the average of the ten ratios for $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb determined. For mass bias correction, a series of six samples were always bracketed by NIST SRM 981. Ratios were corrected independently, i.e. a correction factor was calculated according to the reference value in the standard for each ratio separately. Ratios were corrected assuming a linear drift relative to their measurement position of the bracketing standard samples. The precision based on 37 duplicate pairs was at 2 RSD < 0.22% for $^{206}$Pb/$^{207}$Pb, 2 RSD < 0.17% for $^{208}$Pb/$^{207}$Pb, and 2 RSD < 0.44% for $^{206}$Pb/$^{208}$Pb. The average measured value and absolute precision (2 SD) of the measured ISE 921 sample (n = 45) was 1.166 ± 0.003 for $^{206}$Pb/$^{207}$Pb, 2.444 ± 0.004 for $^{208}$Pb/$^{207}$Pb, and 0.477 ± 0.002 for $^{206}$Pb/$^{208}$Pb. Precision and accuracy are based on the entire analytical procedure starting with the sample splits. Blanks and reagents used were also measured and contained negligible amounts of Pb (<20 ng/kg).

3.3.5 Analysis of manure, N-P fertiliser and coal samples

The manure, N-P fertiliser and coal samples were analysed for trace elements using a Fisons PQ 2+ ICP-MS after microwave enhanced aqua regia digestion. The microwave digestion procedure is described in detail in Spijker (2005). The solutions were analysed using a low uptake 100 µl/min concentric nebuliser. About 75 masses were measured (1 point per mass) with measuring times varying between 0.5 s for masses 23, 26, 27, 39, 43, 44, 55, 56, 57, 85, 86, 88 and 137, 1 s for masses 11, 31, 45, 90 and 206-208 and 2s for masses 7, 9, 47-53, 59-82, 89, 93-133, 139-205 and 209-238.

Three runs were performed for each sample. External calibrations were performed with a procedural blank and 5 multi element calibrations solutions for trace elements and 2 for major elements. These solutions were prepared daily from monthly prepared stock solutions, which were made from 1,000 or 10,000 ppm single element standards (Merck®, Aldrich®, Alpha®, Johnson Matthey®). Indium was added to each sample and calibration fluid as an internal standard. In an analytical series of 54 samples, 6 duplicate samples were placed at the end. Calibration solutions were measured every 30 samples. Resloping by measuring the middle multi-element calibration solution was performed every 10 samples. Resloping was performed by linear extrapolation between the calibration and reslope solutions. After every 10 samples a QC sample was measured, made from a different brand of calibration stock solutions.

All contents are expressed as mg/kg based on dry sample weight. For the element considered in this study – Pb – the relative precision and accuracy of the analyses is 7.4% 2RSD and 5.7% relative bias respectively (based on soil standard ISE 970 and ISE 989 (www.wepal.nl)). Precision and accuracy are based on the entire analytical procedure starting with the sample splits.
3.3.6 Data analysis

3.3.6.1 Correction for the organic fraction

To calculate the additional Pb content and Pb isotope composition of the additional Pb fraction, the topsoil that has undergone soil formation and human influence, will be compared with the parent material (see Section 3.3.6.2). An important aspect of soil formation is the incorporation of organic material (essentially via uptake of CO₂ from the atmosphere by vegetation). To adequately compare trace element contents in topsoil with those in the parent material this added organic fraction should be accounted for in some way. Here, elemental contents are therefore recalculated to an organic free basis:

\[ [C]_{\text{recalc}} = \frac{[C]}{100/(100-\text{OM} \%) } \]  (3.1)

with [C] the content of any constituent (in % or mg/kg) on a dry total mass basis, and \([C]_{\text{recalc}}\) the content on a dry organic free mass basis. OM\% is the content of organic matter on a dry total mass basis. This correction for the organic fraction has no influence on the Pb isotope ratios themselves, as within one sample the correction factor is the same for all analytes.

In principle, recalculation could also have been on a carbonate free basis. This correction was not performed because the corrections would be very minor (on average less than about 1/10th of that for OM) and would require detailed knowledge about the carbonate mineralogy (presence of primary and secondary carbonate and non-unique attribution of Ca to CaCO₃).

3.3.6.2 Calculation of the Pb content and Pb isotope composition of the additional Pb fraction in the topsoil

Topsoils can contain both lithologically inherited Pb and additional Pb (e.g., anthropogenic Pb or naturally enriched Pb). The total measured Pb isotope composition of topsoils is a mixture of the isotopic composition of both the natural and additional Pb fraction. To derive the Pb isotope composition of the additional Pb fraction, it is necessary to account for the amount of lithologically inherited Pb present in the topsoil. The following equation describes this mass balance principle in approximation:

\[ (\delta^{184}\text{Pb}/\delta^{206}\text{Pb})_{a} \times [\text{Pb}_{\text{recalc}}]_{a} = (\delta^{184}\text{Pb}/\delta^{206}\text{Pb})_{t} \times [\text{Pb}_{\text{recalc}}]_{t} - (\delta^{184}\text{Pb}/\delta^{206}\text{Pb})_{li} \times [\text{Pb}_{\text{recalc}}]_{li} \]  (3.2)

in which the letters a, t and li indicate the Pb content \([\text{Pb}_{\text{recalc}}]\) and Pb isotope composition \((\delta^{184}\text{Pb}/\delta^{206}\text{Pb})\) of the additional, total and lithologically inherited Pb fraction, respectively. \((\delta^{184}\text{Pb}/\delta^{206}\text{Pb})_{a}\) and \([\text{Pb}_{\text{recalc}}]_{a}\) of the topsoils are measured in this study. Since \(^{204}\text{Pb}\) is not measured, a small but negligible error is introduced in Eq. (3.2). Because \(^{204}\text{Pb}\) is only a minor percentage (approximately 1.5-1.7%) of the total lead content, and this is present at both sides of the equation, the error made in the mass balance equation is less than 0.2% relative. Because Dutch topsoils are seldom polluted with Al, the lithologically inherited Pb content in the topsoils \([\text{Pb}_{\text{recalc}}]_{li}\) can be calculated based on the correlation between Al\(_{\text{recalc}}\) and Pb\(_{\text{recalc}}\) in Dutch subsoils (Walraven et al., 2013):

\[ [\text{Pb}_{\text{recalc}}]_{li} = 3.61 \times [\text{Al}_{\text{recalc}}] + 2.05 \]  (3.3)
in which \([\text{Pb}_{\text{recalc}}]_{li}\) is the calculated lithologically inherited Pb content on organic free basis in mg/kg in the topsoil, and \([\text{Al}_{\text{recalc}}]\) is the measured Al content on organic free basis in wt.% in the topsoil \((n = 303; R^2 = 0.88; \text{Standard error of estimate is } 3.5 \text{ mg/kg})\). The additional Pb content in the topsoils \([\text{Pb}_{\text{recalc}}]_a\) can then be calculated as follows:

\[
[\text{Pb}_{\text{recalc}}]_a = [\text{Pb}_{\text{recalc}}]_t - [\text{Pb}_{\text{recalc}}]_{li}
\]  

in which \([\text{Pb}_{\text{recalc}}]_a\) and \([\text{Pb}_{\text{recalc}}]_{li}\) (Eq. (3.3)) are the calculated additional and lithologically inherited Pb content on organic free basis in mg/kg in the topsoil, and \([\text{Pb}_{\text{recalc}}]_t\) is the measured total Pb content on organic free basis in mg/kg in the topsoil.

If the Pb isotope composition of the lithologically inherited Pb fraction in the topsoil is also known, the Pb isotope composition of the additional Pb fraction in the topsoil can be calculated (see Eq. (3.2)). The Pb isotope composition of the lithologically inherited Pb fraction can be determined in two ways, (1) by analysing the lithologically inherited Pb isotope composition in the subsoil underlying the topsoil (method 1) or (2) by calculating the lithologically inherited Pb isotope composition based on the \([Zr_{\text{recalc}}]\) and \([\text{Al}_{\text{recalc}}]\) content of the topsoil samples (method 2, Walraven et al., 2013). The correlation between the methods is presented in Fig. 3.3. A good correlation between the Pb isotope ratios of additional Pb, calculated with the lithologically inherited Pb isotope composition based on method 1 and 2, is observed. This suggests that both methods are adequate in estimating the Pb isotope composition of the additional Pb fraction. The calculated correlations (expressed as \(R^2\)), however, depend on the additional Pb content \([\text{Pb}_{\text{recalc}}]_a\) of the topsoils. The higher \([\text{Pb}_{\text{recalc}}]_a\), the better the correlation. It stresses the limitation of calculating the Pb isotope composition of additional Pb in topsoils using the mass balance principle (Eq (3.2)). If the additional Pb content in a topsoil is low compared with the lithologically inherited Pb content, the error in the calculated Pb isotope composition of the additional Pb fraction can be substantial. For example, the calculated lithologically inherited Pb content (Eq. (3.3)) is not a fixed value, but has a standard error of estimate of 3.5 mg/kg \((1 \text{ s})\) (Eq. (3.3)). This means that for calculated additional Pb contents of less than 7 mg/kg \((2 \text{ s})\) the total Pb concentration falls in the normal range for lithologically inherited Pb. Topsoils with a \([\text{Pb}_{\text{recalc}}]_a\) content < 7 mg/kg are therefore not used for the identification of the additional (e.g., anthropogenic) Pb sources.

Although both method 1 and 2 can be used to calculate the Pb isotope composition of additional Pb in topsoils (Fig. 3.3), method 1 is preferred, because it is based on measured Pb isotope data at the same location. However, method 1 can only be used if (i) subsoil data are available, (ii) the subsoil contains only lithologically inherited Pb, and (iii) the lithology of the subsoil is the same as that of the topsoil. In other words, the subsoil must be a ‘true’ C-horizon of the topsoil. In this study method 1 was applied as these criteria are met \((n = 269)\) and method 2 is used for all other samples \((n = 67)\).

### 3.3.7 Data and graphical representation

The Pb isotope ratios are presented in bivariate plots of the Pb isotope ratios (so-called 3-isotope biplots with a common isotope denominator). Both bivariate plots with \(^{207}\text{Pb}\) and \(^{208}\text{Pb}\) as denominator are presented as \(^{207}\text{Pb}\) is commonly used as denominator in environmental Pb isotope studies and plots with \(^{208}\text{Pb}\) as denominator give the highest resolution.
**Fig. 3.3.** Lead isotope composition of the additional Pb fraction in the topsoils \( (^{206}\text{Pb}/^{207}\text{Pb})_a \) based on mass balance calculations (Eq. (3.2)): method 1 versus method 2. In method 1, the lithologically inherited Pb isotope composition of the topsoil \( (^{206}\text{Pb}/^{207}\text{Pb})_{li} \) is assumed to be equal to the analysed Pb isotope composition of the underlying subsoil. In method 2, \( (^{206}\text{Pb}/^{207}\text{Pb})_{li} \) of the topsoil is based on the \([\text{Zr}_{\text{recalc}}] \) and \([\text{Al}_{\text{recalc}}] \) content of the topsoil (Walraven et al., 2013). The mass balance calculations are performed for the topsoil samples with an additional Pb content \([\text{Pb}_{\text{recalc}}]_a > 0, > 7 \) and > 14. The correlation coefficient \( R^2 \) is calculated for each of these scenarios.
The analytical and calculated results, and subsoil versus topsoil bubble plot maps for \([\text{Pb recal c}]_a\), OM, \([\text{Al recal c}]_a\), \([\text{Zr recal c}]_a\), \([\text{Pb recal c}]_a\), \((^{206}\text{Pb}/^{207}\text{Pb})_a\) and \((^{208}\text{Pb}/^{207}\text{Pb})_a\) are provided in an electronic appendix. The data of the subsoil samples are presented and discussed in Walraven et al. (2013).

3.4 Results
3.4.1 Topsoils

Table 3.1 summarises the analytical and calculated results of all topsoil samples. The variation in additional Pb content and its Pb isotope composition is presented in box-whisker plots in Fig. 3.4 for the five land use types and four different lithologies. \([\text{Pb recal c}]_a\) varies between <limit of detection (LOD) and 1863 mg/kg (Table 3.1). The median \([\text{Pb recal c}]_a\) content of arable land, grassland, forest and open nature is remarkable similar (10-15 mg/kg; Table 3.1, Fig. 3.4). Only the median \([\text{Pb recal c}]_a\) content of moor topsoils is higher at 259 mg/kg. This group comprises only three samples, which are all from peat soils (see below). The open nature topsoils in “open” nature areas (mainly heather and grassland) have the lowest \([\text{Pb recal c}]_a\) content while moor topsoils have the highest values (Table 3.1 and Fig. 3.4). No clear difference in \([\text{Pb recal c}]_a\) content between the sand, clays and loess topsoils is observed (Table 3.1 and Fig. 3.4). In contrast, the \([\text{Pb recal c}]_a\) content in peaty soils is much higher than that of the loess, clays and sands (3-1863 mg/kg vs. <LOD-211 mg/kg; Table 3.1 and Fig. 3.4). This is largely the consequence of reporting the Pb content on an organic free soil mass basis. Van der Veer (2006) demonstrated that the additional Pb content as calculated on a volumetric or square area basis is independent of soil type.

The Pb isotope composition of the additional Pb fractions is calculated only for the topsoils with \([\text{Pb recal c}]_a > 7 \text{mg/kg}\) (see Section 3.6.2). This is the case for approximately 80% of all topsoils (265 out of 336). The \((^{206}\text{Pb}/^{207}\text{Pb})_a\) ratios vary between 1.056 and 1.199 with a median of 1.159 (n = 265; Table 3.1, Fig. 3.4). Leaving out the single lowest and highest value (n = 263), the range is between 1.128 and 1.196. Agricultural topsoils – consisting of arable land and grassland (pasture) – have comparable median \((^{206}\text{Pb}/^{207}\text{Pb})_a\) ratios of 1.162 and 1.160 respectively. Natural topsoils – consisting of forest, open nature and moor – also have comparable, slightly lower median \((^{206}\text{Pb}/^{207}\text{Pb})_a\) ratios of 1.151, 1.150 and 1.153 respectively (Table 3.1, Fig. 3.4). This pattern is also observed within the four individual lithologies: on average lower \((^{206}\text{Pb}/^{207}\text{Pb})_a\) ratios are observed in the natural topsoils as compared with the agricultural topsoils. As expected, no dependency is observed for the \((^{206}\text{Pb}/^{207}\text{Pb})_a\) ratios between soils with different lithology. This supports the hypothesis that the calculated ratios truly represent those of additional sources that do not depend on lithological variations.

The \((^{208}\text{Pb}/^{207}\text{Pb})_a\) and \((^{206}\text{Pb}/^{208}\text{Pb})_a\) ratios vary between 2.336-2.486 with a median of 2.441, and between 0.452-0.490 with a median of 0.475, respectively (n = 265; Table 3.1, Fig. 3.4). If the topsoil samples with the lowest and highest ratio are disregarded, the ratios vary between 2.389-2.475, and between 0.463-0.483 (n = 263). Similar patterns are observed for the \((^{206}\text{Pb}/^{207}\text{Pb})_a\), \((^{208}\text{Pb}/^{207}\text{Pb})_a\) and \((^{206}\text{Pb}/^{208}\text{Pb})_a\) ratios. The variations of Pb isotope values are coherent within each land use type but differ between the types.
Table 3.1. Summary of the analytical and calculated results of the rural topsoils in The Netherlands.

<table>
<thead>
<tr>
<th>Measured parameter</th>
<th>Statistic</th>
<th>All</th>
<th>All</th>
<th>Sand</th>
<th>Clay</th>
<th>Peat</th>
<th>Loess</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>G</td>
<td>F</td>
<td>O</td>
<td>M</td>
<td>A</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td>336</td>
<td>112</td>
<td>150</td>
<td>64</td>
<td>7</td>
<td>59</td>
</tr>
<tr>
<td>MIN</td>
<td></td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>184</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td>MED</td>
<td></td>
<td>13</td>
<td>10</td>
<td>15</td>
<td>13</td>
<td>11</td>
<td>259</td>
</tr>
<tr>
<td>MAX</td>
<td></td>
<td>1863</td>
<td>156</td>
<td>315</td>
<td>1863</td>
<td>23</td>
<td>848</td>
</tr>
<tr>
<td>[Pbrecalc] (mg/kg)</td>
<td>MIN</td>
<td>1.056</td>
<td>1.131</td>
<td>1.128</td>
<td>1.056</td>
<td>1.138</td>
<td>1.146</td>
</tr>
<tr>
<td></td>
<td>MED</td>
<td>1.159</td>
<td>1.162</td>
<td>1.160</td>
<td>1.150</td>
<td>1.153</td>
<td>1.161</td>
</tr>
<tr>
<td></td>
<td>MAX</td>
<td>1.199</td>
<td>1.196</td>
<td>1.188</td>
<td>1.159</td>
<td>1.168</td>
<td>1.189</td>
</tr>
<tr>
<td>(206Pb/207Pb)</td>
<td>MIN</td>
<td>2.336</td>
<td>2.412</td>
<td>2.389</td>
<td>2.336</td>
<td>2.421</td>
<td>2.431</td>
</tr>
<tr>
<td></td>
<td>MED</td>
<td>2.441</td>
<td>2.444</td>
<td>2.443</td>
<td>2.434</td>
<td>2.441</td>
<td>2.444</td>
</tr>
<tr>
<td></td>
<td>MAX</td>
<td>2.486</td>
<td>2.475</td>
<td>2.463</td>
<td>2.486</td>
<td>2.440</td>
<td>2.440</td>
</tr>
<tr>
<td>[Zrrecalc] (mg/kg)</td>
<td>MIN</td>
<td>0.490</td>
<td>0.490</td>
<td>0.483</td>
<td>0.475</td>
<td>0.475</td>
<td>0.475</td>
</tr>
<tr>
<td></td>
<td>MED</td>
<td>0.475</td>
<td>0.476</td>
<td>0.476</td>
<td>0.475</td>
<td>0.475</td>
<td>0.475</td>
</tr>
<tr>
<td></td>
<td>MAX</td>
<td>0.490</td>
<td>0.490</td>
<td>0.483</td>
<td>0.475</td>
<td>0.475</td>
<td>0.475</td>
</tr>
<tr>
<td>[Alrecalc] (wt.%)</td>
<td>MIN</td>
<td>0.44</td>
<td>0.44</td>
<td>0.85</td>
<td>0.99</td>
<td>0.44</td>
<td>53.26</td>
</tr>
<tr>
<td></td>
<td>MED</td>
<td>2.11</td>
<td>2.38</td>
<td>3.69</td>
<td>1.19</td>
<td>0.97</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td>MAX</td>
<td>12.56</td>
<td>9.88</td>
<td>12.56</td>
<td>9.18</td>
<td>1.77</td>
<td>4.59</td>
</tr>
</tbody>
</table>

LOD = limit of detection
A = arable land
G = grassland
F = forest
O = open nature
M = moor
Fig. 3.4. Box-whisker plots of [Pb\text{recalcl}]_h, (206\text{Pb}/207\text{Pb})_h, (208\text{Pb}/207\text{Pb})_h and (206\text{Pb}/208\text{Pb})_h in the subsoils and [Pb\text{recalcl}]_a, (206\text{Pb}/207\text{Pb})_a, (208\text{Pb}/207\text{Pb})_a and (206\text{Pb}/208\text{Pb})_a in the topsoils showing the minimum (lower whisker), maximum (upper whisker), median (centre of the box), lower quartile (bottom of box), and upper quartile (top of box) values.
3.4.2 Coals and fertilisers

Table 3.2 summarises the analytical results of the coal, manure and N-P fertiliser samples. The Pb content of the Dutch coal samples varies from 3 to 42 mg/kg. The $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios of the coal samples range between 1.171-1.184, 2.438-2.450 and 0.479-0.484 respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb (mg/kg)</th>
<th>$^{206}$Pb/$^{207}$Pb</th>
<th>$^{208}$Pb/$^{207}$Pb</th>
<th>$^{206}$Pb/$^{208}$Pb</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal 1</td>
<td>25</td>
<td>1.180</td>
<td>2.441</td>
<td>0.483</td>
<td>DouvergenhoutXIX</td>
</tr>
<tr>
<td>Coal 2</td>
<td>42</td>
<td>1.174</td>
<td>2.438</td>
<td>0.482</td>
<td>DouvergenhoutXIX</td>
</tr>
<tr>
<td>Coal 3</td>
<td>19</td>
<td>1.181</td>
<td>2.450</td>
<td>0.482</td>
<td>DouvergenhoutXIX</td>
</tr>
<tr>
<td>Coal 4</td>
<td>6</td>
<td>1.171</td>
<td>2.441</td>
<td>0.480</td>
<td>Bocholtz-GB-111</td>
</tr>
<tr>
<td>Coal 5</td>
<td>4</td>
<td>1.171</td>
<td>2.445</td>
<td>0.479</td>
<td>Bocholtz-GB-111</td>
</tr>
<tr>
<td>Coal 6</td>
<td>3</td>
<td>1.177</td>
<td>2.445</td>
<td>0.482</td>
<td>Bocholtz-GB-111</td>
</tr>
<tr>
<td>Coal 7</td>
<td>18</td>
<td>1.182</td>
<td>2.447</td>
<td>0.483</td>
<td>Winthagen B113</td>
</tr>
<tr>
<td>Coal 8</td>
<td>17</td>
<td>1.180</td>
<td>2.441</td>
<td>0.483</td>
<td>Winthagen B113</td>
</tr>
<tr>
<td>Coal 9</td>
<td>38</td>
<td>1.184</td>
<td>2.446</td>
<td>0.483</td>
<td>Baneheide B115</td>
</tr>
<tr>
<td>Coal 10</td>
<td>10</td>
<td>1.182</td>
<td>2.440</td>
<td>0.484</td>
<td>Baneheide B115</td>
</tr>
</tbody>
</table>

(N, P) fertilisers (on dry basis)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb (mg/kg)</th>
<th>$^{206}$Pb/$^{207}$Pb</th>
<th>$^{208}$Pb/$^{207}$Pb</th>
<th>$^{206}$Pb/$^{208}$Pb</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP 1</td>
<td>14</td>
<td>1.161</td>
<td>2.443</td>
<td>0.475</td>
<td>Nitrogenphosphate</td>
</tr>
<tr>
<td>NP 2</td>
<td>11</td>
<td>1.149</td>
<td>3.022</td>
<td>0.466</td>
<td>Nitrogenphosphate</td>
</tr>
<tr>
<td>NP 3</td>
<td>12</td>
<td>1.173</td>
<td>2.450</td>
<td>0.479</td>
<td>Nitrogenphosphate</td>
</tr>
<tr>
<td>NP 4</td>
<td>10</td>
<td>1.173</td>
<td>2.450</td>
<td>0.479</td>
<td>Nitrogenphosphate</td>
</tr>
<tr>
<td>NP 5</td>
<td>2</td>
<td>3.335</td>
<td>2.202</td>
<td>1.514</td>
<td>Trippelsuperphosphate</td>
</tr>
<tr>
<td>TSP 1</td>
<td>3</td>
<td>2.232</td>
<td>2.347</td>
<td>0.951</td>
<td>Trippelsuperphosphate</td>
</tr>
<tr>
<td>DAP 1</td>
<td>1</td>
<td>1.496</td>
<td>2.561</td>
<td>0.584</td>
<td>Diammoniumphosphate</td>
</tr>
<tr>
<td>DAP 2</td>
<td>1</td>
<td>1.436</td>
<td>2.536</td>
<td>0.566</td>
<td>Diammoniumphosphate</td>
</tr>
</tbody>
</table>

Manure (on dry basis)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb (mg/kg)</th>
<th>$^{206}$Pb/$^{207}$Pb</th>
<th>$^{208}$Pb/$^{207}$Pb</th>
<th>$^{206}$Pb/$^{208}$Pb</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM 1</td>
<td>10</td>
<td>1.154</td>
<td>2.434</td>
<td>0.474</td>
<td>Dairy cattle manure</td>
</tr>
<tr>
<td>DCM 2</td>
<td>29</td>
<td>1.153</td>
<td>2.429</td>
<td>0.475</td>
<td>Dairy cattle manure</td>
</tr>
<tr>
<td>DCM 3</td>
<td>36</td>
<td>1.152</td>
<td>2.423</td>
<td>0.475</td>
<td>Dairy cattle manure</td>
</tr>
<tr>
<td>DCM 4</td>
<td>37</td>
<td>1.164</td>
<td>2.432</td>
<td>0.478</td>
<td>Dairy cattle manure</td>
</tr>
<tr>
<td>PM 1</td>
<td>6</td>
<td>1.160</td>
<td>2.439</td>
<td>0.476</td>
<td>Pig manure</td>
</tr>
<tr>
<td>PM 2</td>
<td>13</td>
<td>1.159</td>
<td>2.442</td>
<td>0.475</td>
<td>Pig manure</td>
</tr>
<tr>
<td>PM 3</td>
<td>8</td>
<td>1.164</td>
<td>2.439</td>
<td>0.477</td>
<td>Pig manure</td>
</tr>
<tr>
<td>PM 4</td>
<td>6</td>
<td>1.177</td>
<td>2.454</td>
<td>0.480</td>
<td>Pig manure</td>
</tr>
<tr>
<td>PM 5</td>
<td>27</td>
<td>1.154</td>
<td>2.430</td>
<td>0.475</td>
<td>Pig manure</td>
</tr>
<tr>
<td>PM 6</td>
<td>9</td>
<td>1.171</td>
<td>2.442</td>
<td>0.479</td>
<td>Pig manure</td>
</tr>
<tr>
<td>PM 7</td>
<td>44</td>
<td>1.153</td>
<td>2.428</td>
<td>0.475</td>
<td>Pig manure</td>
</tr>
<tr>
<td>CM 1</td>
<td>17</td>
<td>1.175</td>
<td>2.447</td>
<td>0.480</td>
<td>Poultry manure</td>
</tr>
<tr>
<td>CM 2</td>
<td>23</td>
<td>1.175</td>
<td>2.442</td>
<td>0.481</td>
<td>Poultry manure</td>
</tr>
</tbody>
</table>

The Pb content of the N-P fertilisers varies from 1 to 14 mg/kg. The Pb content increases in the following order: DAP < TSP < NP. The $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios of the N-P fertilisers range between 1.161-3.335, 2.202-2.561 and 0.475-1.514, respectively. The $^{206}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios increase in the following order: NP < DAP < TSP. The $^{208}$Pb/$^{207}$Pb ratios increase in the following order: TSP < DAP < NP. Only sample NP2 has a lower Pb content and $^{206}$Pb/$^{208}$Pb ratio, and higher $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{207}$Pb ratios compared...
with the other NP samples. Note that the number of artificial fertiliser samples analysed here is very limited, and may not be representative for the several hundred different types of artificial fertilisers that are or have been used in The Netherlands (CBS, 2012).

The Pb content of the manure samples varies from 6 to 44 mg/kg. The $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios of manure samples range between 1.153-1.177, 2.423-2.454 and 0.474-0.481 respectively. No difference in Pb content and Pb isotope composition is observed between the three animal manure types – dairy cattle, pig and poultry. The number of animal manure samples reported here is limited. Given the large quantities of animal feed imported from other countries (Bouwman et al., 2011), the variation in Pb content and Pb isotope composition of manure in The Netherlands is most likely much higher than could be determined in this study.

3.5 Discussion

3.5.1 Origin of additional Pb in rural topsoils in The Netherlands

To trace the sources of additional Pb in rural soils in The Netherlands, $^{208}\text{Pb}/^{207}\text{Pb}$ is plotted versus $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ (Figs. 3.5 and 3.6). These figures also include data of potential anthropogenic Pb sources (e.g., gasoline Pb, Dutch and Belgian coal and galena ore, incinerator ashes, manures and N-P fertilisers). Belgian coal samples and gasoline Pb are reported in Walraven et al. (1997) and Walraven et al. (2014). The Pb isotope composition of Dutch and Belgian galena Pb and incinerator ash in North-Western Europe were determined and published by others (Pasteels et al., 1980; Cauet et al., 1982; Monna et al., 1997; Chiaradia and Cupelin, 2000; Hansmann and Köppel, 2000; Carignan et al., 2005; Cloquet et al., 2006a).

Nature areas

The dominant sources of additional Pb in topsoils in nature areas in The Netherlands (forest, open nature, moor) is atmospheric deposition (Groot et al., 1998). Worldwide atmospheric deposition can contain lead from various activities such as mining and smelting of Pb ores, waste incineration, and the burning of wood, coal and leaded gasoline (Nriagu and Pacyna, 1988; Farmer et al., 1999; Komárek et al., 2008 and references therein). Due to the absence of large scale mining and smelting activities in The Netherlands, the dominant Pb sources in Dutch atmospheric deposition are most likely incinerator ashes/aerosols, coal ashes and leaded gasoline exhaust fume. This conclusion is consistent with data presented in Figs. 3.5 and 3.6, which demonstrate that the Pb isotope composition of additional Pb in topsoils of nature areas differs from the Pb isotope composition of subsoils (lithologically inherited Pb), and is most comparable with incinerator ash. Monna et al. (1997) reported that the Pb isotope composition of fly ash originating from waste incinerators reflects the average Pb isotope composition of industrial Pb, because all waste products are mixed together and burned in the incinerators. In other words, incinerator ash is a mixture of various anthropogenic Pb sources that can also include gasoline Pb, coal and galena. The Pb isotope composition of additional Pb in topsoils of nature areas can also be explained by a mixture of leaded gasoline and coal/galena Pb (Figs. 3.5 and 3.6), with the former being slightly more dominant. Assuming that gasoline Pb and coal/galena Pb are the two dominant anthropogenic Pb sources in nature areas, topsoils in nature areas contain on average 60% gasoline Pb and 40% coal/galena Pb (based on the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios). Some natural topsoils contain mainly gasoline Pb, while others mainly contain coal/galena Pb (Figs. 3.5 and 3.6).
Fig. 3.5. $(^{208}\text{Pb}/^{207}\text{Pb})_a$ versus $(^{206}\text{Pb}/^{207}\text{Pb})_a$ in rural topsoils in The Netherlands. Ellipses represent the lithologically inherited Pb isotope composition of Dutch soils (subsoil) and the Pb isotope composition of potential anthropogenic Pb sources (gasoline Pb, incinerator ash, coal and galena ore). ¹Walraven et al., 2013; ²Walraven et al., 1997 & data this study; ³Pasteels et al., 1980; ⁴Cauet et al., 1982; ⁵Walraven et al., 2014; ⁶Monna et al., 1997; ⁷Chiaradia and Cupelin, 2000; ⁸Hansmann and Köppel, 2000; ⁹Carignan et al., 2005; ¹⁰Cloquet et al., 2006a.
Tracing diffuse anthropogenic Pb

Fig. 3.6. \( \frac{^{206}\text{Pb}}{^{208}\text{Pb}} \) versus \( \frac{^{207}\text{Pb}}{^{208}\text{Pb}} \) in rural topsoils in The Netherlands. Ellipses represent the lithologically inherited Pb isotope composition of Dutch soils (subsoil) and the Pb isotope composition of potential anthropogenic Pb sources (gasoline Pb, incinerator ash, coal and galena ore). \(^1\)Walraven et al., 2013; \(^2\)Walraven et al., 1997 & data this study; \(^3\)Pasteels et al., 1980; \(^4\)Cauet et al., 1982; \(^5\)Walraven et al., 2014; \(^6\)Monna et al., 1997; \(^7\)Chiaradia and Cupelin, 2000; \(^8\)Hansmann and Köppel, 2000; \(^9\)Carignan et al., 2005; \(^10\)Cloquet et al., 2006a.
The contribution of the various anthropogenic Pb sources to the total additional Pb content at a specific (sample) location is most likely related to the distance of a sample location to roads, Pb emitting industries, power plants (coal) and incinerators. This is not further investigated in this study.

Several measures have been taken to reduce emissions of anthropogenic Pb to the atmosphere. Leaded gasoline has been banned since 1989 A.D. and technical measures have been taken to reduce fly ash emissions from incinerators (Lomborg, 1998). In addition, since the late 1960s coal has been replaced by natural gas as the main energy source in The Netherlands. Dutch and Belgian coal mines all closed by the end of the 1990s, but (brown) coal is still being mined and directly burnt for energy production in Germany. Due to the reductive measures, the average annual Pb concentration in the Dutch atmosphere has decreased by ~ 93% since 1984 A.D. (Hammingh et al., 2002).

Although leaded gasoline has been banned in Europe since 1989 A.D., gasoline Pb entered the Dutch environment from its introduction in 1923 until 1989 A.D. (Lomborg, 1998). This study shows that the historic gasoline input forms a dominant part of the total additional Pb observed in topsoils in nature areas. Because gasoline Pb is banned, coal and incinerator Pb are currently the dominant atmospheric Pb sources in nature areas. Eight coal operated power plants and 12 waste incinerators are still operational in The Netherlands (www.compendiumvoordeleefomgeving.nl). Six new coal operated power plants are planned to be built. Although current atmospheric Pb emissions are low compared with the 1980s, the Pb isotope composition of topsoil in nature areas is expected to slowly but progressively change to more radiogenic Pb isotope values as the cumulative proportion of gasoline Pb to coal and incinerator Pb decreases.

Four natural topsoil samples are very different from the other samples in their additional Pb isotope composition. One sample (indicated in Fig. 3.5d as “1.06, 2.34”) has the lowest measured $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios of all topsoil samples (table 3.1). The Pb isotope composition of this sample matches that of Broken Hill Pb ore (Grousset et al., 1994). Since Broken Hill Pb is only encountered in 1 topsoil sample, it can be considered as a local anthropogenic Pb source in one natural area in The Netherlands. The other three topsoil samples have Pb isotope values for the additional Pb that closely match that of lithologically inherited Pb (label n in Figs. 3.5d and 3.6d). These samples appear to be naturally enriched with Pb and not contain elevated amounts of anthropogenic Pb.

**Agricultural areas**

In agricultural areas the main sources of additional Pb besides the atmospheric input, are animal manure and (N-P-K) fertilisers (Groot et al., 1998). The Pb isotope composition of additional Pb in topsoils in agricultural areas is more radiogenic than in nature areas and clearly differs from lithologically inherited Pb in subsoils (Table 3.1, Figs. 3.5 and 3.6). The Pb isotope composition matches most closely the Pb isotope ratios of the majority of the analysed N-P fertilisers and animal manure samples. However, they can also be explained as a mixture of atmospheric sources (among others gasoline Pb, incinerator ashes, coal/galena Pb) and fertilisers (both N-P fertilisers and animal manure). Ellam (2010) discussed the graphical representation of Pb isotope data for environmental source apportionment in detail. According to the study of Ellam (2010) Pb isotope biplots are not always suitable to distinguish more than two sources of environmental Pb. Linear trends in such plots might be a consequence of the co-linearity of terrestrial leads and care should be taken to indicate simple binary mixing
of Pb sources (Ellam, 2010). It is acknowledged that linear trends observed in the plots can be a consequence of the co-linearity of terrestrial lead and can be explained by the mixing of various Pb sources.

If the Pb isotope composition of the fertilisers is fixed, it would be possible to calculate the proportional contribution of atmospheric deposition and fertiliser emission to the total additional Pb input by using the mass balance Eq. (3.2). Unfortunately, the Pb isotope composition of fertiliser samples shows large variations (Table 3.2). This variation is caused by the worldwide origin of the raw materials from which N-P-K fertilisers are made and the worldwide origin of animal feed used in The Netherlands. Around 1900 A.D. N-P-K fertilisers were introduced. Historical data (CBS, 2012) show that the application of (P, K) fertilisers peaked between 1945 and 1955 A.D. (57 and 70 kg ha/yr for P- and K-fertiliser respectively) and then started to decline (to 20 and 26 kg ha/yr for P- and K-fertiliser respectively). The use of (N) fertilisers peaked in 1986 A.D. (251 kg ha/yr), but has declined to approximately 150 kg ha/yr. The Pb isotope composition of N-P-K fertilisers depends on the origin of the raw materials (e.g., phosphate ores) from which the fertilisers are made. Table 3.2 demonstrates that the Pb isotope composition of (P) fertilisers (both DAP, TSP and NP fertilisers) varies considerably. The DAP and TSP fertilisers, for example, are characterized by a high U and Th content (Walraven et al., 2000), and very radiogenic Pb isotope values (Table 3.2), whereas the NP fertiliser samples (NP 1 to NP 5) are characterized by an average U and Th content (Walraven et al., 2000) and Pb isotope ratios that match the values of animal manure (Table 3.2).

Livestock are mainly fed by grazing and/or by crops grown on topsoil. Animal feed is the main raw material of animal manure. Until the 1960s animal feed had a local origin in The Netherlands. From the 1960s onwards, intensive livestock farming increased rapidly and the import of animal feed from other parts of The Netherlands and other countries similarly increased (Bouwman et al., 2011). Since the Pb isotope composition of natural and anthropogenic Pb in soils, within and between countries, can vary considerably (this study; Komárek et al., 2008; Reimann et al., 2011, 2012), the Pb isotope composition of animal feed may also vary considerably.

Animal feed is not analysed in this study and, unfortunately, there are no Pb isotope data of animal feed in the literature. However, the $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios of most animal manure samples, analysed in this study, are lower than that of the Dutch subsoil (Figs. 3.5 and 3.6). This means that the animal feed for pigs, dairy cattle and poultry appears to contain non-lithologically inherited Pb. Animal manure most likely contains anthropogenic Pb present in animal feed originating from The Netherlands or Pb from countries from which animal feed is imported.

Due to the large variability in Pb isotope composition of fertilisers, the proportional contribution of fertilisers (including manure) to the total additional Pb input to Dutch agricultural topsoils cannot be calculated from the present data. However, Groot et al. (1998) and De Jong and Van der Hoek (2009) performed detailed mass balance studies to determine the proportional contribution of various heavy metal sources to Dutch agricultural soils. They determined that the atmospheric deposition to fertiliser and manure input ratio for Pb in Dutch agricultural topsoils is approximately 4 (80%/20%). This ratio can be used to calculate the average Pb isotope composition of the fertiliser plus manure input based on the mass balance principle as used in Eq. (3.2). Making these assumptions, the average Pb isotope composition of the fertiliser plus manure input to Dutch agricultural soils is 1.198, 2.480 and 0.485 for
$^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ respectively (Table 3.3). These values can be explained by a mixture of animal manure and N-P fertiliser as analysed in this study. However, in this study only a limited number of animal manure and N-P fertiliser samples have been analysed. In addition, the samples are all gathered in a short time span (few weeks) and might represent only part of temporally change inputs as the source of fertiliser and feed has changed with time.

Since the Pb isotope composition of animal manure and N-P fertilisers shows a broad range in values, it cannot be used to determine the proportional contribution of the various Pb sources to Dutch agricultural soils exactly. The different contributions of atmospheric Pb, animal manure Pb and N-P fertiliser to the total additional Pb content in topsoils, can only be calculated if more detailed information is available about the quantities and types of animal manure and (N,P,K) fertilisers that are used and how inputs have changed with time.

Table 3.3. Calculated average Pb isotope composition of fertilisers used in The Netherlands.

<table>
<thead>
<tr>
<th>Anthropogenic Pb source</th>
<th>$^{206}\text{Pb}/^{207}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{207}\text{Pb}$</th>
<th>$^{206}\text{Pb}/^{208}\text{Pb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average atmospheric input, calculated as median for anthropogenic Pb in topsoils in nature areas</td>
<td>1.151</td>
<td>2.434</td>
<td>0.473</td>
</tr>
<tr>
<td>Sum of average atmospheric and fertiliser input, calculated as median for anthropogenic Pb in topsoils in agricultural areas</td>
<td>1.161</td>
<td>2.444</td>
<td>0.476</td>
</tr>
<tr>
<td>Average fertiliser/manure, calculated assuming a 80:20 ratio of atmospheric Pb: fertiliser/manure Pb</td>
<td>1.198</td>
<td>2.480</td>
<td>0.485</td>
</tr>
</tbody>
</table>

3.5.2 Spatial distribution of anthropogenic Pb in rural topsoils in The Netherlands

The spatial distribution of (Pb$_{\text{recalc}}$)$_{a}$, ($^{206}\text{Pb}/^{207}\text{Pb}$)$_{a}$, ($^{208}\text{Pb}/^{207}\text{Pb}$)$_{a}$ and ($^{206}\text{Pb}/^{208}\text{Pb}$)$_{a}$ are shown in Fig. 3.7. For this purpose the (Pb$_{\text{recalc}}$)$_{a}$, ($^{206}\text{Pb}/^{207}\text{Pb}$)$_{a}$, ($^{208}\text{Pb}/^{207}\text{Pb}$)$_{a}$ and ($^{206}\text{Pb}/^{208}\text{Pb}$)$_{a}$ values are interpolated using a simple inverse distance approach. Due to the sample density (1 sample per ~70 km$^2$), the accuracy of the interpolated maps is limited and the regional patterns therefore have to be interpreted with caution. Furthermore, it is noted that the maps are based on data from rural areas only, and as such, are not representative for cities and industrial areas.

The peats (n = 20) are omitted from the data analyses that determines the spatial distribution of (Pb$_{\text{recalc}}$)$_{a}$. The majority of the peat samples have anomalously high (Pb$_{\text{recalc}}$)$_{a}$ values (Table 3.1). As already mentioned, this is caused by the low density of peats and further enhanced by the recalculation of the anthropogenic Pb content on an organic-free basis (Eq. (3.1)).

Several areas with high additional Pb contents in the topsoil are observed in The Netherlands. The largest area is observed in the midwestern part of The Netherlands (Fig. 3.7, area 1). This area of The Netherlands, called Randstad, has the highest population as well as traffic density, and hosts a considerable fraction of the chemical industry (De Smit, 1984a,b,c; AVN, 2008). It is therefore likely, that the high intensity of anthropogenic activities in the Randstad resulted in the high (Pb$_{\text{recalc}}$)$_{a}$ content of the topsoils. Other trace metals, e.g., Zn, Cu and Hg, are also enriched in this area (Van der Veer, 2006). Two other
distinct areas with a relatively high \( \text{Pb}_{\text{recalc}} \) content are observed: one in the south (Fig. 3.7, area 2) and one in the east (Fig. 3.7, area 3) of The Netherlands. The area in the south is most likely influenced by atmospheric deposition from Belgium and German mining and chemical industries (Liege area and Ruhr area), and the area in the east by Dutch chemical industries (De Smidt, 1984b).

The coastal dunes and southern, central and northern forests are characterized by a relatively low \( \text{Pb}_{\text{recalc}} \) contents (Fig. 3.7). The population, traffic and industrial density are relatively low in these areas. In addition, the prevailing wind direction is south-west, preventing polluting atmospheric deposition in the near coastal areas. Furthermore, these nature areas are not fertilized with animal manure and/or N-P-K fertilisers, resulting in a lower anthropogenic Pb input. Fig. 3.7 shows that the coastal dunes and southern, central and northern forests have the lowest observed Pb isotope ratios. This is most likely due to the relatively high proportion of gasoline Pb compared with other diffuse anthropogenic Pb sources. The highest number of low \( \text{Pb}_{\text{recalc}} \), \( \text{Pb}_{\text{gas}} \), \( \text{Pb}_{\text{coal}} \) and \( \text{Pb}_{\text{galena}} \) ratios is observed in the southern forests (Fig. 3.7). These forests host the Dutch Zn smelter in Budel and are close to the Belgium Zn smelters in Balen, Lommel, Neerpelt and Overpelt (the Zn smelters in Budel, Balen en Overpelt are still in operation). The southern forests are situated downwind of these Belgium smelters. The processed Zn ores mainly originate from the former Belgium Congo (now Democratic Republic of Congo). The average Pb isotope composition of these ores – 1.135, 2.400 and 0.473 for \( \text{Pb}_{\text{gas}} \), \( \text{Pb}_{\text{coal}} \) and \( \text{Pb}_{\text{galena}} \) respectively (Doe and Rohrbough, 1977; Sonke et al., 2002) – matches that of additional Pb in the topsoils of the southern forests (Fig. 3.7). Most likely the southern forest soils are polluted with Pb from both gasoline Pb and the Pb emissions from the nearby Zn smelters.

The \( \text{Pb}_{\text{gas}} \), \( \text{Pb}_{\text{coal}} \) and \( \text{Pb}_{\text{galena}} \) ratios of the topsoils in the agricultural areas with a high density of chemical industries close by (Fig. 3.7, area 1-3) resemble that of coal/galena and/or animal manure/fertiliser (Figs. 3.5 and 3.6). However, based on the relatively high \( \text{Pb}_{\text{recalc}} \) content and relatively high \( \text{Pb}_{\text{gas}} \), \( \text{Pb}_{\text{coal}} \) and \( \text{Pb}_{\text{galena}} \) ratios in the topsoils of these three agricultural areas – compared with the other agricultural areas – the major additional Pb source is most likely coal/galena. In the agricultural topsoils that are not in the vicinity of Pb emitting industries, the \( \text{Pb}_{\text{recalc}} \) content and \( \text{Pb}_{\text{gas}} \), \( \text{Pb}_{\text{coal}} \) and \( \text{Pb}_{\text{galena}} \) ratios show more intermediate values matching the fertiliser signature more closely (Fig. 3.7).

Reimann et al. (2012) determined Pb and Pb isotopes in agricultural soils of Europe, including The Netherlands. Although they did not perform a total digestion but a digestion with aqua regia for Pb analysis and a 7 N HNO₃ extraction for Pb isotope analysis, and did not account for the presence of lithologically inherited Pb in the topsoil samples, some similarities in spatial distribution of Pb and Pb isotopes are observed. Reiman et al. (2012) also observed the highest Pb content in the Randstad area (area 1) in The Netherlands, and an elevated Pb content in the southern part of The Netherlands (area 2, influenced by Liege and Ruhr industries). In the southern forests Reimann et al. (2012) also observed the lowest \( \text{Pb}_{\text{gas}} \) and \( \text{Pb}_{\text{galena}} \) ratios. Similar low ratios are also observed in Belgium, just across the Dutch border. This is the area where the Dutch and Belgian Zn smelters are located. Although Reiman et al. (2012) measured high Pb contents in the Randstad area, based on Pb isotope composition they could not discriminate the Randstad area, because the isotopic differences between lithologically inherited and additional (anthropogenic) Pb in this area are small.
Fig. 3.7. (a) Land use type at the sample locations (n = 336). Herein, four areas with mainly forests and natural areas are discerned (all on sandy soil). Other (b-e) spatial distribution of $[\text{Pb}_{\text{reca}l}]_a$, $(^{206}\text{Pb}/^{207}\text{Pb})_a$, $(^{208}\text{Pb}/^{207}\text{Pb})_a$, and $(^{206}\text{Pb}/^{208}\text{Pb})_a$ in equally sized classes. Area 1 = Randstad area; Area 2 = influenced by Liege and Ruhr industry; Area 3 = influenced by Dutch and German industries.
3.5.3 Additional Pb in rural subsoils in The Netherlands.

Approximately 8% of the subsoil samples (default sample depth of 100-120 cm) in rural areas in The Netherlands have higher than expected Pb contents (based on their Al content) (Walraven et al., 2013). Some (n = 9) of these only have slightly enhanced Pb contents and Pb isotope ratios that lie within the range of lithologically inherited Pb in Dutch subsoils (Walraven et al., 2013). The Pb content of these subsoils is either naturally enriched, e.g., Pb containing sulphide minerals in peat, or these subsoils contain anthropogenic Pb in such low amounts that it does not result in a clear shift in Pb isotope ratios. However, at 18 sample sites (~5% of all samples) the additional Pb content in the subsoils is substantial (>7 mg/kg) and the Pb isotope composition of the additional Pb fractions of these subsoils differs from the normal, lithologically inherited range found for Dutch subsoils (Fig. 3.8). Figure 3.8 shows that, with 1 exception, topsoils at most of these sample sites also contain enhanced Pb contents. Highest mass based additional Pb contents are observed in areas with a dominantly lithology of peat, followed by clay and sand.

If the additional Pb in the subsoils is of anthropogenic origin, it is quite remarkable that it can reach depths of 100-120 cm below the surface. This can be caused either by man-caused soil disturbance, bioturbation, physical migration or leaching of anthropogenic Pb from the topsoil to the subsoil, or by scavenging of less radiogenic Pb from upward seeping groundwater. Soil profiles in The Netherlands have commonly been disturbed more profoundly than just by common ploughing (Van der Veer, 2006). Historical disturbance of the soil was particularly extensive in (former) peat areas, which were largely excavated (drained lakes, peat quarries). Here the organic layer was removed and the remaining land surface was often raised with sand, clay, dredged mud, or organic waste. Although extensive man-caused disturbance of Dutch soils has been partly incorporated in the 1:50.000 soil map (Steur and Heijnck, 1987) and can often be discerned in the field, it cannot be excluded that some soil profiles used in this study (Van der Veer, 2006) might have been disturbed by human activity.

Physical transport and leaching of anthropogenic Pb in soils does occur (e.g., Dorr and Munnich, 1991; Miller and Friedland, 1994; Erel et al., 1997 and Erel, 1998; Zhang, 2003; Prapaipong et al., 2008). For example, transport velocities of Pb in forests soils were reported to vary between 0.39 and 0.83 mm/y at over 40 forested sites in Europe (Dorr and Munnich, 1991), 5 mm/y in Mediterranean soils (Erel et al., 1997 and Erel, 1998), between 8.2 and 19.7 mm/y at different depths in forest soils in Vermont, USA (Miller and Friedland, 1994), 4 mm/y in mollisols in Illinois, US (Zhang, 2003) and up to ~1 cm/yr in forest soils in southeast Missouri (Prapaipong et al., 2008). The depth at which anthropogenic Pb was reported in these studies, generally did not exceed 30 cm. Migration or leaching of anthropogenic Pb to depths of 100-120 cm in peaty soils has never been reported. Peat and organic matter-rich sediments are known for their ability to retain Pb (e.g., Shotyk et al., 1998; Sonke et al., 2002). The high organic matter content and anoxic conditions of peat and organic matter-rich sediments limit the mobility of Pb through adsorption and sulphide formation processes.

Enrichment of less radiogenic Pb in subsoils can also be caused by scavenging of Pb from upward seeping groundwater. This Pb can have either a natural (leached from geological formations or minerals with less radiogenic Pb isotope values than typical in the subsoils) or anthropogenic origin. Especially in peat and organic matter-rich subsoils, this Pb can be adsorbed, or fixed in secondary sulphide minerals.
Figure 3.8. Sample sites with additional Pb contents >7 mg/kg in the subsoil.
3.6 Conclusions

The additional Pb content, recalculated to an organic free mass basis and the Pb isotope composition of additional Pb\textsubscript{recalc} in rural topsoils in The Netherlands is determined by means of Pb isotope analysis of 336 topsoils and subsoils (default sample depths 0-20 cm and 100-120 cm respectively). The additional Pb\textsubscript{recalc} content in topsoils of Dutch rural regions varies between <LOD and 1863 mg/kg. The median additional Pb\textsubscript{recalc} content of agricultural land (both arable land and grassland) and nature (forest and open nature) is remarkably similar, with values ranging from 10 to 15 mg/kg. No clear difference in additional Pb\textsubscript{recalc} content is observed in topsoil samples overlying different lithologies (sand, clay and loess).

The Pb isotope composition of the additional Pb fraction in the topsoils varies from 1.056-1.199, 2.336-2.486 and 0.452-0.490 for \(^{206}\text{Pb}/^{207}\text{Pb}\), \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) respectively. These Pb isotope ratios differ clearly from lithologically inherited Pb, as observed in subsoils and argues for an anthropogenic origin. On average lower \(^{206}\text{Pb}/^{207}\text{Pb}\), \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) ratios are observed in topsoils of nature areas compared with agricultural areas. The Pb isotope composition of additional Pb in nature areas most likely reflects a mixture of coal/galena, incinerator ashes and gasoline Pb, with the latter two appearing to be the most important. The Pb isotope data show that agricultural topsoils most likely contain the same anthropogenic Pb sources as topsoils in nature areas, but in addition also contain additional Pb from animal manure and N-P fertilisers. The contribution of the various anthropogenic Pb sources identified to the total additional Pb content at a specific rural site is related to, among others, the quantities and types of fertilisers used and the distance of a sample location to roads, Pb emitting industries, power plants (coal) and incinerators. Future research should elucidate the relations and dependencies between the different anthropogenic sources.

Several areas with high additional Pb contents in the topsoil are observed in The Netherlands. Most notable is the Randstad area, which has the highest population and traffic density and hosts a considerable fraction of the Dutch chemical industry, records a high regional influence of industrial Pb on the anthropogenic signal. Two other areas with high additional Pb contents are located near the Dutch border and are most likely influenced by national, German and Belgian industries. The topsoils in the coastal dunes and southern, central and northern forest are characterized by relatively low additional Pb contents. The population, traffic and chemical industry density is low in these areas and negligible quantities of fertilisers are applied. Pb isotope data show that the southern forest area is influenced by Zn smelters, located to windward, which used Zn ores from the former Belgian Congo.

Knowledge of the cause and source of Pb pollution is important in efforts to abate environmental Pb pollution by taking source-related actions. This study shows that additional Pb in Dutch topsoils is most likely related to anthropogenic activities. In addition, multiple anthropogenic Pb sources can be distinguished in Dutch rural topsoils. Several of these sources are still in use, e.g., coal as an energy source and fertilisers for improving the soil quality. This means that pollution of soil with anthropogenic Pb is an ongoing problem. The information obtained in this study can be of use in future studies to predict the effect of the use of anthropogenic Pb sources (e.g., coal and fertilisers) on the quality of the environment.

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References


Appendix 3.1. Database with the analytical and calculated results of the subsoil and topsoil samples (in Excel).

This appendix can be found in the published version in Applied Geochemistry, at http://dx.doi.org/10.1016/j.apgeochem.2013.07.015
Appendix 3.2. Spatial distribution of the $[\text{Pb}_{\text{recalc}t}]$, content of the subsoils and topsoils in The Netherlands.
Appendix 3.3. Spatial distribution of the organic matter (OM) content of the subsoils and topsoils in The Netherlands.
Appendix 3.4. Spatial distribution of the $[\text{Al}_{\text{recalc}}]_t$ content of the subsoils and topsoils in The Netherlands.
Appendix 3.5. Spatial distribution of the $[\text{Zr}_{\text{recalc}}]_t$ content of the subsoils and topsoils in The Netherlands.
Appendix 3.6. Spatial distribution of the $[\text{Pb}_{\text{reac}}]_i$ content of the subsoils and topsoils in The Netherlands.
Appendix 3.7. Spatial distribution of the $({^{206}\text{Pb}}/{^{207}\text{Pb}})_t$ ratios of the subsoils and topsoils in The Netherlands.
Appendix 3.8. Spatial distribution of the \(^{(208}\text{Pb}/207\text{Pb})_t\) ratios of the subsoils and topsoils in The Netherlands.
Appendix 3.9. Spatial distribution of the $(^{206}\text{Pb}/^{208}\text{Pb})_t$ ratios of the subsoils and topsoils in The Netherlands.
Appendix 3.10. Spatial distribution of the \(^{206}\text{Pb}/^{207}\text{Pb}\)_li ratios of the subsoils and topsoils in The Netherlands.
Appendix 3.11. Spatial distribution of the $({^{208}\text{Pb}}/{^{207}\text{Pb}})_{li}$ ratios of the subsoils and topsoils in The Netherlands.
Appendix 3.12. Spatial distribution of the \(^{206}\text{Pb}/^{208}\text{Pb}\)_li ratios of the subsoils and topsoils in The Netherlands.