Chapter 2

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


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Abstract

Knowledge on the lithologically inherited variation in present day Pb isotope ratios in soils is remarkably limited. Such information is essential to determine the anthropogenic Pb fraction and anthropogenic Pb sources in Pb polluted soils. This study presents results of a survey of subsoil samples of approximately 350 rural locations covering the entire Netherlands, for which the bulk geochemical and Pb isotope composition was determined. The sample density was approximately 1 site per 70 km². The aim was to establish a geochemical reference for the lithological inherited variation in Pb isotope ratios in Dutch soils based on the subsoil samples, with which to compare the topsoils (companion paper in this journal issue).

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

2.1 Introduction

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

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

Information on the occurrence, behaviour and fate of the various anthropogenic Pb sources in the environment is considered to be crucial in understanding and abating the lead problem (e.g., Steele et al., 1990; Ruby et al., 1999; Rieuwerts et al., 2000; Hagens et al., 2009). This includes distinguishing historic from recent pollution, as the former of course cannot be further prevented; identifying the source-related chemical form of environmental Pb, as this may influence its toxicity; and the need to sometimes legally identify the origin of Pb pollution.

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 one of the first researchers to show that clues on the Pb provenance could be obtained through the study of four stable Pb isotopes: $^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$. 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. Lead ores, and the products derived from them, have characteristic Pb isotope signatures, depending on the initial U/Pb and Th/Pb ratios of the source rocks and the geological age at which Pb, as daughter, separated from the melt (mother) during ore formation. In their use as geochemical tracers, Pb isotopes are commonly utilised as ratios; with the $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ 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 many environmental studies, Pb isotope analysis proved to be a powerful tool. However, Pb isotope measurements can only be used to trace anthropogenic Pb sources in polluted soils and sediments if:

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

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

To our knowledge, there are few extensive studies on the spatial distribution of the Pb isotope composition of soils. Notable exceptions are Reimann et al. (2011, 2012), who determined Pb contents and Pb isotope ratios in topsoils collected (1) along an east-west transect across the United States at 40 km resolution and (2) in A horizons of agricultural areas in Europe at an average density of 1 site/2500 km². All other studies of Pb in mineral soils are local in nature and based on a limited number of selected profiles that are sampled at various depths, to distinguish the hypothesised anthropogenic Pb isotope signature in the upper (and generally more organic rich) part of the soil from the lithologically inherited signature at depth (Chow, 1970; Gulson et al., 1981; Walraven et al., 1997; Hansmann and Köppel, 2000; Cloquet et al., 2006). Although Reimann et al. (2011, 2012) determined the spatial distribution of the Pb isotope composition in soils, they did not distinguish lithologically inherited from anthropogenic Pb. Their Pb isotope maps consequently represent a mixture of lithologically inherited and anthropogenic Pb in topsoils.

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

2.2 Background information
2.2.1 General geology of The Netherlands

The Netherlands is located in north-western Europe and is bordered by Germany, Belgium and the North Sea (Fig. 2.1). It is part of the subsiding North Sea Basin that is enclosed by the Brabant Massif in the South and the Rhenish Massif in the East. As a result of extensive subsidence and sedimentary infill of the North Sea Basin during the Cenozoic, the subsurface of The Netherlands largely consists of a 200-500 m thick layer of unconsolidated sediments that are of Pleistocene age in the eastern and southern part and of Holocene age in the northern and western part. (see e.g., Zagwijn and Van Staaldhuinen, 1975; Westerhoff et al., 2003).

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

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

**Fig. 2.1.** Left: Overview of north-western Europe showing The Netherlands (darker grey) and surrounding countries (basemap data from www.esri.com). Right: lithological map of the soils in The Netherlands (Dutch coordinate system, Rijksdriehoeks-projection). (source: Van der Veer, 2006; with permission).

### 2.2.2 General pedology of The Netherlands

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

The different types of parent material in The Netherlands are classically grouped into five districts: sand, loess, peat, fluviatile and marine clay. Whereas the largely Pleistocene sand and loess districts are mainly found in the elevated northern, eastern and southern parts of The Netherlands, the Holocene clay deposits are mainly confined to the low lying coastal areas in the 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 over the last centuries (Bazelmans et al., 2011).

Time is an important soil forming factor. Soil formation in The Netherlands started only after ice receded. Therefore soils in The Netherlands are relatively young: 12,000 years for loess to <50 years for marine clay (for details see Van der Veer, 2006). As a result of the restricted age of the parent material and a temperate climate, soils in The Netherlands are poorly developed compared with those in many other parts of the world (Van der Veer, 2006).
Thereby, the human influence on the soil and soil profile (deep-ploughing, mixing, fertilisation) has been so extensive in The Netherlands that it should be considered as a serious soil forming factor in itself (Van der Veer, 2006).

2.2.3 Natural Pb sources

Lead occurs naturally in all soils (de Treville, 1964). Its terrestrial abundance ranges from 1 to 200 mg/kg with most values being 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 (e.g., calcium carbonate and iron oxides). All minerals contain ‘natural’ trace contents of Pb. The Pb content of some dominant minerals that can occur in sedimentary soils is shown in Table 2.1. High Pb contents – up to 10,000 mg/kg – can be encountered in potassium feldspars. In addition, heavy minerals can contain significant amounts of Pb. For example, the Pb content in apatites, pyrites and zircons can vary from 5-2,000 mg/kg, 0.3-1,000 mg/kg and <0.03 to 69 mg/kg respectively (Table 2.1). In addition, Pb, like many other metals, has a high affinity for iron and manganese oxides. The clay fraction of soils contains the residual Pb of weathered rocks from which they have formed. The average Pb content in fluviatile clays and marine clays is 24 and 16 mg/kg respectively (Table 2.1).

<table>
<thead>
<tr>
<th>Group</th>
<th>Mineral</th>
<th>Pb (mg/kg)</th>
<th>n</th>
<th>References</th>
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<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Range</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Quartz</td>
<td>&lt;1.0</td>
<td>0-5</td>
<td>15  Wedepohl and Doe (1974)</td>
</tr>
<tr>
<td>Feldspars</td>
<td>K feldspar, pegmatitic</td>
<td>98</td>
<td>0.9 – 10,000</td>
<td>219 Wedepohl and Doe (1974)</td>
</tr>
<tr>
<td>Feldspars</td>
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<td>53</td>
<td>3-700</td>
<td>419 Wedepohl and Doe (1974)</td>
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<tr>
<td>Feldspars</td>
<td>Plagioclase feldspars</td>
<td>19.5</td>
<td>1-75</td>
<td>61  Wedepohl and Doe (1974)</td>
</tr>
<tr>
<td>Micas</td>
<td>Biotites</td>
<td>21</td>
<td>4-95</td>
<td>259 Wedepohl and Doe (1974)</td>
</tr>
<tr>
<td>Micas</td>
<td>Muscovites</td>
<td>26</td>
<td>5-77</td>
<td>32  Wedepohl and Doe (1974)</td>
</tr>
<tr>
<td>Clay minerals</td>
<td>Florivatile clays</td>
<td>24</td>
<td>6-53</td>
<td>28  Van der Veer (2006)</td>
</tr>
<tr>
<td>Clay minerals</td>
<td>Marine clays</td>
<td>16</td>
<td>6-34</td>
<td>115 Van der Veer (2006)</td>
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<td>Heavy minerals</td>
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<td>6.6</td>
<td>&lt;1-29</td>
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<td>&lt;0.03-69</td>
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<td>5 – 2,000</td>
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<td>Secondary minerals</td>
<td>Pyrites, sedimentary</td>
<td>62</td>
<td>2-1,000</td>
<td>297 Wedepohl and Doe (1974)</td>
</tr>
<tr>
<td>Secondary minerals</td>
<td>Pyrites, sedimentary</td>
<td>-</td>
<td>0.3-666</td>
<td>8    Huisman (1998)</td>
</tr>
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</table>

2.3 Methods

2.3.1 General approach and assumptions

Subsoil samples collected by Van der Veer (2006) were used in this study. Van der Veer (2006) performed a geochemical soil survey of The Netherlands based on a top-bottom sampling approach. One of the aims of the survey of Van der Veer (2006) was to gain an accurate overview of the natural range of the soil composition in The Netherlands. Since the
topsoil layer, also in forests and natural areas, has been affected by anthropogenic input (e.g., Blaser et al., 2000; Baize and Sterckeman, 2001; Anderson et al., 2002; Steinnes, 2001; Hernandez et al., 2003), topsoil is not useful as a proxy for the natural composition of the soil. Van der Veer (2006) therefore used the soil parent material, or C-horizon (called subsoil in this study), as a proxy for the natural composition of soils in The Netherlands. This approach has been used in many regional geochemical surveys in The Netherlands (Mol, 2002; Lamé et al., 2004; Spijker, 2005) as well as abroad (e.g., Salminen and Tarvainen, 1995; Ódor et al., 1997; Reimann et al., 2000; Sterckeman, 2004, 2006a,b). This approach assumes that the effects of diffuse anthropogenic input of elements on average has had a very limited effect on the composition of the deeper soil layer (subsoil). Additionally, Al was used as indicator for textural variation. Van der Veer (2006) and others (e.g., Huisman, 1998; Spijker, 2005) observed linear relationship between the contents of Al and various (trace) elements, including Pb, in the soil parent material (subsoils) in The Netherlands. This correlation is in part based on the joint occurrence of Al and trace metals in alumino-silicates (e.g., feldspars and clay minerals), partly on the presence of high-metal-containing minerals predominantly in the clay fraction and the higher adsorption capacity of clayey soils in comparison to sandy soils. Subsoil samples with a deviating Pb/Al ratio might contain additional, ‘anomalous’ Pb not representing lithologically inherited Pb. Van der Veer (2006) used the relationship between Al and Pb (i.e. Pb/Al ratio) to calculate the enrichment/depletion of Al in topsoils in the Netherlands (see also Walraven et al., 2013). In this study deviating Pb/Al ratios in the subsoil are used to identify outliers in the subsoil (see Section 2.3.5.2).

The sampling approach of Van der Veer (2006) was restricted by time and costs (some 800 samples could be analysed). Since emphasis was put on the spatial variation of the soil composition, sampling density was maximised. Therefore, from each soil profile only two samples were taken; one from the parent material (subsoil) and one from the topsoil layer. In general, the sampling approach and procedures of the survey of Van der Veer (2006) largely conform to international recommendations set for regional geochemical baseline surveys, such as IGCP 259 and FOREGS (Darnley et al., 1995; Plant et al., 1997). The major differences with respect to these recommendations are: (i) no compositing (single spot sample), (ii) a variable depth of the deeper soil sample and (iii) a more narrowly defined target area. IGCP 259 and FOREGS furthermore recommend sampling a wide variety of sample media, such as soil, overbank, litter material and (surface) water. Van der Veer (2006) focused on soil and soil parent material.

2.3.2 Soil sampling

During an extensive soil sampling campaign in The Netherlands, Van der Veer (2006) collected soil samples using a predefined scheme for optimal unbiased sampling. This selection consists of soils used for agricultural and semi-natural purposes, excluding the potentially contaminated soils in urbanised and industrial areas. The predefined area covered by this selection, amounts to about 25,600 km², comprising ~75% of the Dutch land surface (sampling density of ~1 sample per 70 km²).

The predefined sampling area was cross-stratified according to the soil parent material districts in Fig. 2.1 (sand, loess, peat, marine clay and fluviatile clay) as well as to land use type (agricultural and semi-natural). Within these strata, 400 sample locations were randomly allocated, of which finally 358 were sampled (for details see Van der Veer, 2006).

At each sample location, a subsoil sample was taken from the soil parent material (BC, or
C horizon, 100-120 cm by default) as well as from the topsoil (A-horizon, 0-20 cm). In this study we will discuss the results of the 342 subsoil samples that were analysed for Pb isotopes as well as major and trace element composition.

### 2.3.3 Sample preparation

Prior to analysis, soil samples were dried at 40 °C to constant weight, disaggregated and sieved (<2 mm). To create representative subsamples 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, also sample duplicates and a standard sample were inserted for quality evaluation purposes. The subsamples for analysis were thereafter ground (<15 μm) 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).

### 2.3.4 Analysis

The subsoil 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 using over 100 geological reference material samples. For trace elements the Rh-compton peak was used to correct for matrix differences. In addition, the organic matter (OM) contents were established by Thermo-Gravimetric Analysis (LECO 604 TGA). All contents are either expressed as wt.% or as mg/kg, all based on 40 °C dry sample weight.

Although a broad range of elements was analysed (Van der Veer, 2006), only Pb, Al, Zr and OM content are discussed here. The OM content is used to recalculate the Pb, Zr and Al content to an organic free basis (see Section 2.3.5.1). Zr and Al are included because they are independent proxies for lithologically inherited Pb (see Section 2.3.5.3). 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 (www.wepal.nl) – 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 those determined by XRF (logPb_{ICP-MS} = 0.97 × logPb_{XRF} + 0.009; n = 336; R² = 0.91). Lead content determined by XRF is henceforth used in this study. To determine Pb isotope ratios accurately using ICP-MS, a method similar to that described by Krachler et al. (2004) was used. To diminish mass bias due to concentration differences, the HF destruction solutions as obtained for trace element analysis were diluted with 1 M HNO₃ to a Pb concentration of about 50 μg/kg in solution prior to being introduced into 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 $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ determined. For external calibration and drift, a series of six samples was bracketed by NIST SRM 981. Ratios were corrected independently (for mass bias), 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 from both bracketing standard samples. The precision based on 37 duplicate pairs was at 2 RSD < 0.22% for $^{206}\text{Pb}/^{207}\text{Pb}$, 2 RSD < 0.17% for $^{208}\text{Pb}/^{207}\text{Pb}$, and 2 RSD < 0.44% for $^{206}\text{Pb}/^{208}\text{Pb}$. The average measured value and absolute precision (2 SD) of the measured ISE 921 sample ($n = 45$) was $1.166 \pm 0.003$ for $^{206}\text{Pb}/^{207}\text{Pb}$, $2.444 \pm 0.004$ for $^{208}\text{Pb}/^{207}\text{Pb}$, and $0.477 \pm 0.002$ for $^{206}\text{Pb}/^{208}\text{Pb}$. Average and precision are based on the entire analytical procedure starting with the sample splits. Blanks and reagents used were also measured and appeared to contain negligible amounts of Pb (<20 ng/kg). The analytical results of 6 samples out of the 342 in total did not pass the final quality control criteria and were therefore not included in this study.

2.3.5 Data analysis

2.3.5.1 Correction for the organic fraction

Ultimately, the topsoil, which has undergone soil formation and anthropogenic influence, is to be compared with the parent material (companion article by Walraven et al., 2013). To adequately compare trace element contents in topsoil with those in the parent material, the dilution effect by the organic fraction should be corrected for in some way. Here, contents are recalcuated to an organic free basis:

$$[C]_{\text{recalc}} = [C] \times 100/(100-\text{OM}\%) \quad (2.1)$$

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 performed to a carbonate-free basis. This was not done because the corrections would be very minor (on average less than about 1/10th of that for OM; Van der Veer, 2006), and would require detailed knowledge on the carbonate mineralogy (presence of primary and secondary carbonate and non-unique attribution of Ca to CaCO$_3$).

2.3.5.2 Identifying outliers

While the set of subsoil samples is assumed to primarily represent the lithologically derived variation in Pb content and Pb isotope composition, some of the samples might contain additional, ‘anomalous’ Pb. For example, subsoils could be polluted with Pb from anthropogenic sources derived from the topsoil, both naturally and during sampling. Walraven et al. (1997, 2001a, b) showed that Dutch rural soils and sediments can be polluted to depths of 100-120 cm (default subsoil sampling depth in this study) due to human activities. In addition, subsoils might contain Pb that is not representative of the general lithologically inherited variation as a result of precipitation/adsorption of Pb transported by upward seeping groundwater. Since Pb mineralisation does not occur in the shallow subsurface of The Netherlands (<20 m below surface), anomalous Pb isotope compositions in subsoils will not derive from such mineralization.
The presence of even small quantities of anomalous Pb can have a large influence on the overall Pb isotope composition. To minimise the influence of Pb from other origins on the statistical assessment of the lithologically inherited variation in Pb isotope ratios in subsoils, two selection criteria have been formulated to identify such outliers in the dataset. The first criterion is based on total Pb content and the common relationship between Pb and Al in unpolluted soils and sediments (see Section 2.3.1), here expressed as Pbrecalc/Alrecalc, or its equivalent Pb/Al. Sonke et al. (2002) suggested that Al can be enriched at extremely polluted sites and that care should be taken in using Al as a lithogenic proxy to identify Pb pollution. However, the selected sites in this study are all rural sites, not located close to large industrial sites. Subsoils with Pbrecalc/Alrecalc values smaller than the first quartile or larger than the third quartile plus several times the interquartile range are labelled as outliers (Eqs. (2.2) and (2.3)).

\[
Pb_{\text{recalc}}/Al_{\text{recalc}} < P_{25} - f \times (P_{75}-P_{25}) \quad (2.2)
\]

\[
Pb_{\text{recalc}}/Al_{\text{recalc}} > P_{75} + f \times (P_{75}-P_{25}) \quad (2.3)
\]

This procedure is equivalent to calculating the fences for box and whiskers plots according to Tukey (1977). In this formula P denotes a percentile and Pbrecalc/Alrecalc is calculated based on the OM-free Pb and Al content in the subsoils (Eq. (2.1)). The factor f is set to 1.5 as is commonly done for inner fences (Spijker, 2005). The second criterion is based on identifying deviating Pb isotope ratios in the dataset. The same procedure as in criterion 1 is followed (see Eq. (2.2) and (2.3)), but with \(^{206}\text{Pb}/^{207}\text{Pb}, \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) values instead of Pbrecalc/Alrecalc values. All subsoils that passed criteria 1 were tested in criterion 2.

Outliers were not completely removed from the dataset but flagged as such so they could be treated separately. Only the subsoils that passed both criteria were used to determine the general statistics of the lithologically inherited Pb isotope composition of subsoils in The Netherlands.

### 2.3.5.3 Regression model for lithology dependent variation of Pb isotope ratios

Lithology (soil parent material) will probably be of influence on the variation in Pb isotope ratios, but to our knowledge, no systematic studies have been undertaken on this issue. We set out to identify which geochemical proxies or predictors could be used to predict Pb isotope ratios. A power relation (log-log regression) was used rather than a linear relation, as for most trace elements it better describes the relative variability in content. For the Pb isotope ratios, using a log-log relation has the added advantage that the way the ratios are expressed (A/B or B/A) has no influence on the regression results, since the log value of a ratio and its inverse differ only in sign but not in number. To eliminate the effects of outliers, not only of those already identified as being anomalous for Pb or Pb isotope composition, but also of samples being anomalous for the selected predictors, a robust trimmed least squares regression was used (Montgomery and Peck, 1982; Rousseeuw and Van Driessen, 2002; Van Gaans et al., 2007).

Mass bias correction was applied independently for the three Pb-isotope ratios: \(^{206}\text{Pb}/^{207}\text{Pb}, \(^{208}\text{Pb}/^{207}\text{Pb}, \) and \(^{206}\text{Pb}/^{208}\text{Pb}\) (see above). This means that the ratio of \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{208}\text{Pb}/^{207}\text{Pb}\) may slightly differ from the given value for \(^{206}\text{Pb}/^{208}\text{Pb}\) (and similarly for other combinations) as a consequence of measurement error. A model that predicts the isotope ratios based on bulk sediment chemistry of course should observe the actual dependency. Therefore, a combined regression model is formulated as follows:
Lithologically inherited Pb

\[
\log\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right) = a_1 + b_1 \log(X_{\text{recalc}}) + c_1 \log(Y_{\text{recalc}}) + d_1 \log(Z_{\text{recalc}}) + \ldots \quad (2.4a)
\]

\[
\log\left(\frac{^{208}\text{Pb}}{^{207}\text{Pb}}\right) = a_2 + b_2 \log(X_{\text{recalc}}) + c_2 \log(Y_{\text{recalc}}) + d_2 \log(Z_{\text{recalc}}) + \ldots \quad (2.4b)
\]

\[
\log\left(\frac{^{206}\text{Pb}}{^{208}\text{Pb}}\right) = (a_1-a_2) + (b_1-b_2) \log(X_{\text{recalc}}) + (c_1-c_2) \log(Y_{\text{recalc}}) + \ldots \quad (2.4c)
\]

with $X_{\text{recalc}}$, $Y_{\text{recalc}}$, etc. = measured bulk element chemistry based on organic matter-free basis in mg/kg, and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$, $^{206}\text{Pb}/^{208}\text{Pb}$ = measured Pb isotope ratios. All ratio data are combined to calculate the robust optimal values for $a_1$, $a_2$, $b_1$, $b_2$, etc.

2.3.5.4 Graphical representation

The geographical distribution of the Pb isotopes (and relevant bulk geochemical parameters) is presented in the form of bubble plot maps. The Pb isotope ratios are plotted in triangle plots as well as in more common bivariate plots of the Pb isotope ratios (so-called 3-isotope plots 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.

2.4 Results

2.4.1 Analytical results

The results of the outlier identification, as described in Section 2.3.5.2, are visualised in Fig. 2.2.

**Fig. 2.2.** Left: Box-whisker plots of Pb$_{\text{recalc}}$/Al$_{\text{recalc}}$, $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$. Right: Pb$_{\text{recalc}}$ (mg/kg, XRF) versus Al$_{\text{recalc}}$ (wt.%) content for all subsoil samples (default sample depth is 100-120 cm below surface). ● Subsoil samples that have Pb$_{\text{recalc}}$/Al$_{\text{recalc}}$ ratios and Pb isotope ratios characteristic for the lithologically inherited variation in The Netherlands. ● Subsoil samples that have deviating Pb$_{\text{recalc}}$/Al$_{\text{recalc}}$ ratios according to criterion 1 (most likely non lithologically inherited Pb). × Subsoils samples that have deviating Pb isotope ratios according to criterion 2.
Fig. 2.2 shows that the majority (n = 303) of the subsoil samples have Pb\text{recalc}/Al\text{recalc} ratios in a distinct range between 2.5 and 7.7 that represents the lithologically inherited variation in subsoils. A total of 33 samples – 2 fluviatile clays, 13 peats and 18 sands – have deviating Pb\text{recalc}/Al\text{recalc} ratios or Pb isotope ratios (Fig. 2.2). The samples with enhanced Pb\text{recalc}/Al\text{recalc} ratios (n = 27) have relatively low \(^{206}\text{Pb}/^{207}\text{Pb}, \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) ratios (Fig. 2.3), all being indicators for the presence of additional, probably anthropogenic Pb. In addition, the Cu\text{recalc}/Al\text{recalc} ratios (< limit of detection (LOD) to 30 with a median of 4) and Zn\text{recalc}/Al\text{recalc} ratios (< LOD to 626 with a median of 21) of these samples are elevated, which is also indicative for the presence of anthropogenic metal sources (database Van der Veer, 2006). The Cu\text{recalc}/Al\text{recalc} and Zn\text{recalc}/Al\text{recalc} ratios in the other subsoils (n = 303) vary from < LOD to 9 with a median of 1 and < LOD to 52 with a median of 5 respectively. The subsoil samples with deviating Pb isotope ratios have similar Pb\text{recalc}/Al\text{recalc} ratios (n = 6) but show no evidence of added Pb. Most likely the relatively high \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) ratios, and relatively low \(^{208}\text{Pb}/^{207}\text{Pb}\) ratios in these samples are caused by analytical errors or other anomalies.

\[ \text{Pb}_{\text{recalc}} = 3.61 \times \text{Al}_{\text{recalc}} + 2.05 \]  

(2.5)

with Pb\text{recalc} the measured Pb content on organic matter-free basis in mg/kg, and Al\text{recalc} the measured Al content on organic matter-free basis in wt.% (n = 303; \( R^2 = 0.88; \) Standard error of estimate is 3.5 mg/kg).
The relationship between Al and Pb in soils and sediments has also been examined by others (e.g., Huisman, 1998; Spijker, 2005; Van der Veer, 2006). In these studies, the Al and Pb content were not calculated on an organic matter-free basis. Nevertheless, the inter-element relationships in these studies are comparable with the results obtained in this study.

The variation in $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$, $\text{Pb}_{\text{recalc}}$, OM, $\text{Al}_{\text{recalc}}$, and $\text{Zr}_{\text{recalc}}$ content in the sedimentary subsoils of The Netherlands is summarised in Table 2.2 and visualised in box-whisker plots in Fig. 2.4 for the five lithologies distinguished.

### Table 2.2. Summary of the analytical results of the subsoil samples.
MIN = minimum; MED = median; MAX = maximum; OM = organic matter.

<table>
<thead>
<tr>
<th>n</th>
<th>Statistic</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>
<th>$\text{Pb}_{\text{recalc}}$ (mg/kg)</th>
<th>OM (wt.%)</th>
<th>$\text{Al}_{\text{recalc}}$ (wt.%)</th>
<th>$\text{Zr}_{\text{recalc}}$ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>336 MIN*</td>
<td>1.154</td>
<td>2.428</td>
<td>0.473</td>
<td>3</td>
<td>0.24</td>
<td>0.18</td>
<td>37</td>
</tr>
<tr>
<td>303</td>
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<td>1.175</td>
<td>2.441</td>
<td>0.478</td>
<td>3</td>
<td>0.24</td>
<td>0.58</td>
<td>39</td>
</tr>
<tr>
<td>303</td>
<td>MED</td>
<td>1.197</td>
<td>2.468</td>
<td>0.485</td>
<td>9</td>
<td>1.28</td>
<td>1.94</td>
<td>247</td>
</tr>
<tr>
<td>303</td>
<td>MAX</td>
<td>1.221</td>
<td>2.494</td>
<td>0.492</td>
<td>69</td>
<td>88.24</td>
<td>12.92</td>
<td>719</td>
</tr>
<tr>
<td>336</td>
<td>MAX*</td>
<td>1.230</td>
<td>2.494</td>
<td>0.495</td>
<td>288</td>
<td>95.27</td>
<td>12.92</td>
<td>762</td>
</tr>
<tr>
<td>Sand</td>
<td>202 MIN*</td>
<td>1.168</td>
<td>2.428</td>
<td>0.477</td>
<td>3</td>
<td>0.24</td>
<td>0.18</td>
<td>37</td>
</tr>
<tr>
<td>184</td>
<td>MIN</td>
<td>1.175</td>
<td>2.441</td>
<td>0.479</td>
<td>3</td>
<td>0.24</td>
<td>0.58</td>
<td>39</td>
</tr>
<tr>
<td>184</td>
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<td>0.485</td>
<td>7</td>
<td>0.69</td>
<td>1.35</td>
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<tr>
<td>184</td>
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<td>2.493</td>
<td>0.492</td>
<td>22</td>
<td>18.82</td>
<td>4.05</td>
<td>719</td>
</tr>
<tr>
<td>202</td>
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<td>1.230</td>
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<td>0.495</td>
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<td>18.82</td>
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<td>762</td>
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<tr>
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<td>2.462</td>
<td>0.482</td>
<td>13</td>
<td>1.19</td>
<td>1.19</td>
<td>129</td>
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<tr>
<td>22</td>
<td>MIN</td>
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<td>2.462</td>
<td>0.482</td>
<td>13</td>
<td>1.19</td>
<td>3.21</td>
<td>129</td>
</tr>
<tr>
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<td>6.53</td>
<td>232</td>
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<tr>
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<td>2.480</td>
<td>0.488</td>
<td>69</td>
<td>23.63</td>
<td>11.56</td>
<td>351</td>
</tr>
<tr>
<td>24</td>
<td>MAX*</td>
<td>1.209</td>
<td>2.480</td>
<td>0.488</td>
<td>69</td>
<td>23.63</td>
<td>11.56</td>
<td>351</td>
</tr>
<tr>
<td>Marine clay</td>
<td>81 MIN*</td>
<td>1.186</td>
<td>2.451</td>
<td>0.478</td>
<td>9</td>
<td>1.13</td>
<td>2.78</td>
<td>162</td>
</tr>
<tr>
<td>81</td>
<td>MIN</td>
<td>1.186</td>
<td>2.451</td>
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<td>9</td>
<td>1.13</td>
<td>2.78</td>
<td>162</td>
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<tr>
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<td>2.475</td>
<td>0.485</td>
<td>20</td>
<td>3.92</td>
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<tr>
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<td>2.494</td>
<td>0.490</td>
<td>37</td>
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<td>8.32</td>
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</tr>
<tr>
<td>81</td>
<td>MAX*</td>
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<td>2.494</td>
<td>0.490</td>
<td>37</td>
<td>18.42</td>
<td>8.32</td>
<td>653</td>
</tr>
<tr>
<td>Peat</td>
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<td>2.438</td>
<td>0.473</td>
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<td>24.20</td>
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<td>83</td>
</tr>
<tr>
<td>12</td>
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<td>2.459</td>
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<tr>
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<td>8.17</td>
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<td>0.488</td>
<td>50</td>
<td>88.24</td>
<td>12.92</td>
<td>234</td>
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<tr>
<td>25</td>
<td>MAX*</td>
<td>1.218</td>
<td>2.477</td>
<td>0.492</td>
<td>288</td>
<td>95.27</td>
<td>12.92</td>
<td>460</td>
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<tr>
<td>Loess</td>
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<td>1.219</td>
<td>2.484</td>
<td>0.490</td>
<td>19</td>
<td>2.01</td>
<td>5.02</td>
<td>525</td>
</tr>
<tr>
<td>4</td>
<td>MIN</td>
<td>1.219</td>
<td>2.484</td>
<td>0.490</td>
<td>19</td>
<td>2.01</td>
<td>5.02</td>
<td>525</td>
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<tr>
<td>4</td>
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<td>1.220</td>
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<td>0.491</td>
<td>19</td>
<td>2.23</td>
<td>5.34</td>
<td>560</td>
</tr>
<tr>
<td>4</td>
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<td>2.489</td>
<td>0.491</td>
<td>20</td>
<td>2.32</td>
<td>5.63</td>
<td>605</td>
</tr>
<tr>
<td>4</td>
<td>MAX*</td>
<td>1.221</td>
<td>2.489</td>
<td>0.491</td>
<td>20</td>
<td>2.32</td>
<td>5.63</td>
<td>605</td>
</tr>
</tbody>
</table>

*1 Includes all samples defined as outliers

The spatial distribution of the $\text{Zr}_{\text{recalc}}$, $\text{Al}_{\text{recalc}}$ and $\text{Pb}_{\text{recalc}}$ content and the Pb isotope composition in the subsoils in The Netherlands is visualised in bubble maps in Fig. 2.5. Sand samples (n = 184) are characterised by a low $\text{Pb}_{\text{recalc}}$ content and relatively low $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios (Fig. 2.4, Table 2.2). The fluvial (n = 22) and marine (n = 81) clays have a relatively high $\text{Pb}_{\text{recalc}}$ content and relatively high $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and...
$^{206}\text{Pb}/^{208}\text{Pb}$ ratios (Fig. 2.4, Table 2.2). No difference in isotope signature was found between the marine and fluviatile clays. They are therefore combined as one group, called clays. The Pb_{recale} content and the Pb isotope composition of peat ($n = 12$) overlaps with those of sand and clay (Fig. 2.4, Table 2.2). The peat samples more often contain an enhanced Pb_{recale} content than the other samples (Table 2.2). Only 4 loess samples were analysed. These samples are characterised by an intermediate Pb_{recale} content – in between sand and clay – and the highest $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios of all samples (Fig. 2.4, Table 2.2).

**Fig. 2.4.** Box-whisker plots of Pb_{recale} content, $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ in Dutch subsoils classified by lithology.

### 2.4.2 Pb isotope regression results

We first identified the geochemical proxies or predictors that could be used in a regression model for Pb isotope ratios. Preliminary investigation showed that for our parent material data set, the Pb isotope ratios did show a significant dependence on Al_{recale} content (a proxy for clay content), as well as on the Zr_{recale} content (which could be a proxy for U/Th bearing minerals like zircon). Neither Al_{recale} nor Zr_{recale} is subjected to major anthropogenic influence, which makes them suitable as predictors for the lithologically inherited Pb isotope composition, also in anthropogenically influenced situations.
Fig. 2.5. Spatial distribution of the Zr recalculated, Al recalculated and Pb recalculated content, and the Pb isotope ratios of subsoils in The Netherlands.
The probability of other potential mineralogical relations (with e.g., apatite, feldspar or pyrite) could not be established, as most inorganic constituents, including phosphate (all recalculated on an organic free basis), show a very high correlation with Al_{recalc}, and thus have no added value in a regression model.

The regression results yield the following relations for the isotope ratios with Zr_{recalc} and Al_{recalc} as independent variables:

\[
\begin{align*}
\log\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right) &= 0.0590 + 0.00738 \log\left(\frac{\text{Zr}_{\text{recalc}}}{\text{mg.kg}^{-1}}\right) + 0.003325 \log\left(\frac{\text{Al}_{\text{recalc}}}{\%}\right) \quad (2.6.1) \\
\log\left(\frac{^{208}\text{Pb}}{^{207}\text{Pb}}\right) &= 0.3876 + 0.00146 \log\left(\frac{\text{Zr}_{\text{recalc}}}{\text{mg.kg}^{-1}}\right) + 0.003325 \log\left(\frac{\text{Al}_{\text{recalc}}}{\%}\right) \quad (2.6.2) \\
\log\left(\frac{^{206}\text{Pb}}{^{208}\text{Pb}}\right) &= -0.3286 + 0.00591 \log\left(\frac{\text{Zr}_{\text{recalc}}}{\text{mg.kg}^{-1}}\right) \quad (2.6.3)
\end{align*}
\]

The various ratio data are not assigned proportionally to the core dataset in the combined robust regression model (n_{total} = 720; ^{206}\text{Pb}^{207}\text{Pb}, n = 201; ^{208}\text{Pb}^{207}\text{Pb}, n = 289; ^{206}\text{Pb}^{208}\text{Pb}, n = 230). This makes it less straightforward to quantify the variance explained by the set of regression equations, as R^2 obviously varies with the chosen size of the core dataset. Fig. 2.6 presents the variance as a function of the size of the core dataset for the subsets of ratio data. Explained variance for the overall dataset (n = 336) is around 30-40%; for core datasets of n = 240 for the individual ratios the explained variance is 71.3% (^{206}\text{Pb}^{207}\text{Pb}), 70.5% (^{208}\text{Pb}^{207}\text{Pb}), and 63.7% (^{206}\text{Pb}^{208}\text{Pb}). The total explained variance for ^{206}\text{Pb}^{207}\text{Pb} and ^{208}\text{Pb}^{207}\text{Pb} is only about 10% less than the sum of the explained variances by Zr and Al individually, showing that, as expected, these two proxies are largely independent predictors.

![Fig. 2.6. Variance explained in the ratio data subsets as a function of the size of the core data set (from 100% to 50%). The difference between the total explained variance and the sum of variance explained (log-log basis) by Zr and Al separately for the same dataset is shown as well.](image-url)
Fig. 2.7. Measured $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios in the subsoil versus (a) $\text{Al}_{\text{recalc}}$, (b) $\text{Zr}_{\text{recalc}}$, and (c) predicted $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios. Closed symbols represent the data of the combined 70% core dataset, open symbols the 30% non-core data. Lines represent the log-log regression line of the core data.
Plots of predicted versus measured isotope ratios are shown in Fig. 2.7. To clarify the relation of the Pb isotope ratios with Al_{recalc} and Zr_{recalc}, bivariate plots versus these predictors are also given. In general, Zr_{recalc} is the better predictor, although less so for 208Pb/207Pb. The predicting power of Al_{recalc} is highest for 208Pb/207Pb and absent for 206Pb/208Pb. The latter was identified before setting up the final regression model, which therefore included only one regression coefficient for Al_{recalc} \((c_1 = c_2)\) in Eq. (2.4)), within this dataset. However, as a group they clearly have higher 206Pb/207Pb, 208Pb/207Pb and 206Pb/208Pb ratios than predicted. A substantial part of the peat samples (~50%) appear to contain significant non-lithologically inherited Pb. The deviating predicted Pb isotope ratios of these samples can be related to the presence of this additional Pb.

The size of the core dataset in the robust regression procedure was chosen more or less arbitrarily at around 70% of the whole dataset. This ensures a robust regression equation, but does not imply that the 30% non-core data are all outliers. Equations similar to Eq. (2.2) and (2.3) were used to determine what samples would be considered outliers based on the regression results. It turns out that 8 samples, all sands, that are not identified as outliers by the two criteria defined in Section 2.3.5.2, would be identified as outliers based on the regression results. These samples have unexpected Pb isotope ratios in view of their composition in terms of Al and Zr. Put otherwise, for these samples the regression model fails and one or two of the isotope ratios are not predicted well. However, for 13 samples identified as outliers based on criterion 1 the isotope ratios are still reasonably well predicted. These samples have relatively high Pb contents without this having a notable effect on the Pb isotope ratios. All samples identified as outliers based on criterion 2 (extreme isotope ratio) are also considered anomalous based on the regression results. Although the loess samples individually do not appear as statistical outliers, their Pb isotope ratios differ from the other lithologies (Fig. 2.7). They clearly form a distinct group, with higher measured 206Pb/207Pb, 208Pb/207Pb and 206Pb/208Pb ratios than would be predicted based on their Al_{recalc} and Zr_{recalc} contents.

2.5 Discussion
2.5.1 Lithologically inherited Pb isotope signatures

Dutch sediments mainly originate from geological units in central Western Europe. The oldest geological unit in the Dutch hinterland is Variscan granite with 206Pb/207Pb ratios varying between 1.18 and 1.20 (Michard-Vitrac et al., 1981; Steinmann and Stille, 1997). Most post-Variscan sediments in central Western Europe have 206Pb/207Pb, 208Pb/207Pb and 206Pb/208Pb ratios ranging from 1.18-1.22, 2.46-2.48 and 0.481-0.487 respectively (Elbaz-Poulichet et al., 1986; Monna et al., 1995; Steinmann and Stille, 1997). The range in Pb isotope ratios of the subsoils in The Netherlands encompasses this range and is established at 1.175-1.221, 2.441-2.494 and 0.478-0.492 for 206Pb/207Pb, 208Pb/207Pb and 206Pb/208Pb respectively (Table 2.2). The median Pb isotope composition of Dutch subsoils is 1.197, 2.468 and 0.485 for 206Pb/207Pb, 208Pb/207Pb and 206Pb/208Pb respectively (Table 2.2). These values almost exactly match the Pb isotope composition of average common Pb (AC) as given by Stacey and Kramers (1975) and these values are still commonly used in geochemical models, e.g., Teixeira et al. (2011): \((206Pb/207Pb)_{AC} = 1.197; \ (208Pb/207Pb)_{AC} = 2.472\) and \((206Pb/208Pb)_{AC} = 0.484\). This implies that the Dutch sediments are derived from a mixture of rocks/minerals from the Dutch hinterland that together represent average common Pb. The process of rock weathering, transport, size fractionation, deposition and soil formation
Lithologically inherited Pb

apparently did not result in a deviation of the Pb isotope composition from average common Pb. Van der Veer (2006) compared the major and trace element composition of Dutch soils with the average upper continental crust (UCC). According to this study, Dutch soils are on average more sandy and enriched in As and Se, but on the whole are comparable with UCC, especially the clayey soils. This study shows that an average UCC origin also accounts for the median Pb isotope composition of Dutch soils.

The 4 distinguished lithologies of the Dutch subsoils – sand, clay, peat and loess – have distinct chemical compositions (Table 2.2). To illustrate the lithologically inherited variation in Pb isotope composition of the 4 lithologies, the data are shown in a triangular plot (Fig. 2.8). Additionally \(^{208}\text{Pb}/^{207}\text{Pb}\) is plotted versus \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) versus \(^{208}\text{Pb}/^{207}\text{Pb}\) in 3-isotope plots (Fig. 2.9).

**Fig. 2.8.** Triangular plot of the measured \(^{206}\text{Pb}/^{207}\text{Pb}\), \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{208}\text{Pb}\) ratios in subsoils in The Netherlands. The small inset top left shows the full triangle with single-isotope compositions at the apexes. Solid grid lines are lines of equal percentage (apex compositions indicated). Dashed gridlines are lines of equal isotope ratio as indicated along the sides. The grey shade rhomboid areas show that, as \(^{208}\text{Pb}\) dominates here over both \(^{206}\text{Pb}\) and \(^{207}\text{Pb}\), minimal distortion in data presentation will be obtained with a bivariate ratio-plot with \(^{208}\text{Pb}\) as the common denominator (near-square rhomboid), whereas in \(^{206}\text{Pb}\) and \(^{207}\text{Pb}\) common denominator plots the data cloud will be stretched in the direction of the smallest diagonal of the respective rhomboids, which may lead to spurious correlations. AC-Pb = Pb isotope composition of average common Pb (Stacey and Kramers, 1975).
Fig. 2.9. Measured $^{208}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios versus $^{207}\text{Pb}/^{208}\text{Pb}$ ratios in subsoils in The Netherlands. Ellipses represent the lithologically inherited Pb isotope composition of the 4 distinguished lithologies (NL sand = Dutch sands; NL clay = Dutch clays; NL peat = Dutch peat; NL loess = Dutch loess). Outliers marked with the symbol ‘l’ or outliers according to criterion 2.

Fig. 2.8 and 2.9 clearly show higher average $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{209}\text{Pb}$ ratios for the clays than for the sands. Peat samples have Pb isotope ratios comparable to both sands and clays (Fig. 2.8 and 2.9). Lead in peat can be present both in minerals in the peat (e.g., clay minerals, quartz, pyrite, etc.) or bound to organic matter. Loess shows the most distinct Pb isotope ratios (Fig. 2.8 and 2.9). It is noted, however, that the loess group only comprises 4 samples.
2.5.2 Relation of Pb isotope signature to mineralogy

Sedimentary soils contain a variety of minerals and to fully understand the controls of the observed lithologically inherited variation in the Pb isotope composition of sedimentary soils in The Netherlands, the mineralogy and isotope composition of the individual minerals should be known. In the absence of such detailed information, however, some general considerations can be made.

First, we should distinguish between minerals with and without U and Th as major constituents in the mineral lattice. The Pb isotope composition of minerals that contain U and Th, for example zircons, continuously changes in time due to the build up of radiogenic Pb through the decay of $^{235}$U, $^{238}$U and $^{232}$Th. Their present day Pb isotope composition is the result of this cumulative build up since the time they were formed, and further reflects their initial U/Th ratio. The Pb isotope compositions of minerals with essentially no U and Th, for example galena and K-feldspar, have isotopic compositions that do not change in time. Their Pb isotope composition reflects the initial (magmatic) whole rock Pb isotope ratios, which reflect the time integrated build up of Pb until the time they were formed, which in turn depends on the U/Pb and Th/Pb ratios in the source rocks. These minerals are thus comparatively less radiogenic (containing “old” Pb), while the U and Th containing minerals are on average more radiogenic (containing “young” Pb).

Second, secondary minerals such as clay minerals that are formed during weathering should be distinguished from primary minerals. Secondary minerals weather from primary Pb containing minerals and thus will have a similar Pb isotope signature. However, they may additionally include radiogenic Pb that is contemporaneously released, because of lattice disruption, from U and Th containing minerals (e.g., zircons). Secondary minerals therefore are expected to be enriched in Pb specifically low in $^{207}$Pb, because of the notably shorter half life of $^{235}$U.

These considerations explain the observed and modelled Pb isotope signatures (Eqs. (2.6.1)-(2.6.3)). The regression derived dependency of the Pb isotope ratios on Al and Zr is visualised in Fig. 2.10. Arrows indicate the relative increase in the two plotted ratios - for independent increments in either Al or Zr. Higher Zr contents in soils indicate a higher proportion of U and Th containing minerals and hence higher (more radiogenic) $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios (Fig. 2.10). Furthermore, the U/Th ratio of Zr containing minerals is generally higher than that in bulk rock (Hoskin and Schaltegger, 2003; Fig. 2.10). Aluminium content is known to be indicative of the amount of clay minerals in soils. Higher Al contents in soils represent a higher proportion of secondary minerals, and hence a shift towards lower $^{207}$Pb (Fig. 2.10). The lower $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios of the sands compared with clays can be partly attributed to the lower proportion of radiogenic Pb from secondary minerals (clays) as well as to a broader range towards lower Zr contents (Table 2.1, Fig. 2.5).

The regression model for lithology dependent variation of Pb isotope ratios works well for the sands and clays, and for the peats without additional non-background Pb. It is noted, however, that the loess samples have a more radiogenic Pb isotope signature than predicted from their Al$_{recale}$ and Zr$_{recale}$ content. The regression model could be improved if the mineralogy and isotope composition of the individual minerals in the subsoil are known.
2.5.3 Outliers

Based on the $\text{Pb}_{\text{recalc}}/\text{Al}_{\text{recalc}}$ ratios (criterion 1), approximately 8% of the subsoils are flagged as being outliers (Fig. 2.2). The Pb isotope composition of these samples is visualised in Pb-isotope plots (Fig. 2.9). Fig. 2.9 demonstrates that these outliers are predominantly peat and sand (and not clay and loess) samples. The majority of these subsoils only have a slightly enhanced Pb content (<10 mg/kg additional Pb) that does not result in a significant shift in Pb isotope ratios (Fig. 2.9). Most peat samples and three sand samples, however, do show a significant shift in Pb isotope ratios (Fig. 2.9). The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios of these samples are lower than those of the majority of the subsoils, which indicates an anthropogenic or otherwise less radiogenic Pb source (Fig. 2.9). The deviating Pb isotope signatures could for example be caused by man-caused soil disturbance, physical migration or leaching of anthropogenic Pb from the topsoil to the subsoil and subsequent immobilization, or by scavenging of less radiogenic Pb from upward seeping groundwater. The origin of these outliers will be further discussed in the companion article on anthropogenic Pb (Walraven et al., 2013).

2.6 Conclusions

The lithologically inherited variation in Pb isotope ratios in soils in The Netherlands is determined by means of Pb isotope analysis of 342 subsoil samples (default sample depth 100-120 cm). The established Pb isotope signature of subsoils in The Netherlands is 1.175-1.221, 2.441-2.494 and 0.478-0.492 for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ respectively.

The overall average Pb isotope composition of the Dutch subsoils equals present day common Pb, but the four main lithologies of the Dutch subsoils – sand, clay, peat and loess – have distinct chemical and isotopic compositions. Clays have higher average $^{206}\text{Pb}/^{207}\text{Pb}$ and
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$^{208}\text{Pb}/^{207}\text{Pb}$ ratios than sands. Part of the peat samples show Pb isotope ratios that match both sands and clays due to the presence of Pb containing sand and clay minerals in peat. About half of the peat samples, however, show less radiogenic Pb isotope signatures, that indicate the presence of additional, possibly anthropogenic Pb sources. Loess shows the highest average $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ values of all samples and has very distinct Pb isotope ratios. It is noted, however, that the loess group only comprises a limited number of samples.

Multiple regression analysis demonstrates that the lithologically inherited variation in the Pb isotope composition of Dutch subsoils can be partly explained by the Al and Zr content of the subsoils. Al and Zr are mutually independent and not expected to be subjected to anthropogenic influence. The Zr content represents the proportion of U and/or Th containing primary minerals that on average have more radiogenic Pb isotope compositions. The U/Th ratio of zircons is generally much higher than that in the bulk rocks, which explains the trend in Dutch subsoils of lower contributions of $^{208}\text{Pb}$, relative to $^{206}\text{Pb}$, with higher Zr content. The Al content represents the proportion of secondary clay minerals that incorporate the more recently formed radiogenic Pb that is relatively low in $^{207}\text{Pb}$ compared with $^{206}\text{Pb}$ and $^{208}\text{Pb}$. The different, apparently older, isotopic signature of the sands compared with the clays, can thus be attributed to the lower proportion of radiogenic Pb from secondary minerals (clays) as well as a broader range towards lower Zr contents. The more radiogenic signature of the loess samples, compared with the sands and clays, is only partly explained by their relatively high Al and Zr content.

Approximately 8% of the subsoils, mainly peats, contain additional Pb that is assumed to be non-lithologically inherited, possibly anthropogenic. Pollution of these subsoils might be explained by man-caused soil disturbance, by physical migration or leaching of anthropogenic Pb from the topsoil to the subsoil. Alternatively, it could be, among others, the result of scavenging of less radiogenic Pb from upward seeping groundwater.

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