Chapter 8

General discussion

The main aims of this thesis were to map Pb distribution in rural and urban soils in The Netherlands, to unravel Pb sources and to obtain information about the mobility and bioaccessibility of anthropogenic Pb in the Dutch environment. In this final chapter, the results of the six conducted studies are integrated, and related to the general research questions (see Section 1.4) of this thesis.

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

Knowledge on the lithologically inherited variation in present day Pb isotope ratios in soils is remarkably limited (see Section 2.1). Such information is essential to determine the anthropogenic Pb fraction and anthropogenic Pb sources in Pb polluted soils (see Section 1.7). In this thesis the lithological inherited variation in Pb isotope ratios in sedimentary soils was determined by means of Pb isotope analysis of 342 subsoil samples from rural locations covering the entire Netherlands. This is a sample density of approximately 1 site per 70 km². These data served as a geochemical reference that has been used throughout the thesis to allow correction for the presence of lithologically inherited Pb in Pb polluted soils.

The established Pb isotope ratios of lithologically inherited Pb in Dutch sedimentary soils are 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 (Fig. 8.1). The median Pb isotope composition is 1.197, 2.468 and 0.485 for \( ^{206}\text{Pb}/^{207}\text{Pb} \), \( ^{208}\text{Pb}/^{207}\text{Pb} \) and \( ^{206}\text{Pb}/^{208}\text{Pb} \) respectively (Fig. 8.1). 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): \( (^{206}\text{Pb}/^{207}\text{Pb})_{\text{AC}} = 1.197 \), \( (^{208}\text{Pb}/^{207}\text{Pb})_{\text{AC}} = 2.472 \) and \( (^{206}\text{Pb}/^{208}\text{Pb})_{\text{AC}} = 0.484 \). 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 apparently did not result in a deviation of the Pb isotope composition from average common Pb.

The four main lithologies distinguished – sand, clay, peat and loess – have distinct chemical and isotopic signatures (see Table 2.2 and Fig. 2.4). Clays have higher average \( ^{206}\text{Pb}/^{207}\text{Pb} \) and \( ^{208}\text{Pb}/^{207}\text{Pb} \) ratios than sands. Part of the peat samples showed 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, showed less radiogenic Pb isotope signatures, that indicate the presence of additional, possibly anthropogenic Pb sources. Loess showed 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 comprised a limited number of samples (\( n = 4 \)).

Multiple regression analysis demonstrated 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 (see Eq. (2.6.1) to (2.6.3)). Al and Zr were 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, was only partly explained by their relatively high Al and Zr content.

The knowledge on the lithologically inherited Pb isotope composition of Dutch sedimentary soils (Chapter 2) was used throughout the thesis to calculate the Pb isotope composition of the anthropogenic Pb fraction in Pb polluted soils and sediments in The Netherlands. Three methods have been used for this calculation:

1) In method 1 the lithologically inherited Pb isotope composition of the Pb polluted topsoil was assumed to be equal to the analysed Pb isotope composition of the underlying non-polluted subsoil. This method was only used if (i) subsoil data were available, (ii) the subsoil only contained lithologically inherited Pb, and (iii) the lithology of the subsoil was the same as that of the topsoil. In other words, the subsoil must be a ‘true’ C-horizon of the topsoil.

2) In method 2 the lithologically inherited Pb isotope composition of the Pb polluted topsoil was calculated based on the Zr and Al content of the Pb polluted topsoil (see Eq. (2.6.1) to (2.6.3)). This method was used when method 1 could not be used.

3) In method 3 the median lithologically inherited Pb isotope composition of the relevant lithology (sand, clay, peat or loess) was used (Table 2.2) if method 1 and 2 could not be applied.

Method 1 was the preferred method, because it is based on measured Pb isotope data at one sample location.

Besides the lithologically inherited Pb isotope composition, also the lithologically inherited Pb content had to be known to be able to calculate the anthropogenic Pb content and Pb isotope composition of the anthropogenic Pb fraction in Pb polluted soils (e.g., Eq. (2.2) to (2.4)). The lithologically inherited Pb content, also called natural or background Pb content, was calculated based on the common relationship between Pb and Al in unpolluted soils and sediments (e.g., Huisman, 1998; Van der Veer, 2006). In this thesis the relationship between Al and Pb was established based on 303 unpolluted sedimentary soils covering the entire Netherlands (see Chapter 2 and 3). Because soils and sediments in The Netherlands are seldom polluted with Al, the measured Al content was used as a lithogenic proxy for the natural Pb content.

8.2 Anthropogenic Pb content and sources in Pb polluted rural, roadside and urban (top)soils in The Netherlands.

Three types of Pb polluted soils were distinguished and studied in this thesis:
1) 336 rural topsoils in agricultural (arable land and grassland) and in natural (forests, open nature and moor) areas covering the entire Netherlands. The sample density was approximately 1 site per 70 km². All samples sites were located away from industries and main roads (minimum distance of 100 m);

2) roadside topsoils along highway A28 (near Nunspeet) and A58 (near Moergestel) in The Netherlands. Samples were taken at 2 distances from the roads; approximately at 8-10 m and 74-75 m distance.

3) urban topsoils in two cities (Utrecht and Wijk bij Duurstede) and two villages (Fijnaart and Graft-De Rijp) with a long habitation history. The two cities were already inhabited in Roman times (57 B.C. - 350 A.D.) and the two villages were founded around 1600 A.D.

The anthropogenic Pb content in the studied topsoils increased in the following order: rural topsoils < roadside topsoils < urban topsoils (Fig. 8.1). The anthropogenic Pb content in rural topsoils (A-horizon, 0-20 cm) – based on an organic-free basis – varied from <LOD to 1863 mg/kg with a median of 13 mg/kg (Fig. 8.1). The median anthropogenic Pb content of the various land uses (arable land, grassland, forest and open nature) was remarkably similar with values ranging from 10-15 mg/kg (Table 3.1). Only the median anthropogenic Pb content of moor was higher with 259 mg/kg (Table 3.1). This was largely the consequence of reporting the Pb content on an organic-free basis.

Several areas with high anthropogenic Pb contents in the topsoil were observed in The Netherlands (Fig. 8.2b). Most notable is the Randstad area (area A), which has the highest population and traffic density and hosts a considerable fraction of the Dutch chemical industry and several waste incinerators (Fig. 8.2b). The Randstad area records a high regional influence of industrial Pb on the anthropogenic signal. Two other areas with high anthropogenic Pb contents are located near the Dutch border and are most likely influenced by national, German and Belgian industries (area B and C in Fig. 8.2b). The locations of the Dutch waste incinerators are plotted in Fig. 8.2b. The waste incinerators that were already operational before the early 1990s (waste incinerators 1-6) are all located in areas with high anthropogenic Pb contents in the topsoil (>14 mg/kg) suggesting that they might have contributed to the total anthropogenic Pb content. The majority of the waste incinerators that came into operation from the late 1990s onwards (number 7-13; Fig. 8.2b) is not located in areas with high anthropogenic Pb contents (<14 mg/kg). Measures taken in the late 1980s and early 1990s to reduce Pb emissions from waste incinerators to the atmosphere (Janus et al., 1999), or the shorter operation time, might explain the lower anthropogenic Pb contents in rural topsoils near these waste incinerators (number 7-13; Fig. 8.2b). Notable exceptions are the high anthropogenic Pb contents in the rural soils near waste incinerator 8 and 12 (Fig. 8.2b). These soils might have been influenced by Belgian industries (Antwerp area) or Dutch chemical industries. Relatively low anthropogenic Pb contents (<10 mg/kg) were observed in the topsoils in the coastal dunes and southern, central and northern forest (Fig. 8.2). The population, traffic and chemical industry density is low in these areas and negligible quantities of fertilisers are applied.

The studied roadside soils are situated in a forested area of aeolian periglacial deposits (fine sands). The anthropogenic Pb content in the roadside litter and topsoils was higher than the median anthropogenic Pb content in rural sandy topsoils in Dutch forests (12 mg/kg (n = 55), Table 3.1). The highest anthropogenic Pb contents in the roadside soils from Moergestel and Nunspeet were 645 mg/kg and 191 mg/kg respectively (Appendix 5.2 to 5.4). The Pb
content in the litter and topsoils close to the highways (proximal sites) were a factor 2-4 higher than further away (distal sites) (Fig. 5.4). The relatively high anthropogenic Pb contents in roadside litter and topsoils compared with rural topsoils could be attributed to the proximity of roadside soils to one of the major (former) anthropogenic Pb sources in The Netherlands, namely gasoline Pb.

**Fig. 8.1.** Box-whisker plots of [Pb], (206Pb/207Pb), (208Pb/207Pb) and (206Pb/208Pb) of lithologically inherited Pb in rural subsoils and anthropogenic Pb in rural topsoils, lake sediments, roadside litter (Pba ≈ Pb), and urban soils in The Netherlands showing the minimum (lower whisker), maximum (upper whisker), median (center of the box), lower quartile (bottom of box), and upper quartile (top of box) values. li = lithologically inherited Pb; a = anthropogenic Pb; t = total Pb; recalc = re-calculated on an organic-free basis.
The highest anthropogenic Pb contents were measured in the urban topsoils (Fig. 8.1). The contents ranged from <LOD to 5266 mg/kg with a median of 140 mg/kg (Fig. 8.1). This was a factor 10 higher than the median anthropogenic Pb content in rural topsoils in the Netherlands (13 mg/kg; Fig. 8.1). A clear distinction could be made between the 3 distinguished time periods during which anthropogenic Pb entered the urban soils: the median anthropogenic Pb content increased from Roman period (7 mg/kg) to Medieval period (43 mg/kg) to Modern period (235 mg/kg) (Table 6.2). The high anthropogenic Pb content in urban soils is caused by the (visible) presence of Pb sources like glazed potsherds and roof tile fragments, glass fragments, coal ashes, paint flakes and metal slag. The Pb content of these artefacts varies from 3 mg/kg (Medieval production slag) to ~100 wt.% (Modern Pb sheet) (Table 6.3). High Pb contents were measured in glazed potsherds (0.5-8.7 wt.%), glazed roof tiles (1.9-5.9 wt.%), paint (6.0-18.6 wt.%), Pb spool (87.8 wt.%) and Pb sheets (~100 wt.%) (Table 6.3). Even small pieces of these artefacts can increase the soil Pb content significantly.
Like the anthropogenic Pb content, the Pb isotope composition of the anthropogenic Pb fraction in rural, roadside and urban topsoils in The Netherlands also varies considerably (Fig. 8.1 and 8.3). The lowest $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios for anthropogenic Pb were measured in the roadside soils with, for example, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the litter ranging from 1.12 to 1.14 (Fig. 8.1 and 8.3). These values clearly differ from lithologically inherited Pb in sedimentary soils in The Netherlands (Fig. 8.1 and 8.3) and resemble the values for gasoline Pb observed in Belgium ($^{206}\text{Pb}/^{207}\text{Pb} = 1.12-1.14$, Petit et al., 1984) and Germany ($^{206}\text{Pb}/^{207}\text{Pb} = 1.10-1.11$, Krause et al., 1993). According to Petit et al. (1984), Pb added in gasoline in Belgium and neighbouring countries came mainly from Canadian and Australian Pb ores of pre-Cambrian origin having characteristic low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.04-1.07 (Table 5.1). Based on the observed relationship between anthropogenic Pb and the distance to the highway (factor 2-4 higher anthropogenic Pb contents close to the highway than further away) and the observed Pb isotope composition, it was concluded that anthropogenic Pb in the roadside soils is mainly derived from gasoline Pb.

![Fig. 8.3.](image)

$^{(208}\text{Pb}\!/^{207}\text{Pb})_a$ versus $^{(206}\text{Pb}\!/^{207}\text{Pb})_a$ and $^{(206}\text{Pb}\!/^{208}\text{Pb})_a$ versus $^{(207}\text{Pb}\!/^{208}\text{Pb})_a$ in rural subsoils and topsoils, roadside litter ($\text{Pb}_a \approx \text{Pb}_t$), urban soils and lake sediments in The Netherlands. li = lithologically inherited Pb; a = anthropogenic Pb; t = total Pb.

Low Pb isotope ratios were also measured in several rural soils (Fig. 8.3), mainly in forested and open nature areas (Fig. 3.5). The range in Pb isotope ratios of the anthropogenic Pb fraction in Dutch rural topsoils was 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 (Fig. 8.1). The box values (first to third quartile) of these isotopic ratios differ significantly from that of lithologically inherited Pb, as observed for the subsoils (Fig. 8.1). The largest difference is observed for the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, where $\sim$93% of the $^{(206}\text{Pb}/^{207}\text{Pb})_a$ ratios in Dutch rural topsoils are lower than the minimum $^{(206}\text{Pb}/^{207}\text{Pb})_li$ ratio of 1.175, as observed for the subsoils. On average lower $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios were observed in topsoils of nature areas compared with agricultural areas (Fig. 3.5 and 3.6). The Pb isotope composition of
anthropogenic 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, which explains the slightly more radiogenic Pb isotope ratios for agricultural topsoils. The contribution of the various anthropogenic Pb sources 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.

Anthropogenic Pb in urban soils showed the most radiogenic Pb isotope ratios of all studied anthropogenic Pb fractions in Dutch (top)soils (Fig. 8.1 and 8.3). The Pb isotope composition of the anthropogenic Pb fraction in the urban soils varies from 1.111-1.199, 2.367-2.476 and 0.465-0.490 for \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} \), \( \frac{^{208}\text{Pb}}{^{207}\text{Pb}} \) and \( \frac{^{206}\text{b}}{^{208}\text{Pb}} \) respectively, with a median of 1.171, 2.447 and 0.478 respectively (Fig. 8.1). The box values (first to third quartile) of these isotopic ratios differ significantly from that of lithologically inherited Pb in sedimentary soils in The Netherlands (Fig. 8.1). Again, the largest discriminating power (~77%) is observed for the \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} \) ratios (\( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} < 1.175 \)). No clear differences were observed in the Pb isotope composition (and Pb sources) of urban soils polluted in Roman, Medieval or Modern times (Fig. 6.3). The \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} \), \( \frac{^{208}\text{Pb}}{^{207}\text{Pb}} \) and \( \frac{^{206}\text{Pb}}{^{208}\text{Pb}} \) ratios of the potential anthropogenic Pb sources vary between 1.150-1.207, 2.397-2.496 and 0.473-0.488 respectively (Table 6.3). The calculated Pb isotope compositions of anthropogenic Pb in the majority (~75%) of the urban soils appear to represent a mixture of potential anthropogenic Pb sources found in these soils: glazed potsherds, glazed roof tiles, building remnants, metal slag, Pb-based paint, Pb sheets, coal ash and other Pb containing artefacts. These anthropogenic Pb sources most likely entered the urban soils due to historical smelting activities, renovation and demolition of houses, disposal of coal ashes and raising and fertilization of land with city waste.

Knowledge of the cause and source of Pb pollution is important in efforts to abate environmental Pb pollution by taking source-related actions. Some anthropogenic Pb sources – e.g., gasoline Pb, Pb water distribution pipes and Pb-based paint – have already been banned in many countries and accordingly emission from these sources have been reduced significantly (see Section 8.3). Several other sources, e.g., coal and wood as energy source and fertilisers for improving the soil quality, are still in use. In addition careless renovation of (mainly) old houses can also result in anthropogenic Pb (Pb based paint, Pb glazed roof tile and Pb sheets) entering the environment, mainly in urban soils. This means that pollution of soils with anthropogenic Pb is an ongoing problem. The information obtained in this thesis can be of use in future studies to predict the effect of the use of anthropogenic Pb sources (e.g., coal and fertiliser) on the quality of the environment.

8.3 Extent and sources of historical atmospheric Pb deposition in The Netherlands

The sediments of 2 urban Dutch lakes – Lake Vechten and Fort Vechten – have been investigated to reconstruct historical anthropogenic atmospheric Pb deposition and to determine the anthropogenic Pb sources based on Pb isotope analysis. \(^{137}\text{Cs}\) activities showed that the lake sediments were deposited between 1942 and 2002 A.D. Anthropogenic atmospheric Pb deposition rates in the two lakes varied from 12 ± 2 to 69 ± 16 μg cm\(^{-2}\) y\(^{-1}\).
These values are relatively high compared with the atmospheric Pb deposition rates of 0.001 to 27 μg cm⁻² y⁻¹ established by others (e.g., Shotyk et al., 1998; Weiss et al., 1999; Vile et al., 2000; Le Roux et al., 2005). Most of these studies were performed in remote areas (e.g., rural areas in the Czech Republic and Switzerland). High atmospheric deposition rates (24.6 to 162.9 μg cm⁻² y⁻¹ have been reported in organic-rich pool sediments situated close to a Zn-smelter in Belgium (Sonke et al., 2002).

The profiles of reconstructed atmospheric Pb deposition rates in the 2 urban lakes (Fig. 4.3) resemble the profiles determined by others (Shotyk et al., 1998; Weiss et al., 1999; Vile et al., 2000; Le Roux et al., 2005). A peak in atmospheric Pb deposition is observed in the period 1970-1980 A.D. which is linked to the peak in leaded gasoline combustion in Europe (Shotyk et al., 1998; Weiss et al., 1999). Due to the introduction of gasoline with a lower Pb content and ultimately unleaded gasoline, rates of atmospheric Pb deposition decreased spectacularly since 1975-1980 A.D. (Fig. 4.3). Despite the mitigation measures, atmospheric Pb deposition rates in the 2 Dutch urban lakes are still significantly higher (factor 75 to 20,000) than European background fluxes (e.g., Shotyk et al., 1998; Sonke et al., 2002).

The Pb isotope ratios of the anthropogenic Pb fraction in the lake sediments vary from 1.140-1.176, 2.412-2.457 and 0.471-0.481 for ⁰⁰⁶Pb/²⁰⁷Pb, ⁰⁰⁸Pb/²⁰⁷Pb and ⁰⁰⁶Pb/²⁰⁸Pb respectively (Fig. 8.1). These values correspond with the isotopic composition of anthropogenic Pb in rural sedimentary soils in nature areas in The Netherlands (Table 3.1 and Fig. 3.4). These rural soils mainly contain anthropogenic Pb from a mixture of diffuse atmospheric Pb sources (incinerator ash, gasoline Pb and coal/galena). Temporal variation in the deposition of the various diffuse anthropogenic Pb sources could not be derived from the rural soils. The 2 urban lakes provided an unique opportunity to obtain this temporal information. The Pb isotope ratios of the anthropogenic Pb fraction in the lake sediments confirmed that the peak in atmospheric Pb deposition in the period 1970-1980 A.D. was caused by leaded gasoline combustion (Fig. 4.5). In this period the maximum contribution of gasoline Pb to the total anthropogenic Pb content was 53 ± 3% and 75 ± 5% for Fort Vechten and Lake Vechten respectively (Fig. 4.5). Before the massive increase in the usage of leaded gasoline (Fig. 4.7) the major anthropogenic Pb sources in Fort Vechten and Lake Vechten were industrial Pb (incinerator ash signature) and coal/galena respectively with maximum contributions of 99 ± 5% and 100 ± 7% respectively (Fig. 4.5). At the peak of leaded gasoline usage the relative contribution of industrial Pb in Fort Vechten and coal/galena in Lake Vechten has been decreased to 47 ± 2% and 25 ± 2% respectively (Fig. 4.5). After the ban on leaded gasoline, the relative contributions of industrial Pb and coal/galena increased again to 72 ± 3% for industrial Pb in Fort Vechten and 96 ± 6% for coal/galena Pb in Lake Vechten in 2000 A.D (Fig. 4.5). The studied Dutch urban lake sediments proved to be useful natural archives for the reconstruction of historical atmospheric Pb deposition rates and the temporal variation in the relative contribution of the anthropogenic atmospheric Pb sources.

To assess and manage air quality in the European Union, the European Council Directive 1999/30/EC came into force in 1999 A.D. This Directive describes, among others, the numerical limits and thresholds for pollutants including Pb. The limit value for the annual mean air Pb concentration was set at 500 ng/m³. Between 1987 and 2002 A.D. annual mean air Pb concentrations in The Netherlands decreased from approximately 80 to 10 ng/m³ (Hammingh et al., 2002). Since data before 1987 A.D. are lacking it is unknown if air Pb concentrations in The Netherlands were ever higher than 500 ng/m³. Atmospheric Pb deposition rates, based on the urban lake sediments, showed a clear relationship with nearby
measured air Pb concentrations (Fig. 4.6). Since the lake sediments go back to 1942 A.D. it was possible to reconstruct historical air Pb concentrations before 1987 A.D. (Fig. 4.7). Based on the established relationships it was estimated that annual mean air Pb concentrations between 1942 and 2002 A.D. varied between 5 and 292 ng/m$^3$ and did not exceed the EU critical limit of 500 ng/m$^3$. In addition, national and European measures to curtail the emission of lead from leaded gasoline are clearly reflected in the reconstructed air Pb concentrations, including the 1973 and 1979 A.D. oil crisis. This thesis shows that the legal intervention on a national/worldwide level has resulted in the improvement of the air Pb quality within a decade.

8.4 Mobility of anthropogenic Pb in (roadside) soils in The Netherlands

Although atmospheric Pb deposition rates decreased sharply after the ban on leaded gasoline (Fig. 4.7), rural and roadside soils still contain anthropogenic Pb due to the combustion of leaded gasoline in the past (Fig. 3.5 and Fig. 5.3). Early reports suggested that the residence time of Pb in forest floors could be in the order of several hundred years (Benninger et al., 1975; Tyler, 1978; Friedland and Johnson, 1985; Turner et al., 1985). If these estimates are correct, then despite the reduction in Pb deposition due to legislative measures starting in the 1970s to curtail gasoline Pb, the Pb content in soils should increase to potentially toxic levels (Watmough et al., 2004). In this thesis the Pb content and isotopic composition of sandy roadside soils was determined in 1991 and 2003 A.D. (Appendix 5.2 to 5.4). Since gasoline Pb is not emitted to roadside soils anymore, this offered a unique possibility to study the mobility of anthropogenic Pb, mainly gasoline Pb, over a period of 12 year.

Downward Pb migration was calculated to vary from 72 ± 95 to 324 ± 279 mg m$^{-2}$ y$^{-1}$, depending on distance from the highway and type of soil horizon (Table 5.4). Based on estimates of the total atmospheric Pb deposition between 1962/1963 to 2003 A.D. (data Lake Vechten lake sediments; Fig 4.3), it was calculated that 35-90% of the atmospherically derived Pb migrated to groundwater. Lead isotope measurements confirmed the presence of anthropogenic Pb in groundwater (Table 5.2). This study showed that anthropogenic Pb can be highly mobile, resulting in groundwater pollution. The high mobility of anthropogenic Pb in the studied roadside soils was caused by the absence of reactive phases (organic matter, clay, calcium carbonate, reactive iron) in the deeper soils (>15 cm) and the low soil pH (pH-H$_2$O = 4.3-5.0). Only the litter layer and the topsoil (0-15 cm) retained anthropogenic Pb which is strongly associated with organic matter. At depths >15 cm, anthropogenic Pb was no longer retained and migrated towards groundwater.

This study showed that anthropogenic Pb in soils can be highly mobile. Although the measured Pb concentrations in groundwater were lower than the Dutch intervention value of 75 $\mu$g/l (Table 5.2), it concerns anthropogenic Pb that – in a worst-case situation – can end up in our drinking water. To assess the actual risks it would be worthwhile to determine and quantify the factors that determine fluxes of anthropogenic Pb in soils and sediments in more detail.

8.5 Oral bioaccessibility of anthropogenic Pb sources in Pb polluted soils in The Netherlands

In human risk assessment, ingestion of soil is considered a major route of toxic Pb exposure. Due to the frequent hand-to-mouth behaviour of young children, ingestion of Pb
polluted soil is especially an important exposure route for children (Duggan and Inskip, 1985; Davis and Waller, 1990; Calabrese et al., 1997). In addition, children are more sensitive to the toxic effects of Pb than older people and environmental exposure may cause chronic health effects (see Section 1.2).

Various in vitro tests have been developed to determine the oral bioaccessibility of Pb in media like food, suspensions, liquids and soils. Oral bioaccessibility is defined as the fraction of Pb that is mobilized from the medium (e.g., Pb polluted soil) into the lumen (chyme). The fraction of an orally administered Pb dose that is mobilized and actually reaches systemic circulation is defined as oral bioavailability. The bioaccessible fraction is considered to represent the maximum amount of Pb available for intestinal absorption. Therefore, oral bioaccessibility is always larger than or equal to oral bioavailability.

In this study the oral bioaccessibility of Pb in 28 soils polluted with various Pb sources (e.g., Pb bullets and pellets, car battery Pb, gasoline Pb and city waste with among others remnants of Pb glazed potsherds and roof tiles, Pb based paint flakes, and Pb sheets) was determined with an in vitro digestion model developed and tested by Oomen (2003). In addition, the influence of the Pb pollution characteristics (chemical composition and particle size of the anthropogenic Pb fraction) and soil characteristics (pH, total Pb, organic matter, clay, calcium carbonate, and reactive iron content) on the oral bioaccessibility was determined. The relative oral bioaccessibility of the Pb polluted soils varied from 0.5% to 79% and decreased in the following order:

Pb bullets and pellets > Car battery Pb > Made ground Pb ≈ Gasoline Pb ≈ Diffuse Pb > City waste (among others remnants of Pb glazed potsherds and roof tiles, Pb based paint flakes, and Pb sheets)

This differed from the expected oral bioaccessibility as predicted from the chemical composition and particle size of the anthropogenic Pb sources (not taken into account soil processes). The oral bioaccessibility of Pb was expected to decrease in the following order:

Gasoline Pb > Diffuse Pb > Made ground ≈ City waste > Car battery Pb ≈ Pb bullets and pellets

Based on the relative soluble Pb halides, oxides and sulfates, and their small particle size (see Section 7.5.2.1), it was presumed that (combusted) gasoline Pb would be the most bioaccessible Pb source. Lead bullets and pellets were expected to be the least bioaccessible Pb source based on the relative insolubility of metallic (native) lead and the large particle size of Pb bullets and pellets. The observed differences between the expected and measured oral bioaccessibilities are a strong indication of the importance of the influence of soil composition on bioaccessibility of Pb. Statistical analysis indicated that oral bioaccessibility of Pb depended on soil pH, and the content of organic matter and reactive Fe. Time is probably also an important factor in determining oral bioaccessibility of Pb in polluted soils. In time, the bioaccessible Pb fraction is leached from the soil and stable secondary Pb phases will remain. Two soil samples were polluted between 500 and 1000 A.D. These soils had relative oral bioaccessibilities of 1.6-5.7% which are among the lowest measured oral bioaccessibilities.
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The Dutch intervention value for Pb is 530 mg/kg for standard soils (25% clay and 10% organic matter). Soils with a higher Pb content than the intervention value are classified as ‘seriously’ contaminated (Swartjes, 1999). In case of a serious soil contamination, the contaminated site has, in principle, to be remediated. However, the need for remediation is decided on the basis of actual risk to humans and ecosystems and the actual risk due to migration of the contamination. Dutch risk assessment for Pb is based on criteria laid down by FAO/WHO (1993) and IPCS (1995). It is recommended to avoid Pb blood levels above 50 μg/l, resulting in a provisional tolerable weekly intake (PTWI) of 25 μg/kg body weight per day⁴, which is based on absorption of 40% dietary Pb. This value for the absorption of dietary Pb is based on toxicity studies. Media that are typically employed in toxicity studies are food, suspensions, and liquids such as water (see Section 7.5.3). The results of this thesis show that in current risk assessment in The Netherlands, the risk of Pb polluted soil to children is in general overestimated. In 85% of the studied samples (24 out of 28) the ‘in vitro based’ bioavailability was lower than the bioavailability based on the toxicity studies (<40%). However, in 15% of the studied samples (4 out of 28), the risk to children may be underestimated in current Dutch risk assessment (>40%). For this reason, the remediation urgency of these sites should be reconsidered. Currently, several thousand Dutch sites are still polluted with Pb. The knowledge gained in this thesis can be used to prioritize the need to remediate these locations.

8.6 Findings of this thesis in the context of the current practice of risk assessment of lead in soils in The Netherlands

The current practice of risk assessment of Pb in soils in The Netherlands is illustrated in Fig. 8.4. The total soil Pb content is measured to determine if a soil is polluted with Pb. A soil with a Pb content exceeding the intervention value of 530 mg/kg for standard soils (25% clay and 10% organic matter) is classified as ‘seriously’ contaminated (Swartjes, 1999). When this intervention value is not exceeded, no further action is required unless there is a specific ‘sensitive’ situation, such as a vegetable garden (Fig. 8.4). In case of a serious soil contamination (Pbstandard soil > 530 mg/kg), the contaminated site has, in principle, to be remediated. However, the need for remediation is decided on the basis of actual risks to humans and ecosystems and the actual risk due to migration of the contamination. This risk assessment is performed in The Netherlands with the decision-support tool Sanscrit. Two main aspects of the tool can be distinguished (Van Kesteren et al., 2014): 1) the relevant human exposure scenario can be calculated and 2) soil-specific evaluation can be performed by determining the relative bioavailability factor (Rel F). This factor is introduced to compare oral bioavailability of Pb in soils with bioavailability of Pb based on toxicity studies with food, liquids and suspensions on which ‘legal’ threshold values are based (see Section 7.5.3). For made grounds a Rel F of 0.4 is currently used in Dutch soil policy (Van Kesteren et al., 2014). A site-specific Rel F may also be calculated by determining the bioavailability of Pb in Pb polluted soils by using an in vitro digestion model.

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⁴ The European Food Safety Authority’s (ESFA) Panel on Contaminants in the Food Chain decided in 2010 that a PTWI for Pb was no longer appropriate since there is no evidence for a threshold for a number of critical endpoints including development neurotoxicity and adult nephrotoxicity (Van Kesteren et al., 2014 and references therein). As an alternative measure ESFA identified a 95th percentile lower confidence limit of the benchmark dose of 1% extra risk (BMDL01) of 0.50 mg/kg body weight per day for neurotoxicity in young children (Van Kesteren et al., 2014 and references therein).
This thesis showed that,

1) anthropogenic Pb can be far more mobile than previously thought. This means that actual risks due to migration of Pb pollution might be underestimated in current risk assessment

2) relative oral bioaccessibilities of Pb polluted soil can vary considerably (0.5-79%) and depend on the chemical composition and specific reactive surface of the anthropogenic Pb sources and the characteristics of the soil in which the anthropogenic Pb source resides (soil pH, and the content of organic matter and reactive Fe). This urges for the determination of the site specific bioavailability of Pb –using in vitro digestion models – instead of using an average Rel F of 0.4 to determine human risks. Another possibility is to increase Rel F to avoid (any) risk of oral exposure.

Recently, the Dutch National Institute for Public Health and the Environment (RIVM) studied the bioavailability of Pb from Dutch made grounds using 3 in vitro digestion models and an in vivo study with juvenile swine (Van Kesteren et al., 2014). This study showed that the in vitro method ‘unified BARGE method (UBM)’ predicts the bioavailability of Pb in made grounds in young children best (i.e. agreed best with the in vivo study results). The relative bioavailability of Pb in made ground determined in the in vivo juvenile swine study
and with the in vitro UBM method varied from 47-95% and 10-74% respectively. This RIVM study confirms that bioavailability of Pb in polluted soils can vary considerable. This shows that actual risks for young children can only be determined well when site-specific measurements of Pb bioavailability are performed, e.g., using an in vitro digestion model. When the current generic value for Rel F is used the bioavailability of Pb can be underestimated bringing young children at risk. Van Kesteren et al. (2014) therefore concluded that the current Rel F (for made grounds) needs to be revised.

‘Prevention is better than cure’ also accounts for environmental Pb pollution. The highest anthropogenic Pb contents were measured in urban soils (see Section 8.2). Major anthropogenic Pb sources in these urban soils are Pb-based paints chips, remnants of Pb-glazed roof tiles and ceramics, and Pb sheets. These Pb based artefacts can have entered the soil during renovation or demolition of ‘old’ houses. Since many houses still contain Pb-based building materials and since some of these materials are still for sale, careless renovation or demolition of (mainly old) houses can cause new or more extensive Pb polluted soils. When these Pb sources end up in (back)yards they can pose a direct threat to young children playing in these yards. Public awareness programs can help to avoid Pb pollution in soils where young children are playing. ‘Een beter milieu begint bij jezelf (VROM, 2014’).

8.7 References


