



MacKinnon, G., MacKenzie, A.B., Cook, G.T., Pulford, I.D., Duncan, H.J., and Scott, E.M. (2011) Spatial and temporal variations in Pb concentrations and isotopic composition in road dust, farmland soil and vegetation in proximity to roads since cessation of use of leaded petrol in the UK. *Science of the Total Environment*, 409 (23). pp. 5010-5019. ISSN 0048-9697

Copyright © 2011 Elsevier

A copy can be downloaded for personal non-commercial research or study, without prior permission or charge

The content must not be changed in any way or reproduced in any format or medium without the formal permission of the copyright holder(s)

When referring to this work, full bibliographic details must be given

<http://eprints.gla.ac.uk/59075/>

Deposited on: 4 June 2013

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk>

Spatial and temporal variations in Pb concentrations and isotopic composition in road dust, farmland soil and vegetation in proximity to roads since cessation of use of leaded petrol in the UK.

G. MacKinnon^{a†}, A.B. MacKenzie^a, G. T. Cook^a, I. D. Pulford^b, H. J. Duncan^b, and E. M. Scott^c

^a Scottish Universities Environmental Research Centre, East Kilbride, G75 0QF, Scotland, UK. E-mail: Gillian.MacKinnon@glasgow.ac.uk; Angus.MacKenzie@glasgow.ac.uk, Gordon.Cook@glasgow.ac.uk

^b School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, Scotland, UK. E-mail: Harry.Duncan@glasgow.ac.uk, Ian.Pulford@glasgow.ac.uk

^c School of Mathematics and Statistics, University of Glasgow, Glasgow, G12 8QQ, Scotland, UK. E-mail: Marian.Scott@glasgow.ac.uk

† corresponding author

Tel: 00 44 (0) 1355 270 142, Fax: 00 44 (0) 1355 229 898

Abstract.

Results are presented for a study of spatial distributions and temporal trends in concentrations of lead (Pb) from different sources in soil and vegetation of an arable farm in central Scotland in the decade since the use of leaded petrol was terminated. Isotopic analyses revealed that in all of the samples analysed, the Pb conformed to a binary mixture of petrol Pb and Pb from industrial or indigenous geological sources and that locally enhanced levels of petrol Pb were restricted to within 10 m of a motorway and 3 m of a minor road. Overall, the dominant source of Pb was historical emissions from nearby industrial areas. There was no discernible change in concentration or isotopic composition of Pb in surface soil or vegetation over the decade since the ban on the sale of leaded petrol. There was an order of magnitude decrease in Pb concentrations in road dust over the study period, but petrol Pb persisted at up to 43% of the total Pb concentration in 2010. Similar concentrations and spatial distributions of petrol Pb and non petrol Pb in vegetation in both 2001 and 2010, with enhanced concentrations near roads, suggested that redistribution of previously deposited material has operated continuously over that period, maintaining a transfer pathway of Pb into the biosphere. The results for vegetation and soil transects near minor roads provided evidence of a non petrol Pb source associated with roads/traffic, but surface soil samples from the vicinity of a motorway failed to show evidence of such a source.

Keywords

Pb, farmland, vegetation, soil, sources, temporal variations

1. Introduction

In most industrialised countries, atmospheric deposition of Pb increased from the start of the industrial revolution, reached peak values in the mid 20th century then declined as increasing awareness of the potential health implications of environmental contamination led to the progressive introduction of measures to reduce emissions from major sources such as industry, power generation, transport and domestic heating (Nriagu, 1988, 1989, 1990). Temporal variations in atmospheric deposition of Pb in the UK followed such a trend and have been well characterized on the basis of studies of peat and sediment cores and other environmental archives (eg MacKenzie et al., 1997, 1998; Farmer et al., 1996, 2005; Cloy et al., 2008). Vehicle exhaust emissions constituted a major source of Pb during the period of use of leaded petrol from the 1920s until the end of the 20th century, generating high concentrations of Pb in soil and vegetation in the vicinity of roads as the result both of runoff affecting the immediate roadside environment and of atmospheric dispersion giving longer range transport (Harrison and Johnston, 1985, Zupančič, 1999, Legret and Pagotto, 2006, Preciado et al., 2007; Yesilonis et al., 2008, Zehetner et al., 2009).

Characteristic differences between the stable isotope composition of petrol Pb and that of other major contaminant sources and of indigenous geological materials have been widely utilised in investigations of the origins and behaviour of Pb in soils (*e.g.* Erel et al., 1997, Hansmann and Köppel, 2000, Teutsch et al., 2001, Novak et al., 2003, Watmough and Hutchinson, 2004, Klaminder et al., 2005) and in reconstructing historical trends in contaminant Pb deposition from different sources using peat or lake sediment cores (*e.g.* MacKenzie et al., 1997, 1998, Shotyk et al., 2002, Farmer et al., 2005; Steinnes et al., 2005, Cloy et al., 2008). The situation in the UK was highly favourable for such studies, with petrol Pb having an average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.076 (Sugden et al., 1993, Farmer et al.,

2000), while indigenous geological materials, industrial emissions and coal typically have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.17 or greater (Farmer et al., 2000).

Despite the cessation of use of leaded petrol at the start of 2000, road and vehicular traffic related releases still continue to provide a source of Pb which will contribute incrementally to the extant environmental inventory. Road runoff, corrosion of crash barriers, wear of tyres and engine components and exhaust emissions have been identified as minor, but finite, contemporary sources of Pb (eg Hjortenkrans et al., 2006). For example, Chen and Jiang (2009) reported Pb concentrations of 21.6 to 32.3 $\mu\text{g l}^{-1}$ in diesel, 41.3 $\mu\text{g l}^{-1}$ in biodiesel, 1.8 $\mu\text{g l}^{-1}$ in unleaded gasoline and 4.5 $\mu\text{g l}^{-1}$ in engine oil in Taiwan, while Kummer et al. (2009) gave an average value of 17 $\mu\text{g l}^{-1}$ for the Pb concentration in unleaded gasoline in Europe. Kummer et al. (2009) also estimated Pb emission factors of 0.0016 and 0.0049 mg km^{-1} for tyre wear for cars and heavy duty vehicles, respectively, and corresponding figures for brake wear of 0.0049 and 0.023 mg km^{-1} . Such emissions represent a source of Pb that is likely to continue indefinitely in the future and which will have operated in the past, but at a level that was largely masked by the much larger releases from the use of leaded petrol. Evidence of this was provided by Bacon (2002) in a study of stable Pb isotope ratio trends for grass from two sites in Scotland over the period 1989 to 2001, which indicated that, in addition to petrol Pb, road/traffic related emissions contained another, isotopically distinct, component and Bacon (2002) introduced the term “traffic Pb” for this component.

Past releases have left a legacy of a large environmental burden of contaminant Pb which will contribute to chronic, long term human intake, in particular in situations where entry into the food chain is possible. Redistribution from sites with higher levels of contamination is potentially important in this context, as illustrated by Young et al. (2002) who reported that resuspension of soil near industrial facilities and highways resulted in Pb concentrations in PM_{10} particles ranging from 79.4 to 2283 mg kg^{-1} .

Evaluation of the long term implications of Pb contamination will therefore require both investigation of the distribution and behaviour of historically deposited Pb and characterisation of contemporary sources, particularly in situations that could lead to human intake. The objective of the present study was to characterise the distribution of Pb from different sources in soil and vegetation of an arable farm influenced by both vehicular and urban/industrial emissions shortly after the cessation of sale of leaded petrol and to evaluate changes in these sources and distributions in the subsequent decade.

2. Materials and Methods

2.1 Study Site and Sample Collection

The study site, located in central Scotland approximately 15 km to the west of the centre of the City of Glasgow, is an arable farm, which is bordered directly by a motorway with average daily traffic flow of about 54,000 vehicles in each direction (www.scotlandtransport.gov.uk, 2011) and is traversed by minor roads with a much lower volume of traffic (Fig. 1). The soil at this site, belonging to the Dreghorn Series which is part of the Dreghorn Association (Ragg et al., 1976), is a sandy loam (32.7% coarse sand, 35.3% fine sand, 16.3% silt and 15.7% clay) with 6.5% Loss on Ignition (LOI%), 0.17% total nitrogen (Kjeldahl N) and a pH of 6.86 (1:2.5 water) (Metwaly, 1999).

Samples from within the fields were collected from uncultivated boundary areas. Although there are no formal records, the landowner has indicated that these areas had not been cultivated and had been left under natural vegetation for approximately forty years prior to the first sampling date. Four transects of surface soil (0 - 3 cm depth, using plastic corers to minimise disturbance), and vegetation (mixed grasses/legumes, removed carefully using

scissors to avoid any soil contamination) were collected in spring 2001 to investigate the spatial distribution and isotopic composition of Pb relative to the road systems. This sampling was repeated again in 2010 from approximately the same locations using identifiable features in the field boundaries to locate the transect positions. In 2001, transects 1 and 2 (T1 and T2) extended 50 m from the motorway into the field, with a verge constituting the first 5 m of each transect and the field being separated from the verge by a well established hedge of height ~ 2 m. In 2010, vegetation samples could be collected only to a distance of 30 m at these transect positions because of a greater extent of ploughing of the field. For transects 3 and 4 (T3 and T4) vegetation extended 35 m and 50 m respectively but soil sampling extended to 50m in both transects. This field was adjacent to a minor road, with the verge occupying 3 m and 1.5 m, for T3 and T4 respectively, and was bordered by a post and wire fence with small, intermittent lengths of hedge of less than 1 m height. Samples of road dust, which is a potential source material for Pb transferred to adjacent soil, were collected from a single location on the motorway hard shoulder between the positions of transects 1 and 2 and from the road edge at the positions of each of transects 3 and 4. A soil core was collected on the line of each transect from a position 7.5 m from the road edge. The cores were obtained by excavating a pit using a stainless steel spade then progressively collecting sections of area 20 cm x 20 cm and depth 5 cm to a depth of 30 cm using a stainless steel trowel. Upon removal, the core sections were sealed in polythene bags for return to the laboratory

2.2 Analytical Procedures

High purity 'Primar' HCl and HNO₃ (Fisher Chemicals) were used for analyses and Millipore milli-U10 purified water was used for dilutions. Approximately 1 g subsamples of sieved, air dried soil or road dust, or 0.25 – 0.50 g of oven dried (70° C), homogenised vegetation, was

digested using Aqua Regia (5h reflux on hotplate), taken to dryness and redissolved in 0.5 M HCl. Pb concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS) using a Perkin Elmer 1100B instrument. Pb isotope ratio analyses were performed using a VG Plasma Quad PQII ICP-MS. Precision was monitored by running a set of Pb standards at the beginning of each run using solutions prepared from a Johnson Matthey standard solution. For Pb isotope ratios, a solution of the NIST Pb reference material 981 was run after every third sample to compensate for any mass bias and to assess precision which was better than 0.5%. Bi was used as an internal standard to compensate for any change in instrument sensitivity during the run. Accuracy of Pb concentration measurements was determined by analysing a subsample of NIST SRM 1648 Urban Particulate Matter along with each sample run, giving satisfactory agreement with the certified concentration range (certified Pb $6550 \pm 80 \text{ mg kg}^{-1}$; observed range 6053 – 6586 mg kg^{-1}). As a secondary check of accuracy, a suite of subsamples was also analysed for Pb using both FAAS and ICP-MS, giving average agreement within 10% ($n = 24$) for the two methods, giving further confidence in the analytical data.

3. Results and discussion

3.1 Road dusts

The road dust samples had similar Pb concentrations at the three different locations within each year of sampling (Table 1), but the mean concentration decreased from 117 mg kg^{-1} in 2001 to 14.2 mg kg^{-1} in 2010, consistent with the trend observed in other studies in the UK. Thus, concentrations observed for road dusts in Glasgow in 1976 ranged from 150 to 2,300

mg kg⁻¹ (Farmer and Lyon, 1977) while those for Edinburgh in 1991 were in the range 99 to 1194 mg kg⁻¹ (Sugden, 1993; Sugden et al., 1993). A series of studies of urban street dusts in Manchester, NW England, revealed: (i) mean concentrations of 941 mg kg⁻¹ in 1975 and 569 mg kg⁻¹ in 1997 (Nageotte and Day, 1998), (ii) concentrations at three locations decreasing from 447 to 215 mg kg⁻¹, from 467 to 247 mg kg⁻¹ and from 451 to 216 mg kg⁻¹, respectively, from May 1999 to September 2000 (Massadeh and Snook, 2002) and (iii) a range of 89 to 234 mg kg⁻¹, with one anomalous value of 433 mg kg⁻¹, for 2001 (Robertson and Taylor, 2007). The concentrations observed in the present work are therefore consistent with this decreasing trend, but are substantially lower than those observed in the above studies of road dust from urban areas.

A number of studies have demonstrated that in central Scotland non-petrol lead was deposited into soil predominantly during the industrial era, and that this lead originated mainly from the use of local lead ores and Scottish coals (Farmer et al, 1996, 2005, 2006, MacKenzie et al, 1997, 1998, Cloy et al., 2008). In the plot of ²⁰⁶Pb/²⁰⁷Pb against ²⁰⁸Pb/²⁰⁷Pb (Figure 2) the values for the road dust samples lie on a straight line ($R^2 = 0.99$) between end members represented by the ratios for petrol Pb and those for industrial emissions and indigenous geological materials, represented here by average values for Scottish coal (Farmer et al., 1999) and ore from the abandoned Leadhills mine in SW Scotland (Sugden et al., 1993, Farmer et al., 1999, 2000). Assuming that the total Pb is a binary mixture of petrol Pb and “industrial Pb” (with an isotopic composition assumed here to be the average of that of Scottish coal and indigenous Pb ore), indicates that in 2001 the Pb in the dust from the minor roads (T3 and T4) was approximately 50% petrol derived, with the motorway sample (T1/T2) having a slightly lower petrol contribution of 38%. Refinement of this apportionment calculation including the small contribution from pedogenic lead resulted in no significant

difference to these values (< 1%). By 2010, the petrol Pb contribution to the minor road samples had decreased to 22% for T3 and 13% for T4, whereas the motorway sample had a value of 43%, which is similar to that observed in 2001. Thus, while Pb concentrations decreased at all three locations, the isotope data reveal a pronounced decrease in the relative contribution of petrol Pb at the minor road but not at the motorway.

3.2 Soil and vegetation transects

Table 2 shows Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for the transect soil and vegetation samples. The motorway transects had soil Pb concentrations ranging from 59.3 to 388 mg kg⁻¹, with the minor road transects having a similar range of 49.1 to 260 mg kg⁻¹, with the exception of samples within 3 m of the road edge in T4, where higher values of up to 703 mg kg⁻¹ were observed. The concentrations in the soils close to the road for T4 were consistently lower in 2010 than in 2001, but overall there was no systematic difference between the transects sampled ten years apart. This suggests a high degree of heterogeneity in the lead concentrations in the soils, and so individual samples cannot be compared on a temporal basis. The soil transects exhibit generally higher soil Pb concentrations close to the roads, but with irregular variations both within individual transects and between transects. The observed range of concentrations is similar to the ranges that have been reported for surface soil in parks in Glasgow over a period of some thirty years. Farmer and Lyon (1977) reported values for 1976 of 93 – 424 mg kg⁻¹ (mean 196) for central areas of parks and 321 – 744 mg kg⁻¹ (mean 584 mg kg⁻¹) for areas within 5 m of roads and Gibson and Farmer (1985) reported a range of 22 – 1260 mg kg⁻¹ (mean 226 mg kg⁻¹) for 1981. Ajmone-Marsan et al. (2008) reported a range of 53–553 mg kg⁻¹ (mean 178 mg kg⁻¹) for Pb in Glasgow park soils for 2003, with similar ranges being reported for other European cities: Aviero 33 – 234 mg

kg⁻¹ (mean 86 mg kg⁻¹); Ljubljana 80-306 mg kg⁻¹ (mean 102 mg kg⁻¹), Seville 46-340 mg kg⁻¹ (mean 157 mg kg⁻¹) and Turin 85-839 mg kg⁻¹ (mean 235 mg kg⁻¹).

Figure 3 shows the plot of ²⁰⁶Pb/²⁰⁷Pb ratio versus ²⁰⁸Pb/²⁰⁷Pb ratio for the soil transect samples. In all cases, the data points lie on the petrol Pb – industrial Pb tie line, with a general, but irregular, trend with samples closer to the roads lying closer to the petrol value. There was no systematic difference between transects from different positions or between samples from the same transect lines in different years. Taken together, the concentration and isotope ratio data are therefore consistent with the soil Pb at all locations being derived from a binary mix of petrol and industrial sources, but with no systematic temporal variations in either concentrations or isotope ratios and with irregular trends in distribution, limiting the value of interpreting trends in individual transects. Because of the high spatial variability, the average of the petrol Pb and non-petrol Pb concentrations in 2001 and 2010 were calculated for the motorway transects and for the minor road transects in order to show the trend in variation in Pb concentration relative to the roads. These trends are shown in Figure 4, along with calculated petrol Pb and non petrol Pb concentrations. For the motorway transects, the mean concentrations of total Pb ranged from a maximum of 208 mg kg⁻¹ at 1 m from the road edge to a minimum of 92.3 mg kg⁻¹ at 20 m. Petrol Pb was dominant within 10 m of the road, but non petrol Pb dominated at greater distances. The petrol Pb concentration decreased from a maximum of 150 mg kg⁻¹ at 1 m to 20.2 mg kg⁻¹ at 50 m, with an approximately exponential trend characterised by a halving distance (analogous to half life in radioactive decay) of 9 m. The mean concentration of non petrol Pb was relatively uniform (range 54 – 59.3 mg kg⁻¹) within 20 m of the road, but then gradually increased with increasing distance to a maximum of 131 mg kg⁻¹ at 50 m. Mean concentrations of total Pb for the minor road transects decreased from 287 mg kg⁻¹ at 1 m from the road to a minimum of 102 mg kg⁻¹ at

50 m (Figure 4b). Petrol Pb exhibited a sharp exponential decrease from 210 mg kg⁻¹ at 0.15 m to 14.3 mg kg⁻¹ at 50 m, with a calculated halving distance of 1.5 m, with the result that petrol Pb was dominant only within 3 m of the road. The larger halving distance (9 m) for the motorway transects than the minor road (1.5 m) reveals greater dispersion of Pb at the motorway, possibly related to greater traffic speed. The maximum non petrol concentration of 143 mg kg⁻¹ was at 4 m, with lower values closer to the road and a gradual decrease with increasing distance into the field, reaching a minimum of 87.7 mg kg⁻¹ at 50 m. The trend of non petrol Pb concentrations within the field adjoining the minor roads could be taken to indicate a traffic Pb component as proposed by Bacon (2002), but there is no evidence of this in the mean concentrations for the motorway transects.

A general trend of decreasing Pb concentration with increasing distance from the road is apparent in the vegetation samples (Table 2), with the exception of T4 in 2001, where the maximum value was observed at 5 m from the road and T1 in 2010 where the 10 m sample was anomalously high. Despite contemporary low levels of atmospheric deposition of Pb, there was no systematic decrease in concentrations of Pb in the vegetation between 2001 and 2010. The plot of ²⁰⁶Pb/²⁰⁷Pb ratio versus ²⁰⁸Pb/²⁰⁷Pb ratio for the vegetation samples reveals that the 2001 samples plot on the petrol Pb – industrial Pb tie line with a trend generally consistent with greater petrol Pb influence closer to the roads (Figure 5). The results for 2010 also lie on or close to the petrol-industry tie line, but show a greater spread than those for 2001. With the assumption that Pb in the vegetation is derived from deposition rather than uptake (Bacon et al., 2005), this suggests continuing aerial deposition up to 2010 of both petrol and non-petrol Pb, implying redistribution of previously deposited material. Figure 6 shows the average total, petrol and non petrol Pb concentrations in vegetation for the Motorway transects for 2001 and 2010. For the 2001 samples, the total Pb concentration exhibited an exponential decrease with increasing distance from the road and this trend was

paralleled by both the petrol and non petrol Pb, giving respective halving distances of 3.8, 3.2 and 4.6 m respectively. The halving distance observed for petrol Pb in the vegetation of 3.2 m, indicating the influence of contemporary redistribution processes, is smaller than that of 9 m observed for surface soil, which would have been influenced by historical emission related processes. In contrast, similar halving distances were observed for petrol Pb and non petrol Pb in the vegetation, possibly indicating similar redistribution processes influencing both components. Similar concentrations and trends were observed in 2010, but with greater irregularity caused by higher concentrations of petrol Pb at 10 m and of non petrol Pb at 10 and 30 m. Figure 7 shows the average total, petrol and non petrol Pb concentrations for vegetation from the minor road transects for 2001 and 2010. In both years, total, petrol and non petrol Pb concentrations all exhibited a very rapid decrease with increasing distance from the road edge, reaching a total concentration of less than 10 mg kg^{-1} and petrol and non petrol concentrations of less than 5 mg kg^{-1} within 3 m of the road. This very rapid decrease makes calculation of halving distances impractical in this case, with the available spacing of samples. Concentrations of both petrol Pb and non petrol Pb were generally less than 5 mg kg^{-1} for samples from within the field except for non petrol Pb in 2010 where samples from 20 – 50 m had slightly higher concentrations of $6.8 - 8.2 \text{ mg kg}^{-1}$. There was no correlation between the soil and vegetation Pb concentrations, with vegetation:soil concentration ratios ranging from 0.006 to 0.5 in 2001 and from 0.02 to 0.5 in 2010. In 2001, the vegetation from within 10 m of the motorway had systematically higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios than the soil samples, revealing the greater influence of historically accumulated petrol Pb in the soil relative to more recently deposited material on the vegetation. A similar effect was observed at the minor road, but only within 2 m of the road edge. At greater distances than 10 m from the motorway or 2 m from the minor roads, there was no apparent relationship between the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the soil and the vegetation. In 2010 there was less systematic difference

between the soil and vegetation ratios close to the road, with some of the soil samples having higher ratios, consistent with a relative decrease in petrol Pb contribution, and some of the vegetation samples having low ratios, indicative of deposition of redistributed petrol Pb. The average $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for the vegetation samples in 2001 and 2010 of 1.136 ± 0.008 and 1.137 ± 0.012 , respectively, revealed no systematic difference despite the intervening period of 9 years in which there had been no use of leaded petrol. Within the field, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for the vegetation were all lower than the typical Scottish geological value of approximately 1.17, implying persistence of previously deposited petrol Pb or contemporary deposition of Pb with a lower ratio. The latter process would be consistent with the suggestion by Bacon (2002) that incinerator ash with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the approximate range 1.14 to 1.15 could, in the post petrol Pb era, represent a significant component of atmospheric deposition. The absence of any relationship between the soil Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and those of the vegetation is also consistent with the conclusion of Bacon et al. (2005) that Pb in grass is derived from deposition rather than uptake from the soil.

3.3 Soil cores

The plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio against $^{208}\text{Pb}/^{207}\text{Pb}$ ratio for the four soil core samples (Figure 8) confirms that the data all lie on the petrol-industry tie line with the cores from the positions of the motorway transects having a greater proportion of petrol Pb than those from the vicinity of the minor road. Total Pb concentrations are plotted for the cores in Figure 9 along with petrol and non petrol concentrations calculated using the above binary mixture assumption. Cores 1 and 2 exhibited similar profiles for non petrol Pb with relatively small variations in the range 37 to 61 mg kg^{-1} . Maximum petrol Pb concentrations for these cores were observed from 0 to 10 cm, with concentrations in the range 66 to 81 mg kg^{-1} , but with lower

concentrations being detectable to the base of both cores. Resultant total Pb concentrations in the 0 to 10 cm depth ranged from 103 to 129 mg kg⁻¹, with trends paralleling those of petrol Pb. Core 3 had markedly higher concentrations of both petrol Pb (range 108 to 165 mg kg⁻¹) and non petrol Pb (434 mg kg⁻¹ at 0-5 cm to 678 mg kg⁻¹ at 25–30 cm). The total Pb concentration increased from 576 mg kg⁻¹ at 0–5 cm to 786 mg kg⁻¹ at 25-30 cm depth. These high concentrations were verified by independent analysis by FAAS and ICP-MS which were within 10% agreement. There is no obvious explanation for these high values but these data and the high concentration of Pb close to the road in Transect 4 (up to 703 mg kg⁻¹) clearly illustrate heterogeneously distributed, highly localised anthropogenic disturbance of the soil at these points within a few metres of the road. In contrast, core 4 had much lower concentrations, with petrol Pb in the range 2 to 9 mg kg⁻¹, non petrol Pb 37 to 76 mg kg⁻¹ and total Pb 39 to 84 mg kg⁻¹. Thus, petrol Pb was only dominant in the 0-10 cm sections of the cores from close to the motorway and industrial Pb was dominant in all other samples. Pb inventories (g m⁻²) for the four cores are presented in Table 3 and in order to provide an indication of regional levels of Pb in areas remote from roads and towns, data are also provided for a peat core from a hill farm at Carbeth in central Scotland ((NS 524 758) and two cores (core 1: sandy-loam; core 2: sandy-clay-loam) from a field at the Scottish Agricultural College, Auchincruive in South West Scotland (NS 385 227). The inventories for the cores from the study site, ranging from 25.1 to 260 g m⁻², are all substantially higher than those for the remote sites, with both petrol Pb (range 3.4 to 12.2 g m⁻²) and non petrol Pb (range 14.0 to 208 g m⁻²) being elevated relative to the remote sites. Petrol Pb constituted 43 % and 44 % of the total in the cores from close to the motorway. However, the lower contributions of 9% and 20% for the cores from close to the minor road were similar to that of 15% for Carbeth, from a position downwind of the Central Scotland industrial belt, but higher than that of 3% for Auchincruive, upwind of the industrial belt. The fact that the

inventory for core 3 is an order of magnitude greater than those of the other cores indicates a highly localised input of Pb at this location. Thus, the results for the cores are consistent with the conclusion from the transect studies that locally enhanced petrol Pb deposition is restricted to within 10 m of the motorway. The concentrations and inventories for the cores, along with those for the surface soils, reveal a heterogeneous distribution of both petrol and non petrol Pb in the soil of the study site.

4. Conclusions

The isotopic composition of Pb in all of the samples analysed (road dusts, soil and vegetation) was consistent with a binary mix of petrol Pb and industrial Pb, both shortly after cessation of use of leaded petrol and also a decade after cessation. The most obvious change over that decade was a significant decrease in Pb concentrations in road dust from a mean of 117 mg kg⁻¹ in 2001 to 14.2 mg kg⁻¹ in 2010. However, the percentage of lead in road dust accounted for by petrol Pb remained at about 40% for the motorway samples, but fell from about 50% to 20% or less for the samples from the minor roads. In contrast, there was no systematic decrease in Pb concentrations or change in isotopic composition in either surface soil or vegetation between 2001 and 2010.

Trends for the transects confirmed that Pb concentrations in soil and vegetation are locally enhanced around roads, but the isotopic analyses revealed that the local enhancement of petrol Pb is restricted to within 10 m of the motorway and 3 m of the minor road. At distances greater than these, non petrol sources make the dominant contribution to contaminant Pb levels. Different trends were observed in the distribution of petrol and non petrol Pb in soil with increasing distance from roads, consistent with historical inputs. In contrast, petrol Pb

and non petrol Pb in vegetation exhibited similar distributions in both 2001 and 2010, implying redistribution of both, with no discernible change in the process in the 10 years since cessation of sales of unleaded petrol. The lack of correlation between concentrations and isotope ratios in soil, and corresponding values for vegetation, supports the suggestion by Bacon et al. (2005) that Pb in grass is derived from deposition rather than uptake.

Despite the proximity to motorway and roads, non petrol Pb from historical, industrial and coal-burning emissions was the dominant component except for very limited areas in the immediate vicinity of roads.

The concentration trends for the vegetation and soil transects at the minor roads were compatible with the suggestion by Bacon (2002) of “traffic Pb” input, as distinct from “petrol Pb”, but there was no evidence of this in the motorway soil transects.

This study revealed a heterogeneous distribution of both petrol Pb and non petrol Pb, highlighting the difficulty in formulating an adequate sampling strategy to assess the distribution of Pb. Overall the study demonstrated that past inputs of both petrol and industrial Pb have persisted in surface soil and that redistribution processes have maintained levels in vegetation over the 10 year period since the cessation of use of leaded petrol.

5. Acknowledgements

Thanks are expressed to the UK Food Standards Agency for partial financial support of this research under contract number CO1030.

6. References

- Ajmone-Marsan F, Biasioli M, Kralj T, Grčman, Davidson CM, Hursthouse A S, Madrid L, Rodrigues S. Metals in particle-size fractions of the soils of five European cities. *Environ. Poll.* 2008;152:73-81.
- Bacon JR. Isotopic characterisation of lead deposited 1989 – 2001 at two upland Scottish locations. *J Environ Monitoring* 2002;4:291–299.
- Bacon JR, Hewitt IJ, Cooper P. Lead in grass in the Scottish uplands: deposition or uptake? *J Environ Monit* 2005;7:785-791.
- Cloy JM, Farmer JG, Graham MC, MacKenzie AB, Cook GT. Historical records of atmospheric Pb deposition in four Scottish ombrotrophic peat bogs: an isotopic comparison with other records from western Europe and Greenland. *Global Biogeochemical Cycles*, 2008;22 GB2016, doi:10.1029/2007GB003059.
- Chen F-Y, Jiang S-J. Determination of Hg and Pb in fuels by inductively coupled plasma mass spectrometry using flow injection chemical vapour generation. *Anal Sci* 2009;25:1471-1476.
- Erel Y, Veron A, Halicz K. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotope ratios. *Geochim Cosmochim Acta* 1997;61:4495–4505.
- Farmer JG, Lyon TDB. Lead in Glasgow street dirt and soil. *Sci Total Environ* 1977;8:89–93.

Farmer JG, Eades LJ, Graham MC. The lead content and isotopic composition of British coals and their implications for past and present releases of lead to the UK environment. *Environ Geochem Health* 1999;21:257–272.

Farmer JG, Eades LJ, MacKenzie AB, Kirika A, Bailey-Watts TE. Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. *Environ Sci Technol* 1996;30:3080-3083.

Farmer JG, Eades LJ, Graham MC, Bacon JR. The changing nature of the $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratio of lead in rainwater, atmospheric particulates, pine needles and leaded petrol in Scotland. *Journal of Environmental Monitoring* 2000;2:49–57.

Farmer JG, Graham MC, Bacon JR, Dunn SM, Vinogradoff S, MacKenzie AB. Isotopic characterisation of the historical lead deposition record at Glensaugh, an organic-rich, upland catchment in rural N.E. Scotland. *Sci Total Environ* 2005;346:121 – 137.

Farmer JG, Graham MC, Yafa C, Cloy JM, Freeman AJ and MacKenzie AB. Use of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to investigate the surface integrity of peat cores used to study recent depositional history and geochemical behaviour of inorganic elements in peat bogs. *Global and Planetary Change* 2006; 53:240 - 248.

Gibson MJ, Farmer JG. A survey of trace metal contamination in Glasgow urban soils. *Proc Int Conf. Heavy Metals in the Environment*. 1985. CEP Consultants Ltd. Edinburgh. Vol 2, 1141-1144.

Hansmann W, Köppel V. Lead-isotopes as tracers of pollutants in soils. *Chemical Geology* 2000;171:123–144.

Harrison RM, Johnston WR. Deposition fluxes of lead, cadmium, copper and polynuclear aromatic hydrocarbons (PAH) on the verges of a major highway. *Sci Total Environ* 1985;46:121 – 135.

Hjortenkrans D, Bergbäck B, Häggerud A. New metal emission patterns in road traffic environments. *Environ Monit Assess* 2006;117:85-98.

Klaminder J, Bindler R, Emteryd O, Renberg I. Uptake and recycling of lead by boreal forest plants: quantitative estimates from a site in northern Sweden. *Geochim Cosmochim Acta*.2005;69;2485–2496.

Kummer U, Pacyna J, Pactna E, Friedrich R. Assessment of heavy metal releases from the use phase of road transport in Europe. *Atmos Environ*2009;43:640-647.

Legret M, Pagotto C. Heavy metal deposition and soil pollution along two major rural highways. *Environmental Technology* 2006;27,247–254.

Massadeh AM, Snook RD. Determination of Pb and Cd in road dusts over the period in which Pb was removed from petrol in the UK. *J Environ Monitoring* 2002;4:567–572.

Nageotte SM, Day JP. Lead concentrations and isotope ratios in street dust determined by electrothermal atomic absorption spectrometry and inductively coupled plasma mass spectrometry. *The Analyst* 1998;123:59–62.

MacKenzie AB, Farmer JG, Sugden CL. Isotopic evidence for the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats. *Science of the Total Environment* 1997;203:115–117.

MacKenzie AB, Logan EM, Cook GT, Pulford ID. Distribution, inventories and isotopic composition of lead in ^{210}Pb -dated peat cores from contrasting biogeochemical environments: implications for lead mobility. *Sci Total Environ* 1998;223: 25-35.

Metwaly HAH. A study of groundwater contamination and bioremediation treatment using natural soil and vegetation. Ph. D. Thesis, University of Glasgow, 1999.

Nriagu JO Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 1988;333:134-139.

Nriagu JO A global assessment of natural sources of atmospheric trace metals. *Nature* 1989;338:47-49.

Nriagu JO 1990. The rise and fall of leaded gasoline. *Sci Total Environ* 1990;92:13-28.

Novak M, Emmanuel S, Vile MA, Erel Y, Véron A, Pačes T, Wieder RK, Vaněček M, Štěpápanová M, Břizová E, Hovorka J. Origin of lead in eight European peat bogs

determined from isotope ratios, strengths and operation times of regional pollution sources. *Environ Sci Technol* 2003;37:437–445.

Preciado, H. F., Li, L. Y. and Weis, D. Investigation of past and present multi-metal input along two highways of British Columbia, Canada, using lead isotope signatures. *Water, Air and Soil Pollution*, 2007;184, 127 – 139

Ragg J M, Shipley BM, Duncan NA, Biddy JS, Merrilees DW. Map sheet 31, Airdrie, Soil Survey of Scotland. The Macaulay Institute for Soil Research, Aberdeen. 1976.

Robertson D. Taylor KG. Temporal variability of metal contamination in urban road deposited sediment in Manchester, UK: implications for urban pollution monitoring. *Water, Air Soil Pollution* 2007;186:209–220.

Shotyk W, Weiss D, Heisterkamp M, Cheburkin AK, Appleby PG, Adams FC. New peat bog record of atmospheric lead pollution in Switzerland: Pb concentrations, enrichment factors, isotopic composition and organolead species. *Environ Sci Technol* 2002;36:3893–3900.

Steinnes E, Sjøbak TE, Donisa C, Bränvall M-L. Quantification of pollutant lead in forest soils. *Soil Sci Soc America J* 2005;69:1399 – 1404.

Sugden CL. Isotopic studies of the environmental chemistry of lead. PhD thesis, University of Edinburgh 1993. pp 252.

Sugden CL, Farmer JG, MacKenzie A B. Isotopic ratios of lead in contemporary environmental materials from Scotland. *Environ Geochem Health* 1993;15:59–65.

Teutsch N, Erel Y, Halocz, L, Banin A. Distribution of natural and anthropogenic lead in Mediterranean soils. *Geochim Cosmochim Acta* 2001;65:2853–2864

Watmough, S. A. and Hutchinson, T. C. The quantification and distribution of pollution Pb at a woodland in rural south central Ontario, Canada. *Environ Pollut* 2004;128: 419–428.

www.scotlandtransport.gov.uk/road/traffic-count/map-application (accessed 27 April 2011)

Yesilonis ID, Pouyat RV, Neerchal NK. Spatial distribution of metals in soil in Baltimore, Maryland: role of native parent material, proximity to major roads, housing age and screening guidelines. *Environmental Pollution* 2008;156:723–731.

Young TM, Heeraman DA, Sirin G, Ashbaugh LL. Resuspension of soil as a source of airborne lead near industrial facilities and highways. *Environ Sci Technol* 2002;36:2484-2490.

Zehetner, F., Rosenfellner, U., Mentler, A. and Gerzabek, M. H. 2008. Distribution of road salt residues, heavy metals and polycyclic aromatic hydrocarbons across a highway-forest interface. *Water, Air, Soil Pollut.* 2009;198: 125-132.

Zupančič N. Lead contamination in the roadside soils of Slovenia. *Environ Geochem Health* 1999;21:37 – 70.

Transect position	2001 samples				2010 samples			
	Pb mg kg ⁻¹	$\frac{^{206}\text{Pb}}{^{207}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{207}\text{Pb}}$	Petrol Pb (%)	Pb mg kg ⁻¹	$\frac{^{206}\text{Pb}}{^{207}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{207}\text{Pb}}$	Petrol Pb (%)
T1/T2	120	1.137	2.422	38	18.5	1.132	2.416	43
T3	117	1.125	2.410	51	10.8	1.153	2.440	22
T4	113	1.127	2.399	49	13.2	1.162	2.455	13

Table 1. Pb concentrations (mg kg⁻¹), $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios and calculated % petrol Pb for road dust samples from the positions of transects T1/T2, T3 and T4.

Transect and sample number	Distance (m)	Soil Pb mg kg ⁻¹ 2001	Soil Pb mg kg ⁻¹ 2010	Soil ²⁰⁶ Pb/ ²⁰⁷ Pb 2001	Soil ²⁰⁶ Pb/ ²⁰⁷ Pb 2010	Veg Pb mg kg ⁻¹ 2001	Veg Pb mg kg ⁻¹ 2010	Veg ²⁰⁶ Pb/ ²⁰⁷ Pb 2001	Veg ²⁰⁶ Pb/ ²⁰⁷ Pb 2010	
T1	1	0.1	194	115	1.107	1.127	37.6	39.7	1.119	1.131
	2	1	351	59.3	1.094	1.165	35	26.6	1.118	1.116
	3	2	388	238	1.091	1.106	19.9	22.1	1.125	1.112
	4	4	165	282	1.113	1.101	5.0	6.8	1.134	1.128
	5	10	108	83.6	1.123	1.123	3.9	32.4	1.141	1.131
	6	20	62.2	119	1.141	1.141	1.7	2.9	1.132	1.138
	7	30	101	189	1.158	1.101	3.7	19.5	1.150	1.157
	8	50	181	73	1.159	1.164	2.0		1.157	
T2	1	0.2	207	97.5	1.108	1.126	24.9	29.7	1.130	1.128
	2	1	286	136	1.097	1.119	13.2	34.4	1.131	1.130
	3	4	82.4	203	1.128	1.097	14.2	11.4	1.134	1.104
	4	10	156	145	1.130	1.117	6.5	7.4	1.136	1.118
	5	20	119	68.8	1.130	1.134	3.6	5.5	1.137	1.133
	6	30	172	76.1	1.163	1.157	4.7	6.6	1.141	1.149
	7	50	269	80.3	1.163	1.163	4.5		1.138	
T3	1	0.2	106	63	1.118	1.118	53.1	31.1	1.130	1.138
	2	1	94.7	176	1.124	1.101	21.0	18.1	1.131	1.133
	3	3	92.3	260	1.147	1.150	5.7	7.8	1.131	1.143
	4	5	139	156	1.147	1.145	6.9	4.1	1.135	1.137
	5	10	120	217	1.159	1.164	4.1	5.0	1.144	1.148
	6	20	85.6	210	1.154	1.157	4.4	8.9	1.139	1.150
	7	30	58	170	1.134	1.165	2.9	6.6	1.140	1.156
	8	50	49.1	177	1.143	1.167				
T4	1	0.6	703	276	1.096	1.113	4.3	23.0	1.134	1.122
	2	1.5	388	140	1.111	1.124	4.8	6.0	1.139	1.126
	3	3	453	107	1.130	1.142	2.6	5.8	1.134	1.137
	4	5	251	92.9	1.133	1.153	10.5	6.5	1.140	1.149
	5	10	195	105	1.152	1.155	4.4	4.3	1.141	1.153
	6	20	126	71.1	1.160	1.151	4.2	12.6	1.140	1.155
	7	30	99.8	93.4	1.163	1.155	2.6	8.9	1.142	1.156
	8	50	94.7	88.0	1.165	1.160	4.4	11.7	1.148	1.152

Table 2. Pb concentrations and ²⁰⁶Pb/²⁰⁷Pb ratios for soil and vegetation for transects T1 and T2 adjacent to the motorway and T3 and T4 adjacent to the minor road.

Core	Total Pb	Petrol Pb		Non petrol Pb	
		Inventory	% of total	Inventory	% of total
1	25.1	11.1	44	14.0	56
2	28.3	12.2	43	16.1	57
3	260	52	20	208	80
4	36.7	3.4	9	33.3	91
Carbeth	11.9	1.8	15	10.1	85
Auchincruive 1	10.2	0.3	3	9.9	93
Auchincruive 2	11.5	0.3	3	11.2	93

Table 3. Total Pb inventories (g m^{-2}) and calculated petrol and non petrol inventories for soil cores 1 - 4 from the study site and for comparison, data for cores from Carbeth and Auchincruive.

Figure Captions

Figure 1. Study site location

Figure 2. Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio against $^{208}\text{Pb}/^{207}\text{Pb}$ ratio for road dust samples from the positions of transects T1, T2, T3 and T4. (01) indicates 2001 samples (10) indicates 2010 samples.

Figure 3. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$ for soil samples from (a) T1, (b) T2, (c) T3 and (d) T4 (★ petrol Pb, ♣ Leadhills ore; ✖ Average Scottish coal; closed circles 2001 samples, open circles 2010 samples; sample numbers as indicated in Table 1).

Figure 4. Mean Pb concentrations and calculated petrol and non petrol Pb concentrations for soil samples from (a) the motorway transects and (b) the minor road transects.

Figure 5. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$ for vegetation samples from (a) T1, (b) T2, (c) T3 and (d) T4 (★ petrol Pb, ♣ Leadhills ore; ✖ Average Scottish coal ; closed circles 2001 samples, open circles 2010 samples; sample numbers as indicated in Table 1).

Figure 6. Variations in mean Pb concentrations in vegetation with distance from the motorway: (a) total Pb, (b) petrol Pb and (c) non petrol Pb

Figure 7. Variations in mean Pb concentrations in vegetation with distance from the minor roads: (a) total Pb, (b) petrol Pb and (c) non petrol Pb

Figure 8. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$ for soil core samples from the positions of transects T1 (Core 1), T2 (core 2), T3 (core 3) and T4 (core 4). Labels indicate core number followed by depth: 1 (0-5 cm), 2 (5-10 cm) 3 (10 – 15 cm), 4 (15 -20 cm), 5 (20-25 cm) and 6 (25-30 cm) (★ petrol Pb, ♣ Leadhills ore; ✖ Average Scottish coal).

Figure 9. Pb concentration profiles for soil cores collected at 7.5 m from the road at the positions of (a) T1, (b) T2, (c) T3 and (d) T4. (Total concentration ■; Petrol Pb ●; non petrol Pb ○).

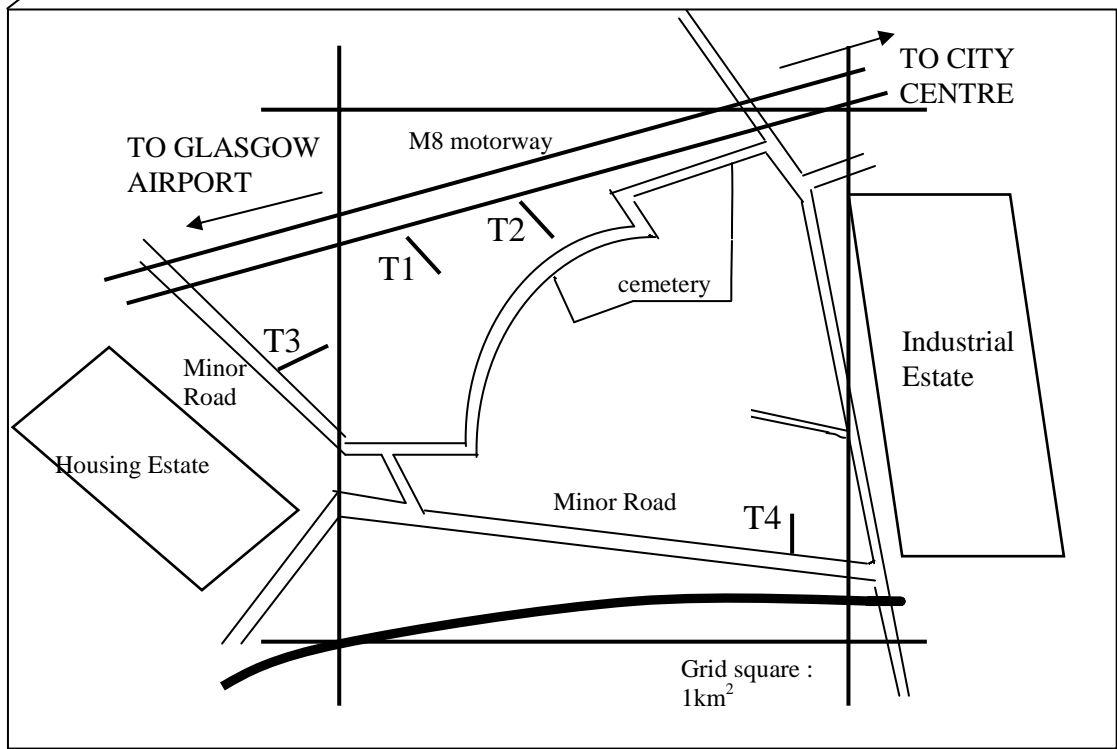
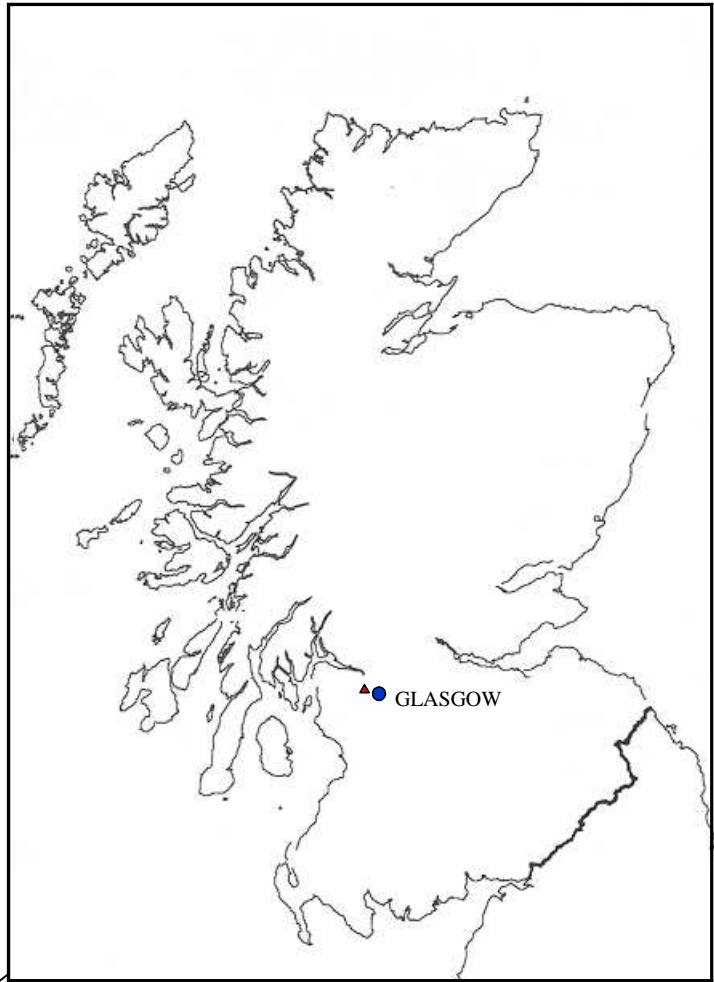


Figure 1. Study site location

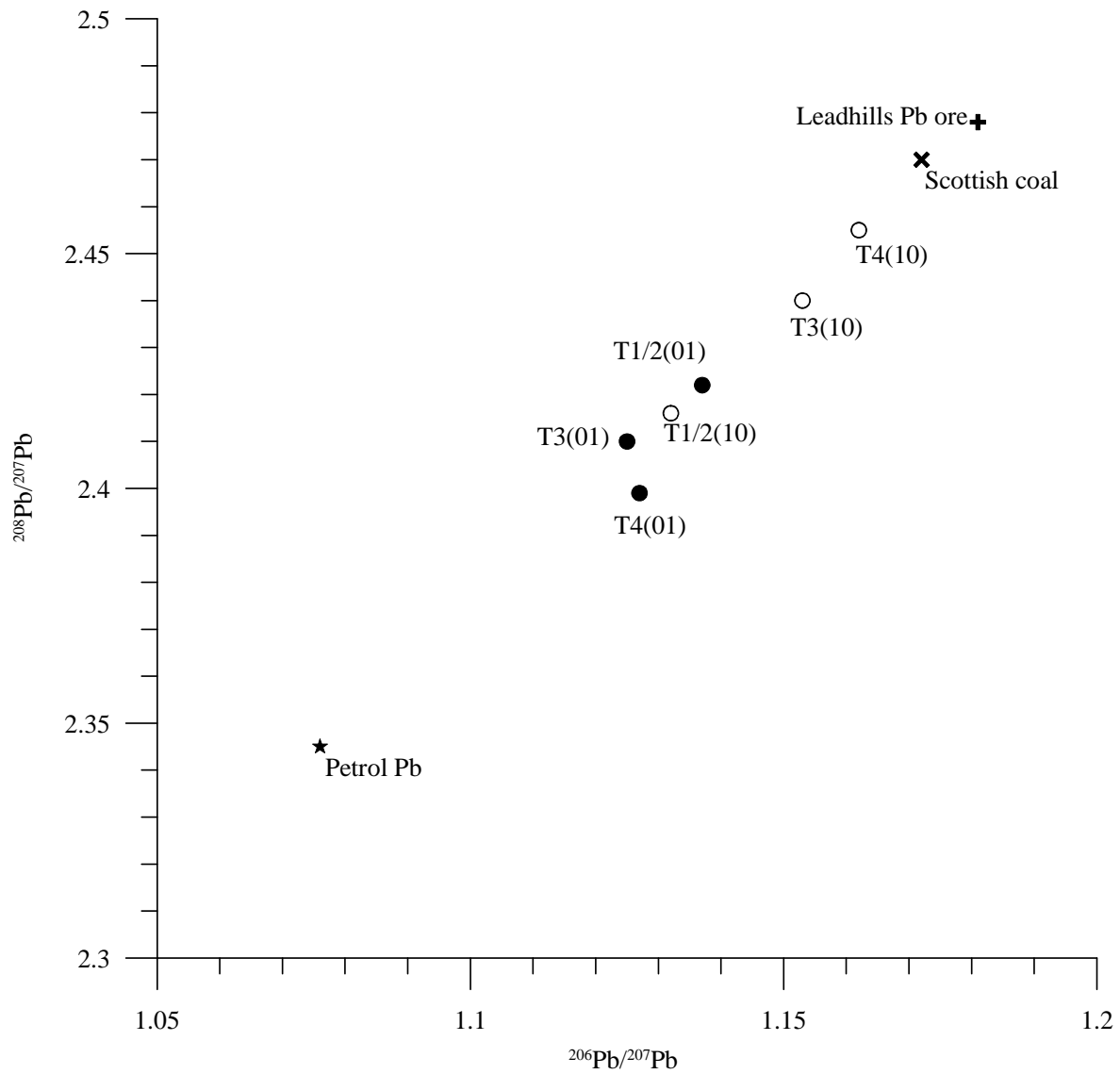


Figure 2. Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio against $^{208}\text{Pb}/^{207}\text{Pb}$ ratio for road dust samples from the positions of transects T1, T2, T3 and T4. (01) indicates 2001 samples (\bullet) and (10) indicates 2010 samples (\circ).

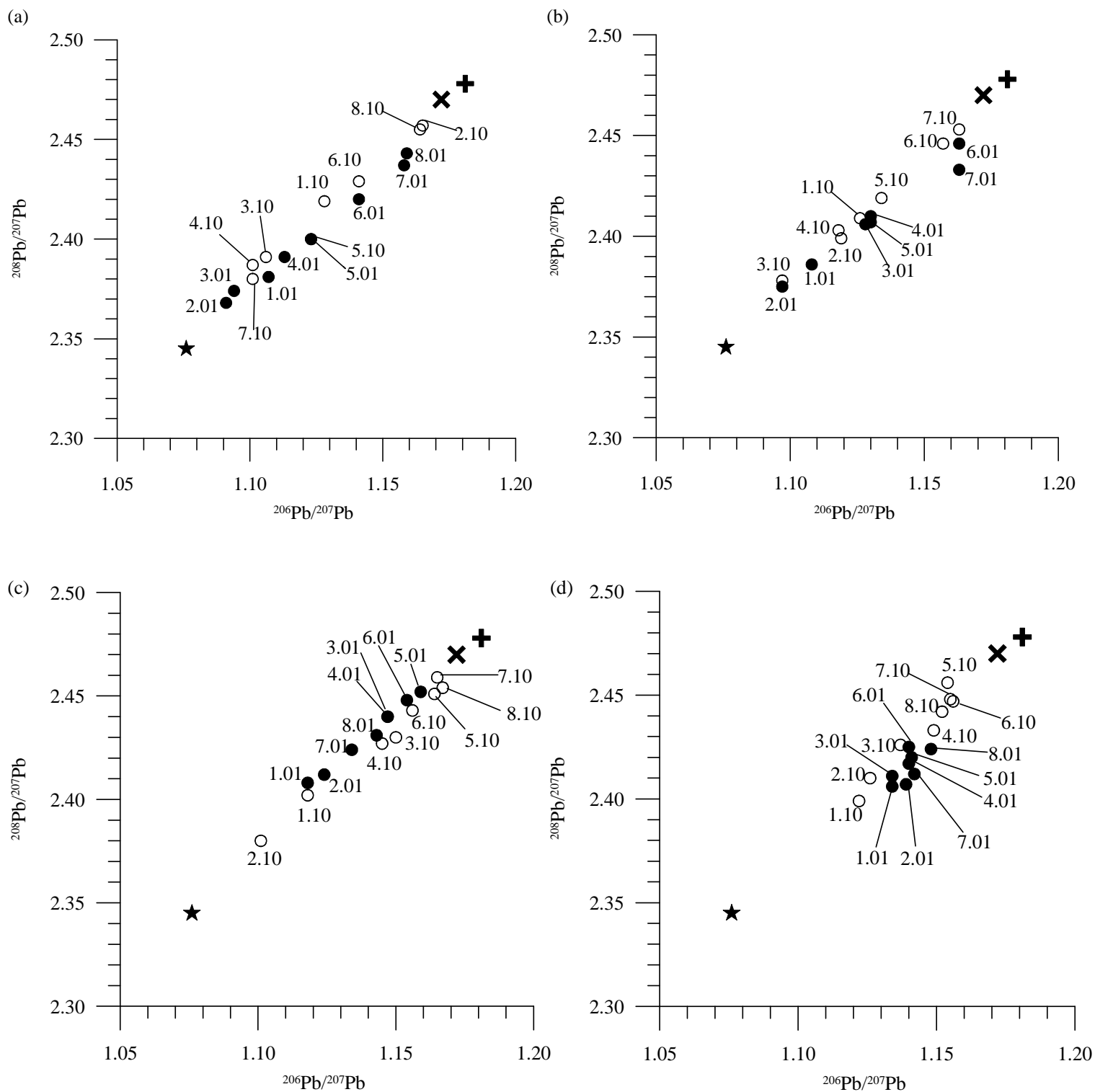


Figure 3. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$ for soil samples from (a) T1, (b) T2, (c) T3 and (d) T4 (★ petrol Pb, + Leadhills ore; ✕ Average Scottish coal; closed circles 2001 samples, open circles 2010 samples; sample numbers as indicated in Table 1).

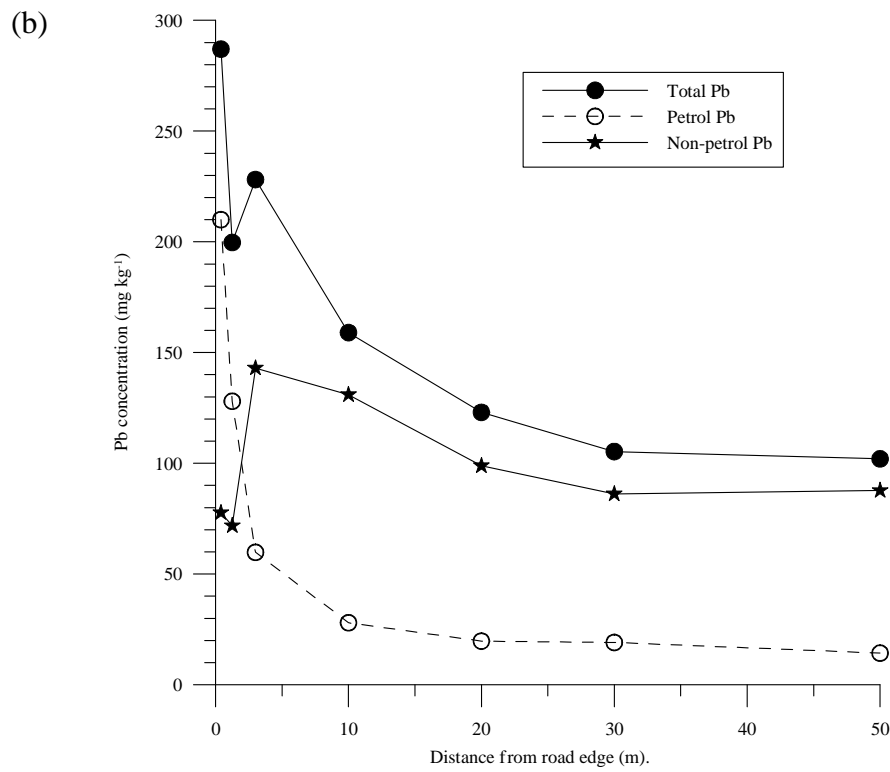
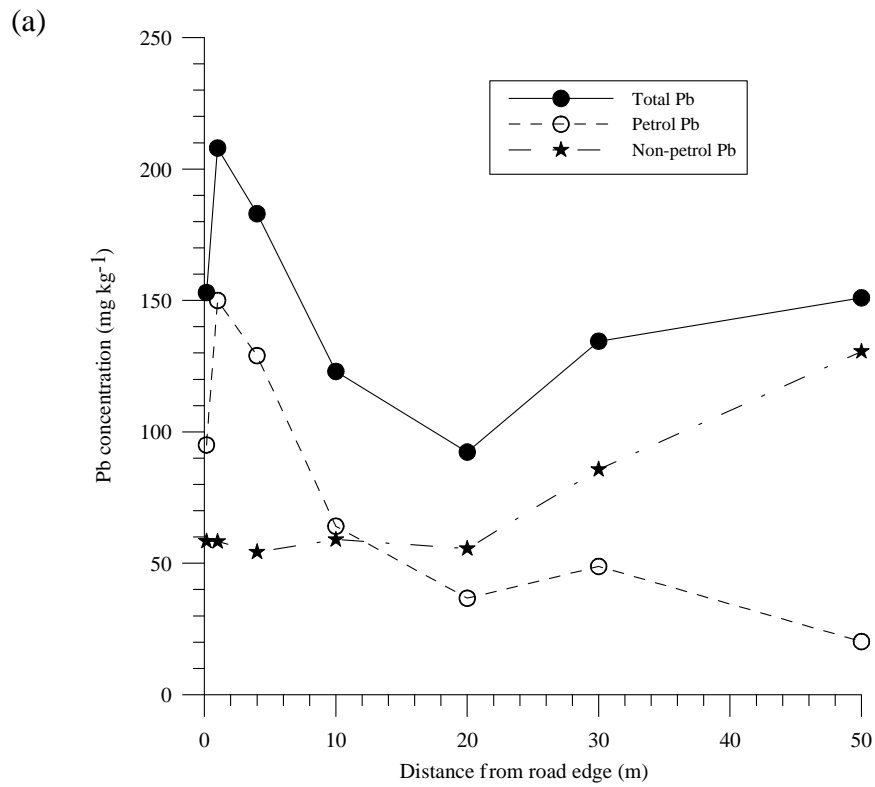


Figure 4. Mean Pb concentrations and calculated petrol and non petrol Pb concentrations for soil samples from (a) the motorway transects and (b) the minor road transects.

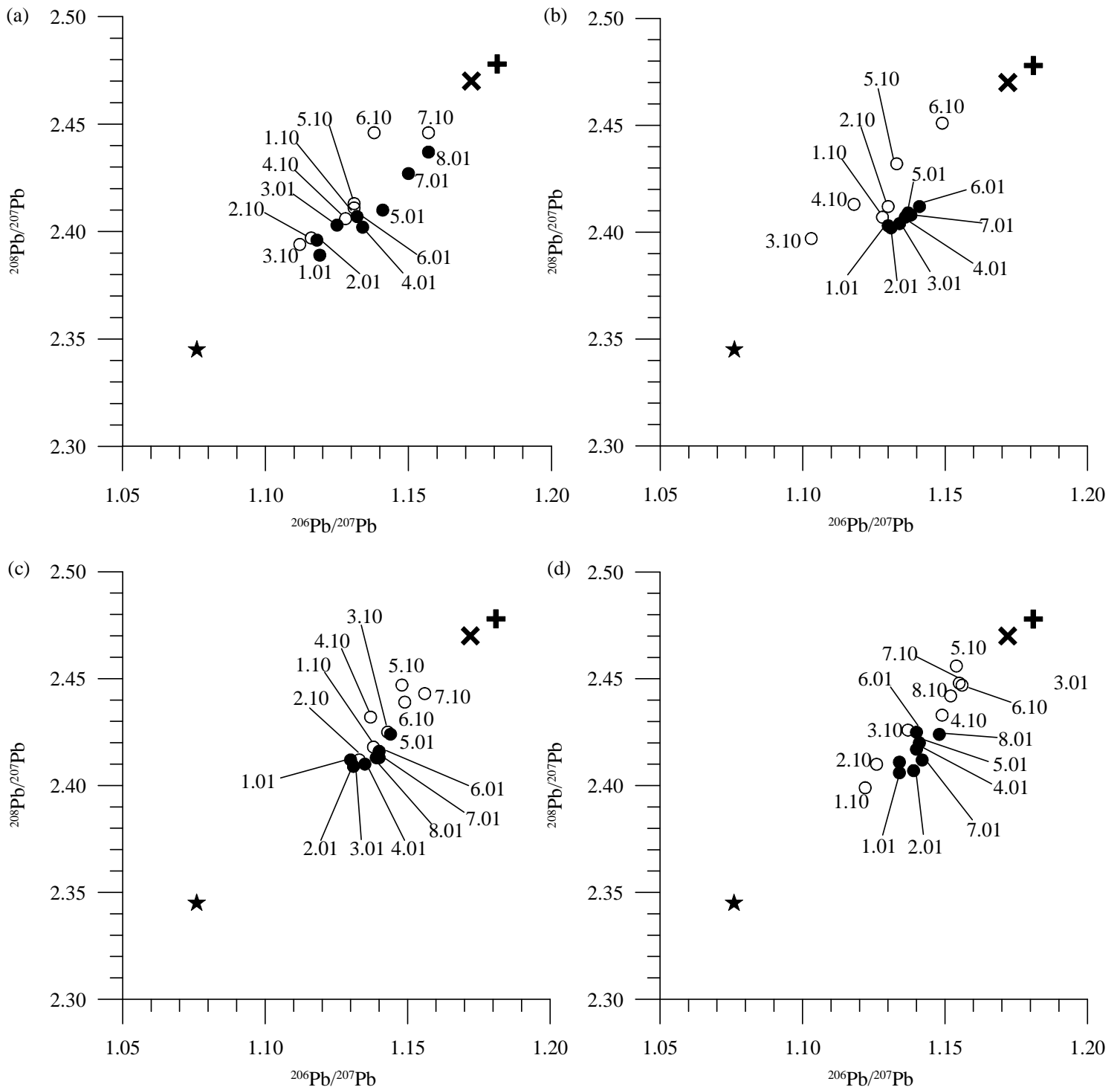


Figure 5. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$ for vegetation samples from (a) T1, (b) T2, (c) T3 and (d) T4 (★ petrol Pb, + Leadhills ore; x Average Scottish coal; closed circles 2001 samples, open circles 2010 samples; sample numbers as indicated in Table 1).

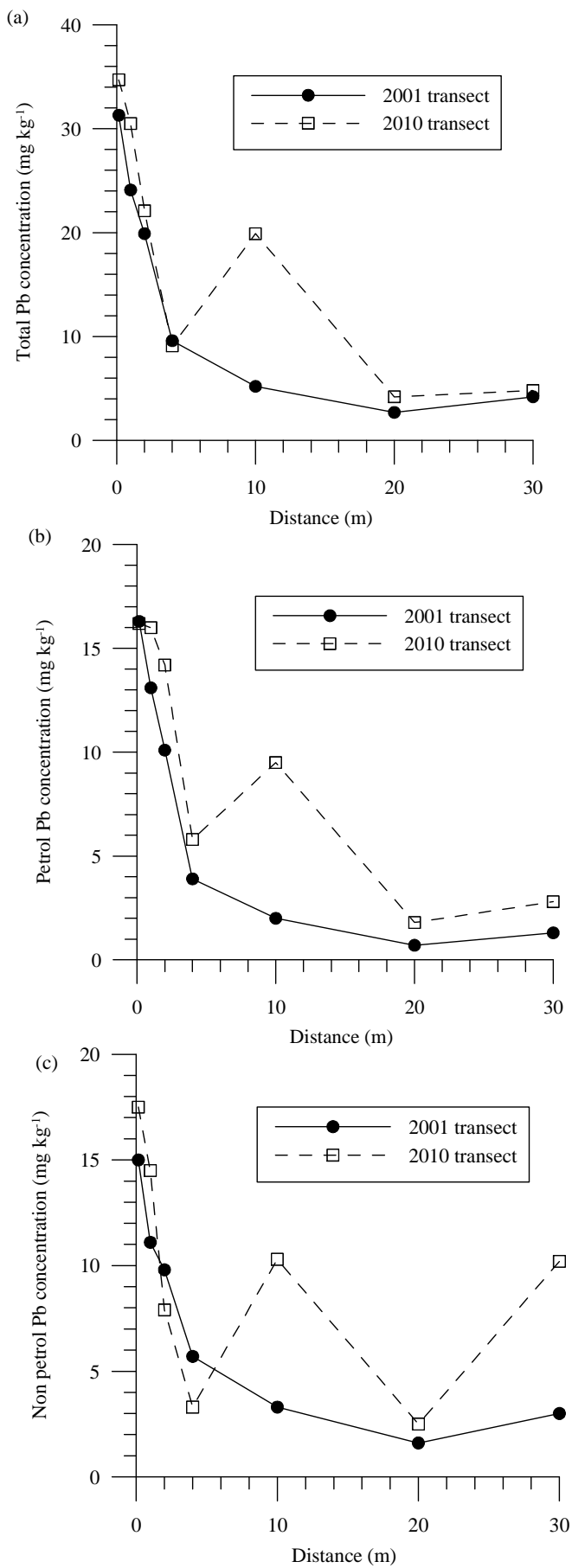


Figure 6. Variations in mean Pb concentrations in vegetation with distance from the motorway: (a) total Pb, (b) petrol Pb and (c) non petrol Pb

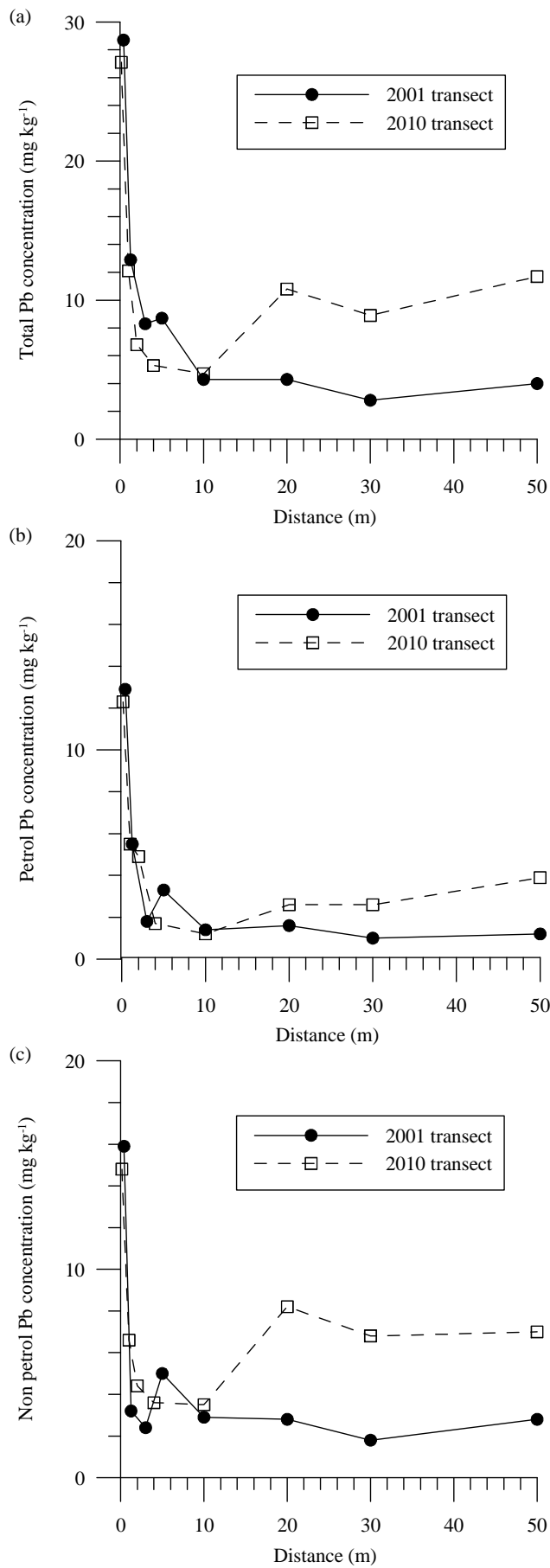


Figure 7. Variations in mean Pb concentrations in vegetation with distance from the minor roads: (a) total Pb, (b) petrol Pb and (c) non petrol Pb

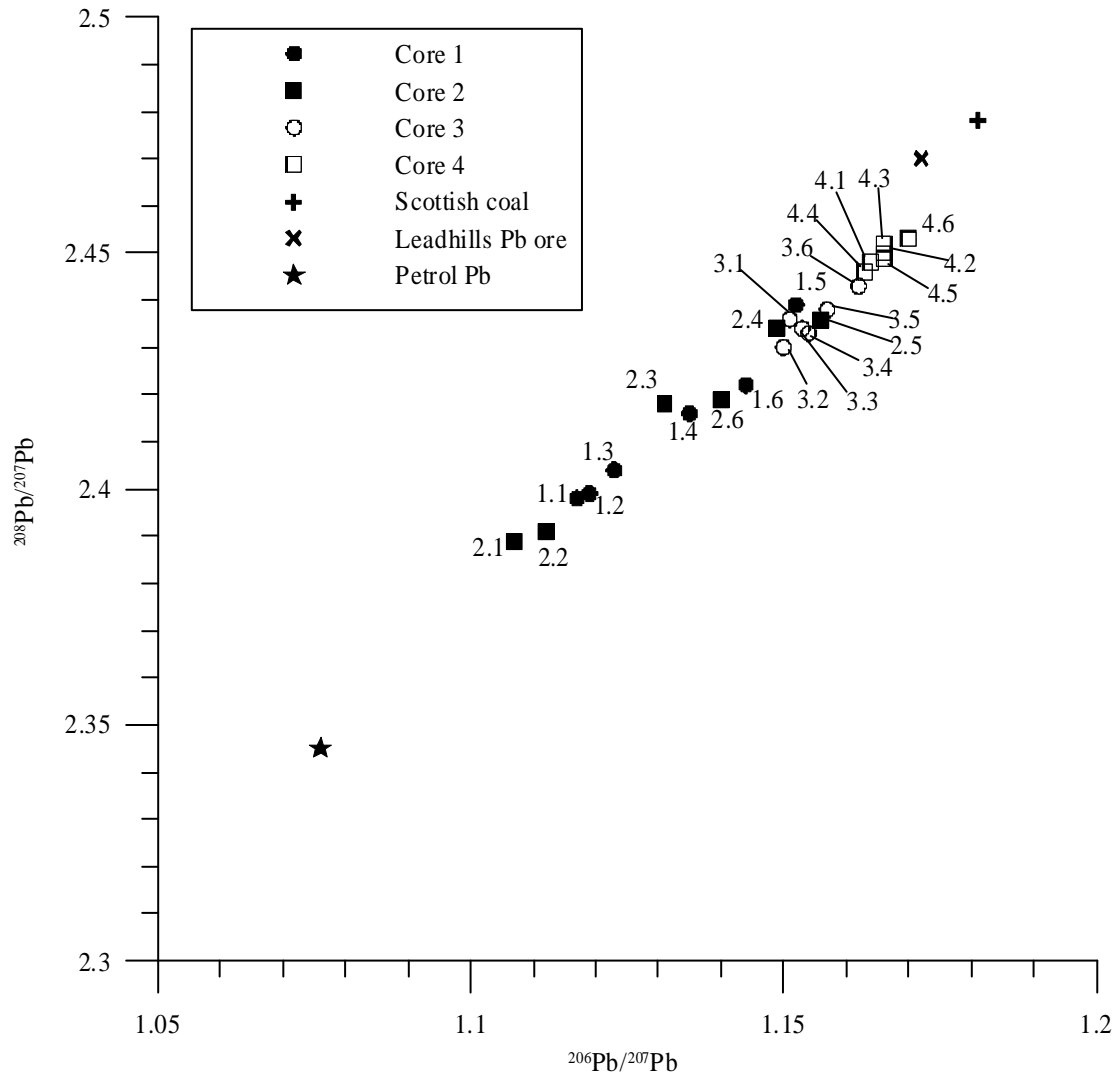


Figure 8. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$ for soil core samples from the positions of transects T1 (Core 1), T2 (core 2), T3 (core 3) and T4 (core 4). Labels indicate core number followed by depth: 1 (0-5 cm), 2 (5-10 cm) 3 (10 – 15 cm), 4 (15 -20 cm), 5 (20-25 cm) and 6 (25-30 cm) (★petrol Pb, + Leadhills ore; x Average Scottish coal).

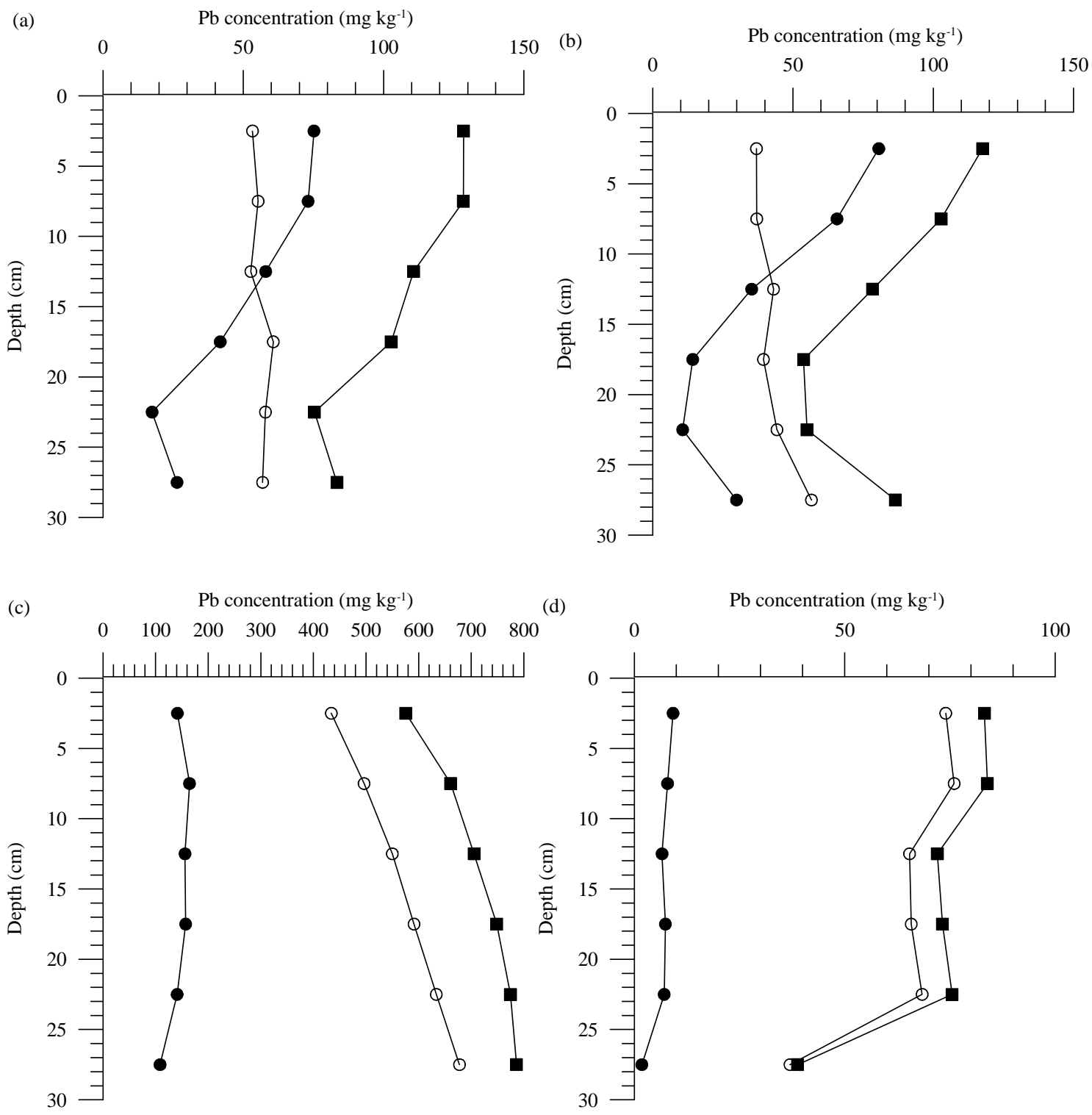


Figure 9. Pb concentration profiles for soil cores collected at 7.5 m from the road at the positions of (a) T1, (b) T2, (c) T3 and (d) T4 (Total concentration ■; Petrol Pb ●; non petrol Pb ○).