Sources and Background Concentrations of Lead

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Presentation Overview

1. Lead – the basics
2. Sources of lead
   i. Natural
   ii. Anthropogenic
3. But what is *natural*?
4. The need to consider “background”
5. Background levels of lead
   i. National\ Regional
   ii. Urban\ Rural comparisons
   iii. Determining a background concentration?
6. A local authority perspective on lead
7. Conclusion

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Lead – The basics

- Lead is a common heavy metal with the symbol Pb from the Latin word *plumbum* for soft metal.
- It has two oxidation states, +2 and +4, with +2 being the most common.
- Four naturally occurring stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb.
- Lead has been commonly used for thousands of years because it is widespread, easy to extract, easy to work with, is highly malleable and ductile, easy to smelt and is resistant to corrosion.
- The largest pre-industrial producer of lead were the Romans, with an estimated output per annum of 80,000t.

Source: http://en.wikipedia.org/wiki/Lead

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Lead – The basics

-The mobility of Pb in the environment is limited, mainly by the low solubility of its sulphate and carbonate compounds.

- Pb also has a strong affinity for sorption by secondary iron and manganese oxides and by humic organic matter.

- Pb is biologically non-essential and is well known for its toxic properties

- Environmental lead – inorganic (e.g. PbS, PbO, $PbSO_4$)
- Organic lead (e.g. tetraethyl lead $(CH_3CH_2)_4Pb$) - occupational exposure

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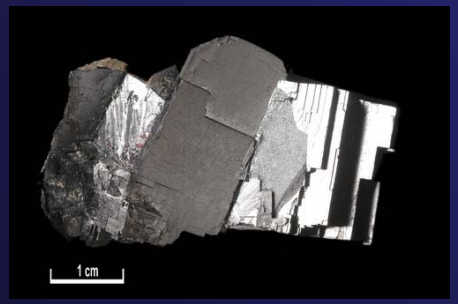
Natural sources of lead; minerals

- Chalcophile metallic element forming several important minerals:

-Galena (PbS)



-Anglesite ($PbSO_4$)

- Cerrussite ($PbCO_3$)

Source: webmineral.com/specimens/photos/Cerrussite

-Minium (Pb_3O_4)

Source: webmineral.com/specimens/photos/Minium

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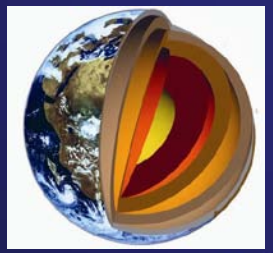
Natural sources of lead; trace levels

- Lead is also present at trace levels in a range of other minerals:
    - e.g. K-feldspar, plagioclase, mica, zircon and magnetite.

- Pb^{2+} ion intermediate in size, replaces K^{+} and Ca^{2+} in K-feldspar, micas etc… therefore:
    -Pb enriched in felsic rocks (light coloured, silica rich igneous) relative to mafic rocks (dark coloured, pyroxene and olivine rich)

Crustal abundance	13 mg kg^{-1} Pb
Basalt	6 mg kg^{-1} Pb
Granite	15 – 19 mg kg^{-1} Pb



-Lead is mobile in late-stage magmatic processes

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Natural sources of lead;
Sedimentary rocks and sediment

Limestone	*Ca.* 5 mg kg^{-1} Pb
Quartzitic sandstone	6 mg kg^{-1} Pb
Shale & Greywacke	23 mg kg^{-1} Pb

- Sedimentary rocks with the highest Pb concentrations are black shales, reflecting the affinity of Pb for organic matter

-In stream sediments around 35% of Pb occurs in the sand fraction but the majority in the silt and clay fractions

-Due to association with kaolinite & mica, and secondary iron oxide precipitates

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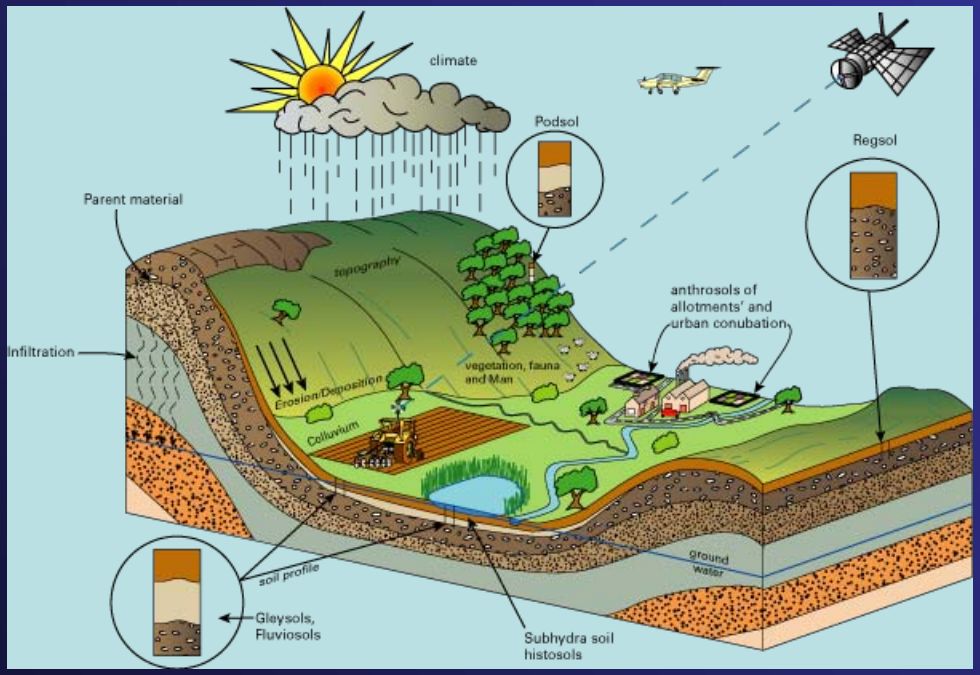
Natural sources of lead; in soil

- In soil, Pb concentration is linked to geological parent material

-Species varies with soil type

-Mainly associated with clay minerals, Mn Oxides, Fe and Al hydroxides and organic matter



-Can concentrate in Ca carbonates particles or phosphate concentrations

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Anthropogenic sources of lead

- Urban surveys of soils have reported lead levels significantly higher than the surrounding rural areas
- Lead is considered to be one of the most immobile elements in soil
- Soil therefore acts as a significant sink for anthropogenic lead

Lead Mining in the UK

- Since the Iron Age (Mendip Hills)
- Gained momentum in early 1800s
- By1950s mainly secondary processing
- Environmental lead emissions from mining, milling, haulage, smelting, refining

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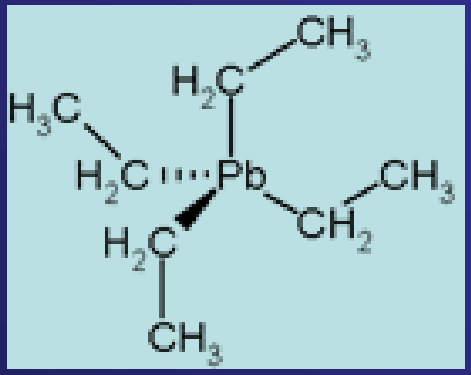
Anthropogenic sources of lead

Atmospheric deposition

- Deposition of inorganic lead emitted to the atmosphere is the major contributor of environmental lead



1. Vehicle emissions – leaded petrol
   - Tetraethyl lead $(CH_3CH_2)_4Pb$
   - Anti-knock fuel additive
   - 5-star petrol 0.8g/L
   - At its height (1973) 380,000t used worldwide
   - 70% entered the environment immediately after combustion
   - Limit of 0.15g/L by 31 December 1985
   - Phased out by 1 January 2000
   - Main area of deposition within 30m of the road

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Anthropogenic sources of lead

Atmospheric deposition

2. Industrial emissions
- Processing of alkyllead additives
- Metal mining, smelting and refining operations
- Primary lead (ore)
- Secondary lead (scrap)
- Localised elevated levels, depending on stack height

3. Combustion of fossil fuels
- Combustion of coal (~25mg/kg Pb)
- Combustion of oil (~0.3mg/kg Pb)

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Anthropogenic sources of lead

Chemical Industry

http://en.wikipedia.org/wiki/Lead_paint

1.Paint

- Used as paint pigments
- White lead (lead carbonate). Internal and external use, over wood and metal. Used on doors, radiators, pipes, plaster walls.
- Red lead (lead tetroxide). Used in the painting of steel as an anti-corrosive paint.
- Chrome yellow (lead(II) chromate). Yellow pigment.

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Anthropogenic sources of lead

Chemical Industry

1.Paint
- Weathers over time
- Estimated that 50% is removed in 7 years
- Heavy lead contamination reported in the soil and dust of houses painted with lead paints

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Anthropogenic sources of lead

Chemical Industry

2. Insecticides
- Lead arsenate $PbHAsO_4$
- Used against the codling moth
- Used up until 1966

Source: http://vtpp.ext.vt.edu/

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Anthropogenic sources of lead

Chemical Industry

3. Fertilizers

- Superphosphate applied in vast quantities (trace Pb levels of 7-92 mg/kg)
- Steel industry wastes (recycled into fertilizers for their high levels of zinc)

4. Lime

- Limestone, often crushed and applied to soil to neutralise soil acidity, is known to contain lead (~9 mg/kg)

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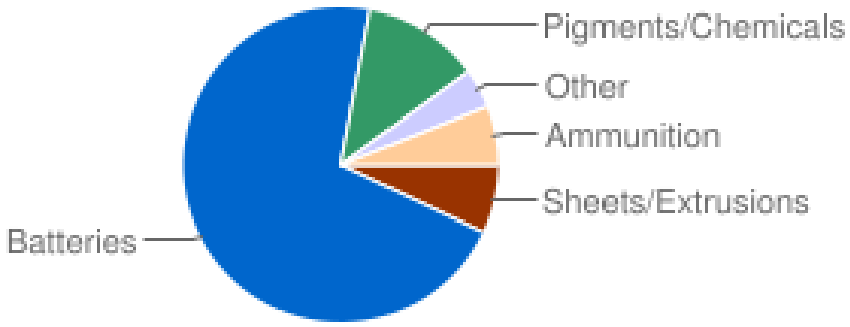
Anthropogenic sources of lead

Miscellaneous Industry



Industry	%
Batteries	71
Pigments/Chemicals	12
Sheets/Extrusions	7
Ammunition	6
Other	4
Total	100

Source: Standard CIB Global Research www.standardbank.co.za

1. Lead batteries

- Largest worldwide consumption of lead
- Auto industry (lead-acid batteries)
- Metallic lead and lead oxides
- Secondary lead (battery recycling)

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Anthropogenic sources of lead

Miscellaneous Industry

2. Building, construction, manufacturing
- Resistant to corrosion
- Roofing, flashings, sound insulation, wall cladding
- Plumbing
- Printing (process and inks)
- Electronic circuit boards
- Radiation shielding
- Solder
- Welding

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Anthropogenic sources of lead

Miscellaneous Industry

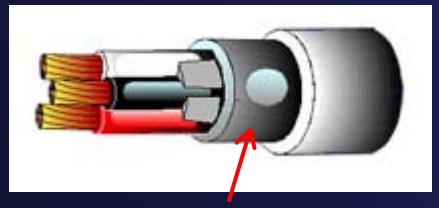
3. Ammunition
 - Lead shot
 - Rifle ranges

Lead shot

4. Lead glass and glazes
 - Lead glass: 18-40% PbO
 - Lead crystal: 24-35% PbO
 - Lead glazes: up to 60% PbO

Lead crystal

5. Cable sheathing
 - Underground cables & power distribution of 10kV or higher
 - Alloyed and unalloyed lead



Cable sheathing

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Anthropogenic sources of lead

Miscellaneous Industry

6. Lead alloys
 - Lead forms alloys readily and has been used in solder, bearing metals, brasses, collapsible tubes, plates, ornaments, cutlery
 - Babbit, pewter, solder, terne, cerrosafe, rose metal, Wood's metal, molybdochalkos

Waste disposal

1. Mine dumps
2. Processing waste
3. Smelter emissions
4. Ship breaking
5. Municipal incinerators
6. Sewage sludge application

Pewter vase

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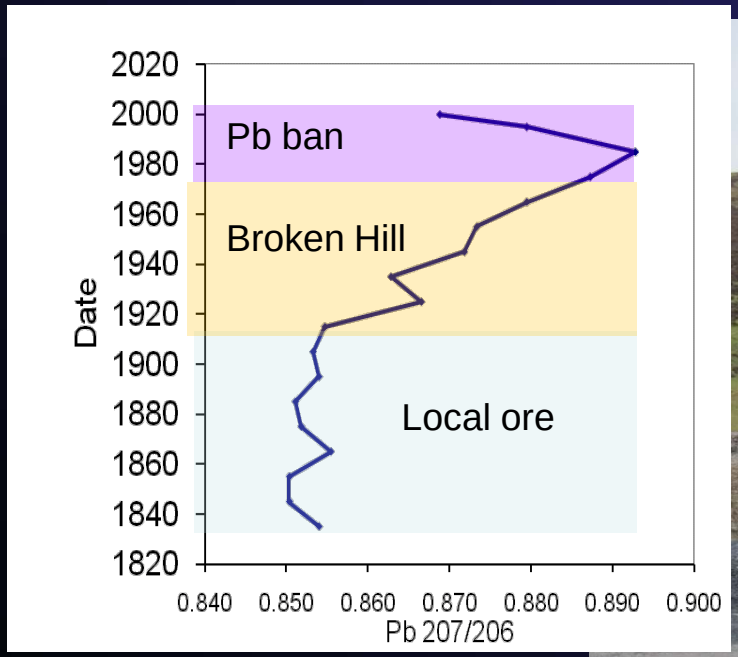
But, what is *natural*?

- Man has been altering the environment for thousands of years

- Lead isotopes can help us distinguish between natural and anthropogenic sources



Her
show pe
ratios have varied over
the last two centuries
as a consequence of
changing source(s) of
Pb ore used

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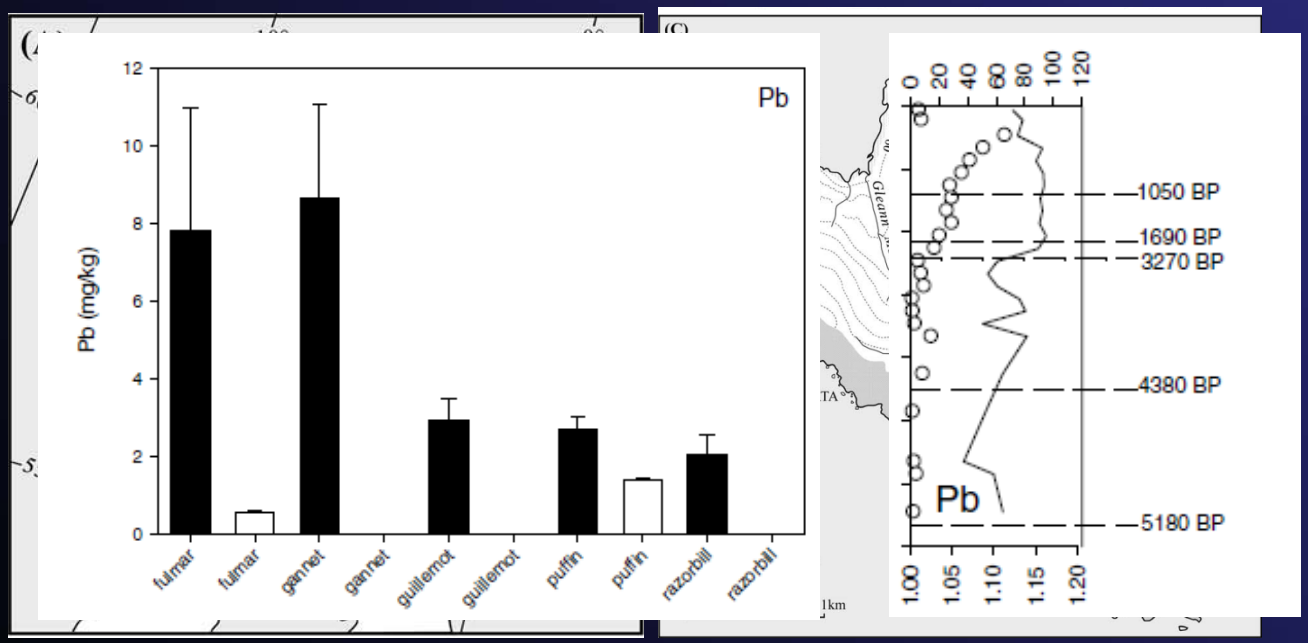
Lead pollution not a new phenomenon

Ancient manuring practices pollute arable soils (inc. lead) at the St Kilda World Heritage Site, Scottish North Atlantic



Meharg et al., 2006. Ancient manuring practices pollute arable soils at the St Kilda World Heritage Site, Scottish North Atlantic. Chemosphere **64**, 1818 – 1828

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The need to consider background levels

-DEFRA revision of the statutory guidance

- "Normal" levels of contamination are not to be caught up in the Part 2A regime

- Sites close to background levels of contamination should normally be dismissed from further investigation

- "Background levels" = levels of contaminants are not significantly different to those likely to be widespread within a local authority's area, or in other similar areas, that are common or usual across England/Wales.

- This might include: - elevated natural background levels
  - elevated levels of contaminants caused by common human activity

- Should be exceptionally unusual for LA's to determine sites close to background levels

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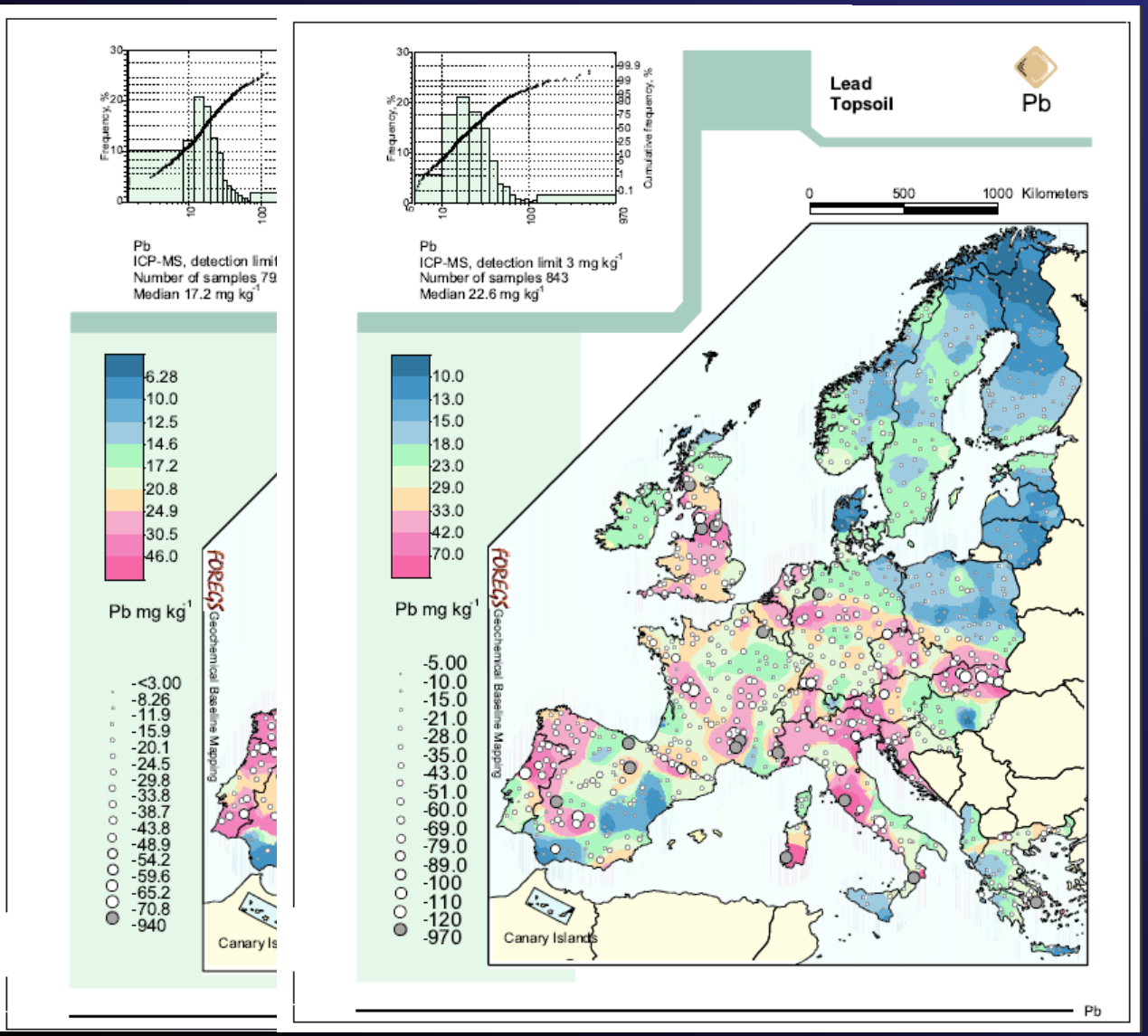
Background concentration information

European Scale information on background concentrations



Continental scale variation controlled by parent material (bedrock and superficial geology)

National Background Levels

Sediments, but shows natural Variation at the national scale

Variation over several orders of magnitude

Min	**<1** mg/kg Pb
Max	**22982** mg/kg Pb
Median	**33.8** mg/kg Pb
Mean	**84.6** mg/kg Pb
Std Dev	**535**

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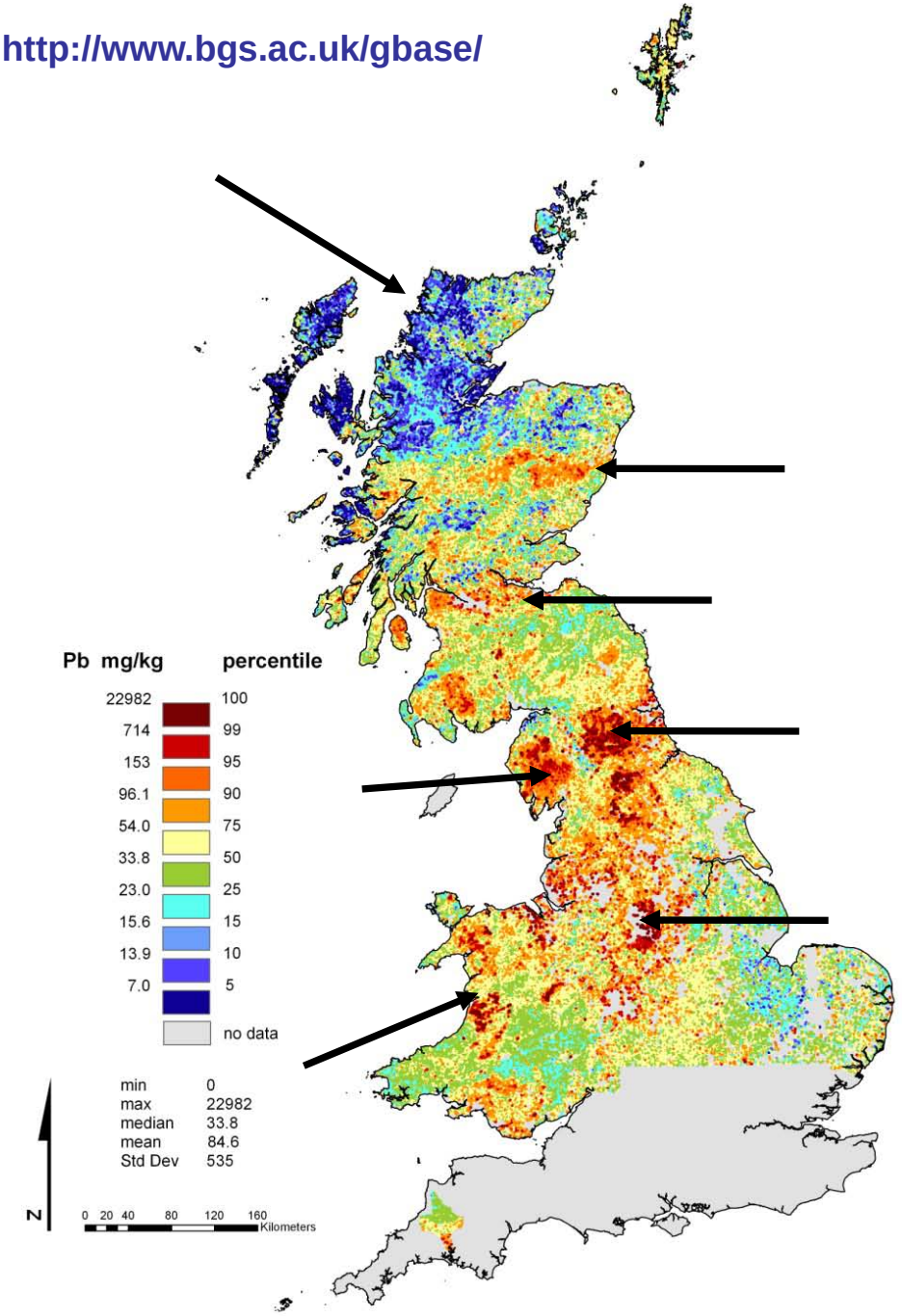
http://www.bgs.ac.uk/gbase/

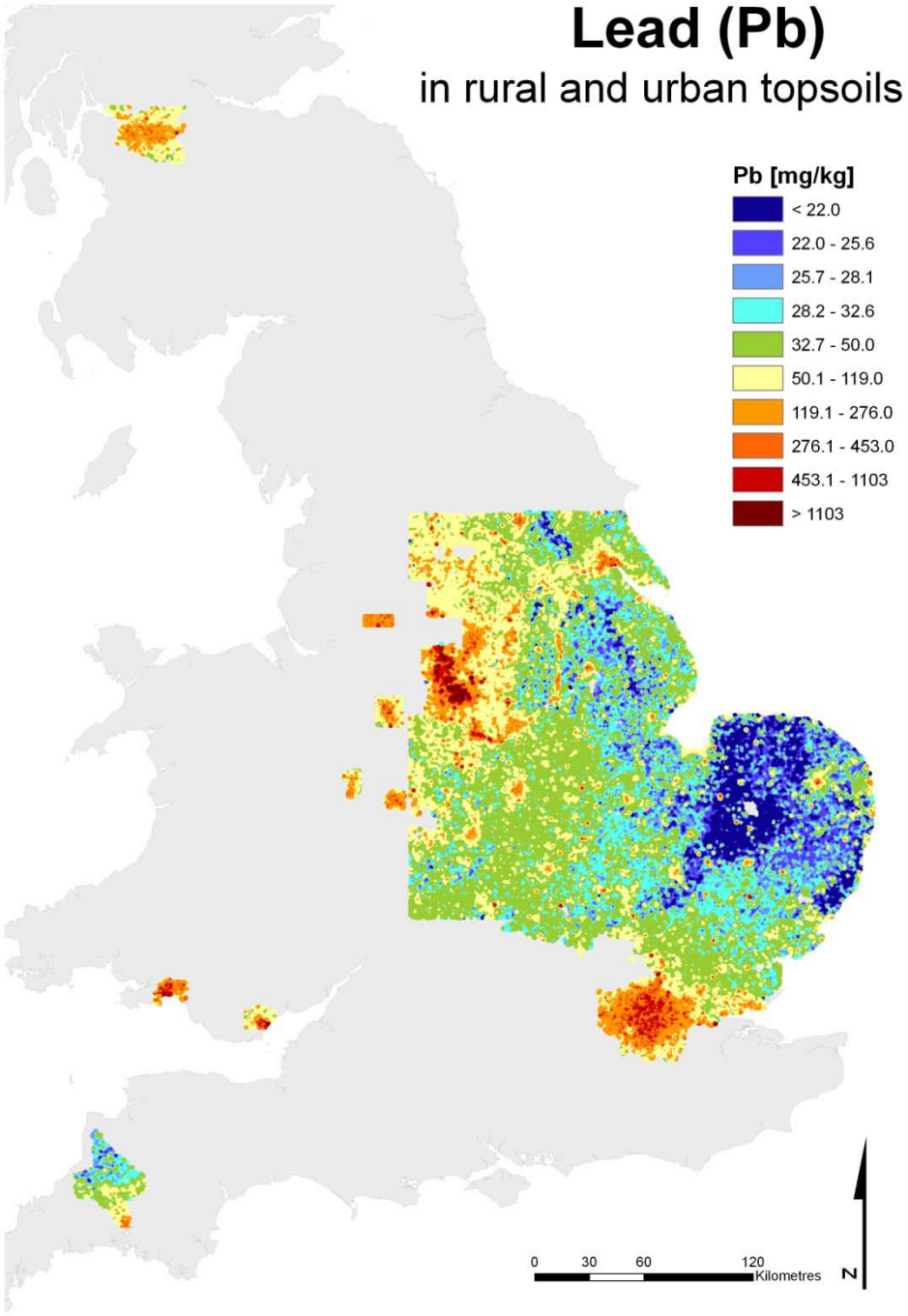


National Background Levels

Soil, shows natural variation and urban/rural contrast

Topsoils 5 – 20 cm, 5-point composite sample, <2mm fraction, XRFS

Min	**<1** mg/kg Pb
Max	**35930** mg/kg Pb
Median	**50** mg/kg Pb
Mean	**129.4** mg/kg Pb
Skew	**43.4**
Std Dev	**388.2**



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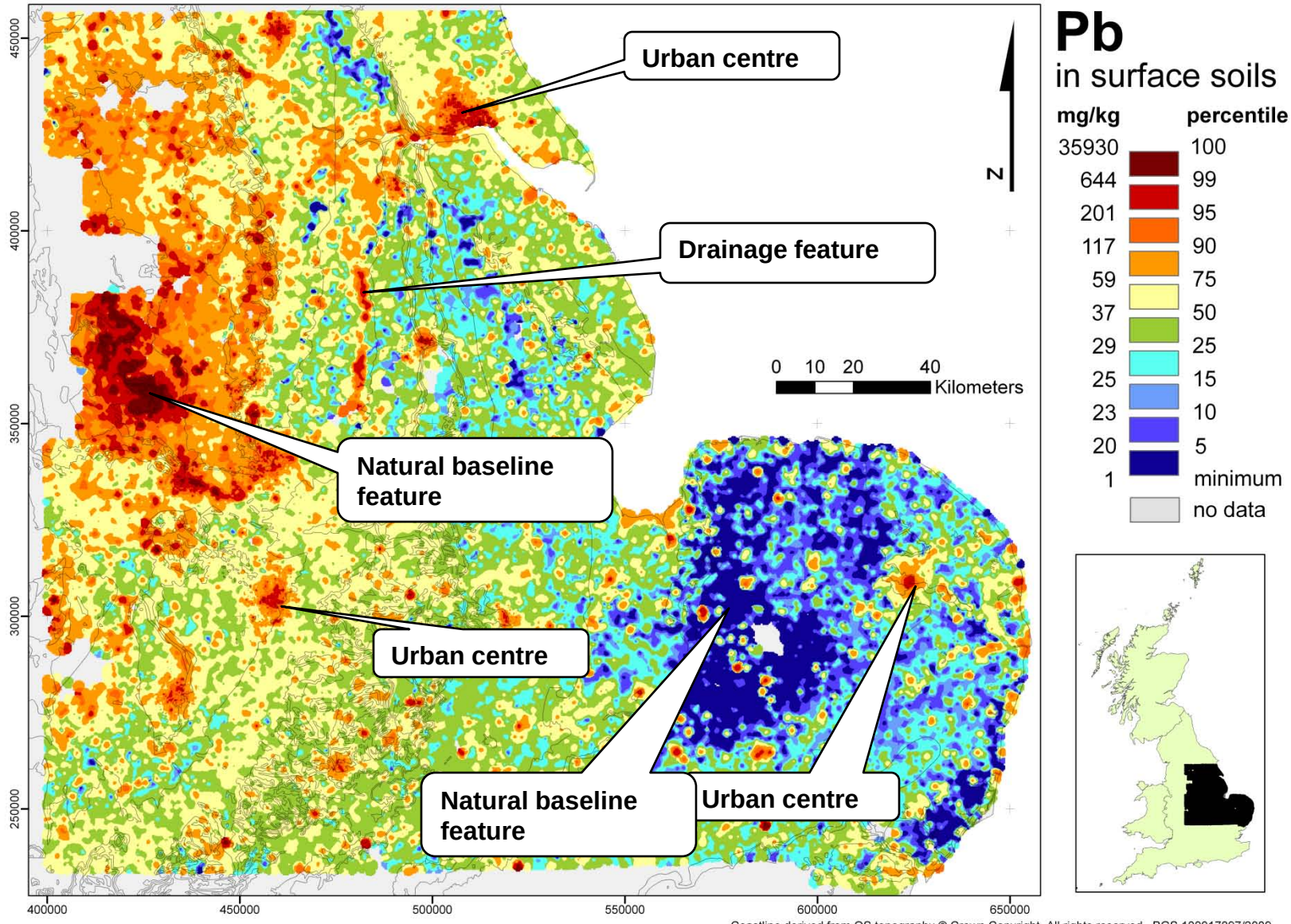
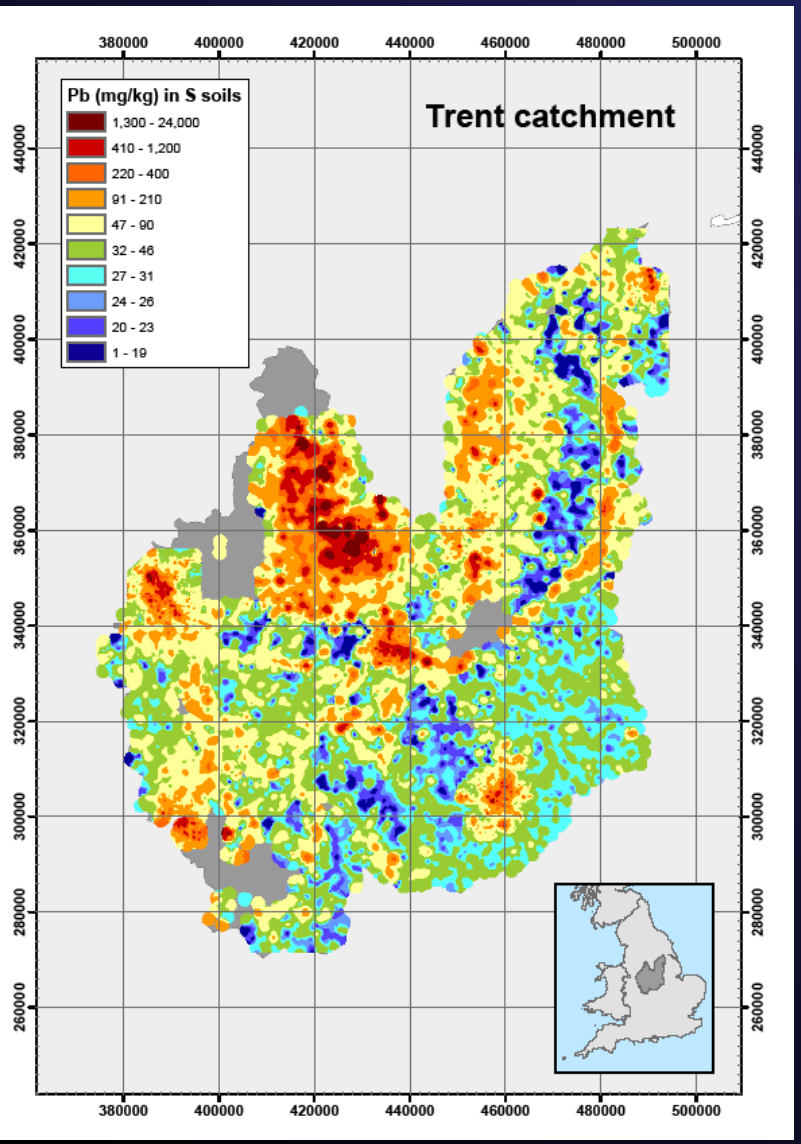
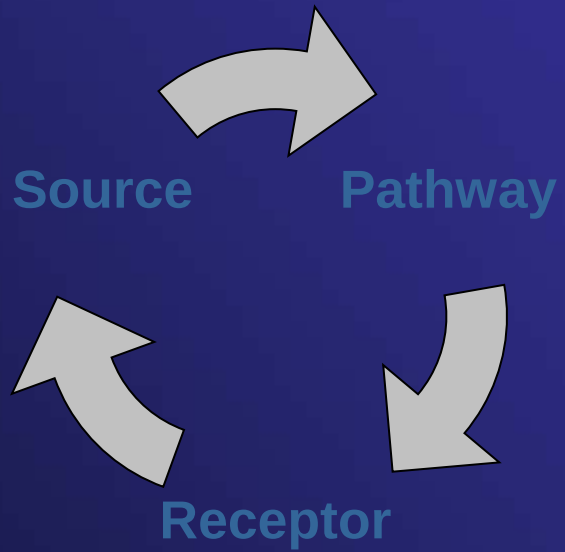
Regional soil geochemical baseline

Natural and anthropogenic controls

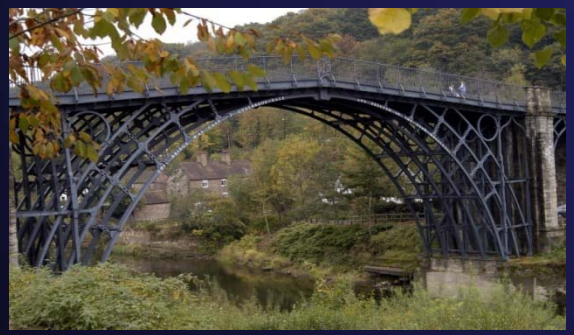


Natural Transport mechanisms





Centres of urban development, settlement & industry



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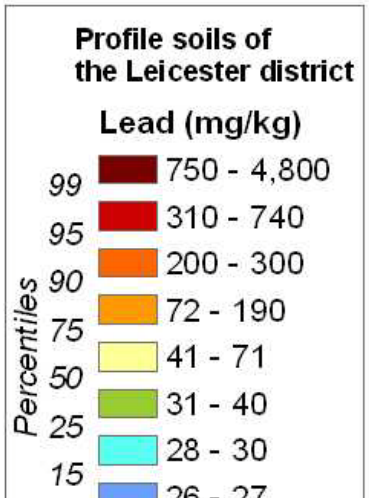
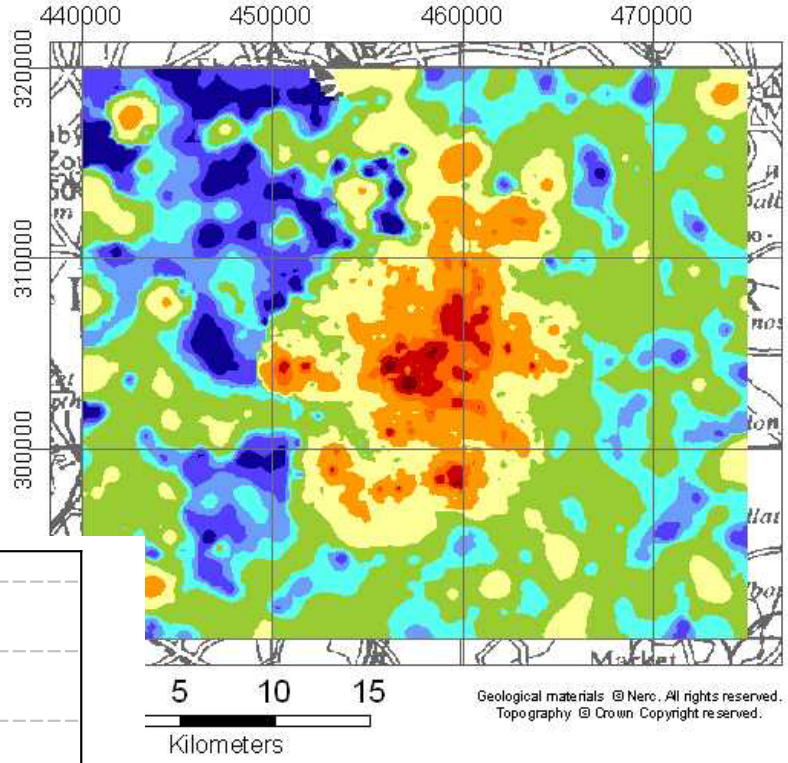
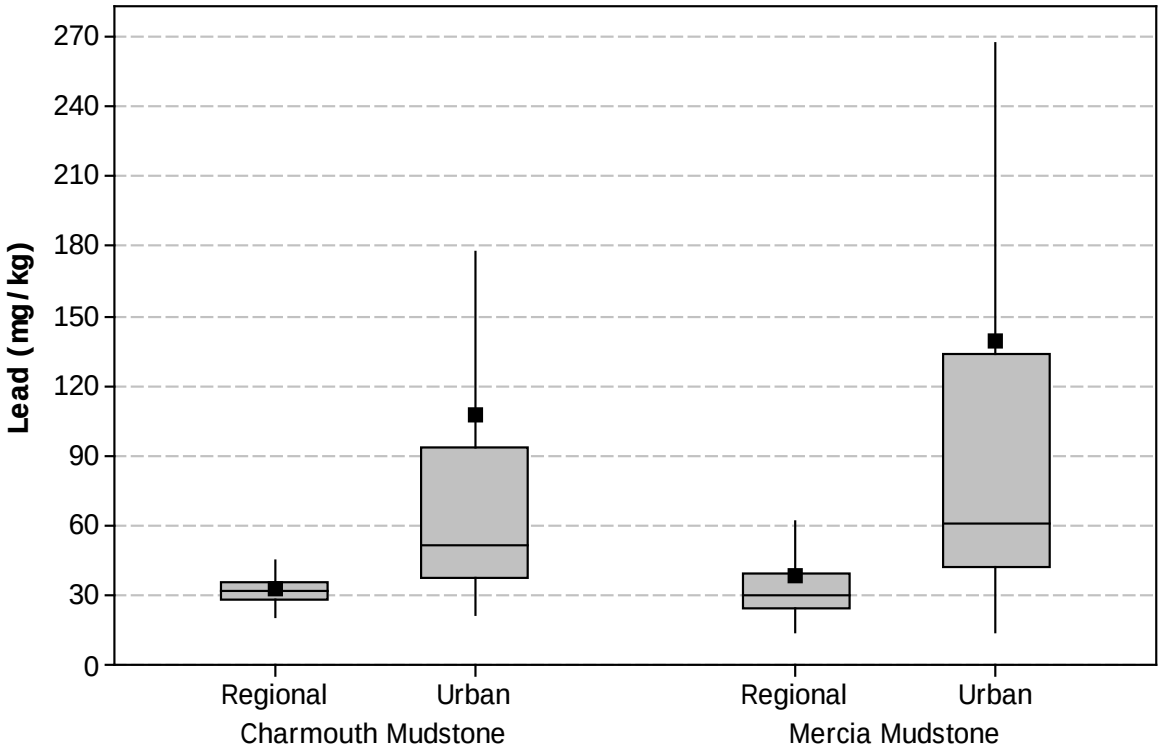
Leicester and surrounding area

- Concentrations systematically and significantly higher in the urban area







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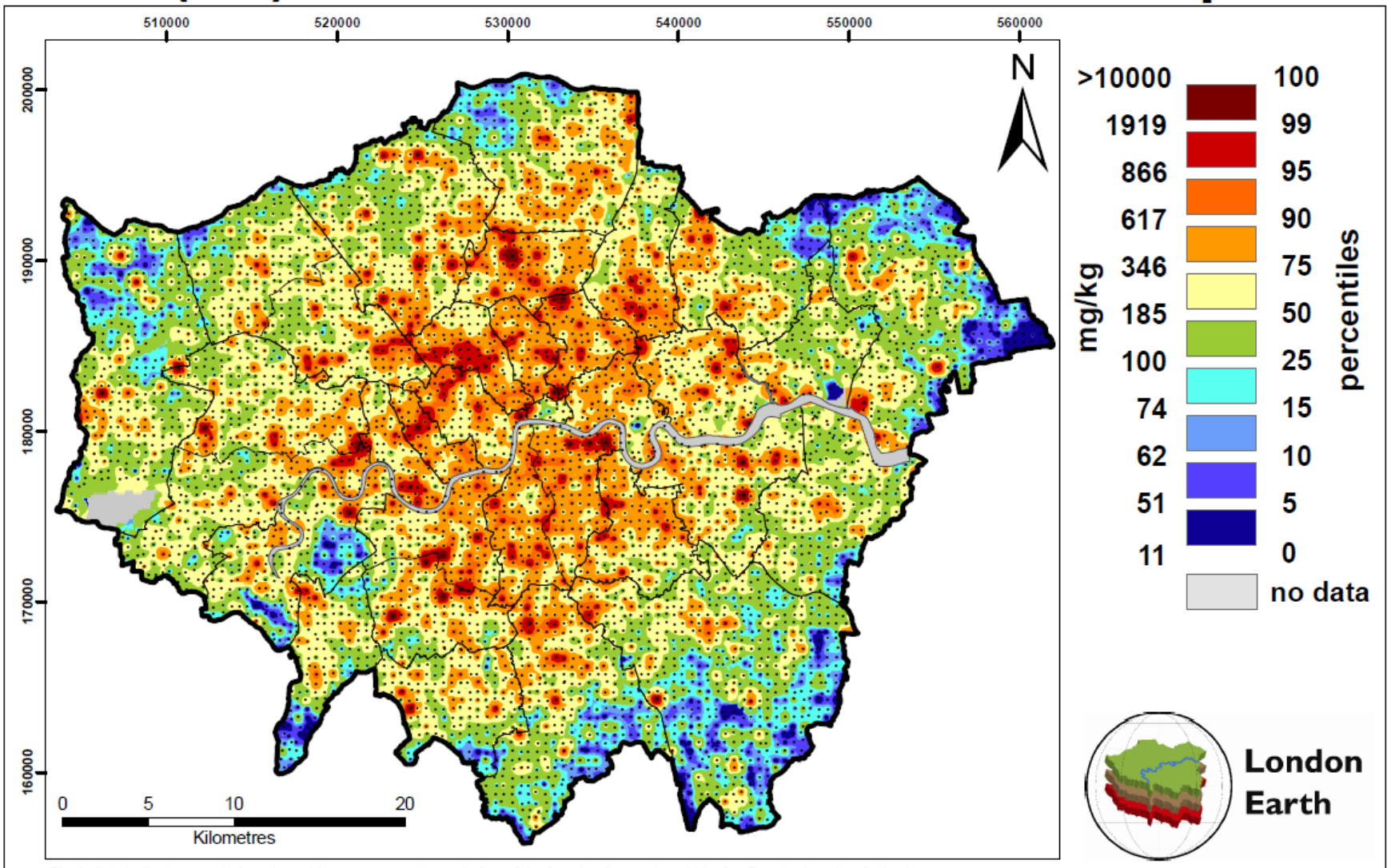
Median element concentrations for the East Midlands regional and urban soils (Median values where urban > regional, highlighted in red)

Analyte	Unit	East Mids	Corby		Coventry		Derby		Leicester		N'hampton		N'ham	P'borough	
		S	A	S	A	S	A	S	A	S	A	S	A	A	S
Al_2O_3	wt %	14.7	13.3	14.4	10.5	13.2	11.6	11.7	13.1	13.4	11.2	13.4	NR	12.4	12.7
As	mg/kg	15.8	**19.3**	**22.5**	9.0	11.0	15.7	12.8	12.9	**16.6**	**30.2**	**35.3**	13.0	**17.0**	**18.6**
CaO	wt %	0.89	**3.40**	**4.00**	0.51	0.54	**1.81**	**1.32**	**1.06**	**1.16**	**1.81**	**2.54**	0.82	**2.77**	**3.59**
Cd	mg/kg	0.8	0.3	0.3	0.3	0.3	**2.0**	**1.2**	0.7	0.5	0.3	0.3	**2.0**	0.3	0.3
Cr	mg/kg	94	90	**102**	64	82	67	73	73	89	**98**	**122**	67	78	90
Cu	mg/kg	22.5	20.5	**22.5**	**31**	**33.0**	**40.1**	**37.1**	**28.8**	**35.4**	**24.1**	**26.2**	**36.0**	**25.4**	**26.4**
Fe_2O_3	wt %	6.24	5.93	**6.65**	4.06	4.98	4.46	4.50	4.7	5.70	**7.56**	**9.19**	3.95	6.00	**6.50**
K_2O	wt %	2.16	1.92	1.95	2.10	**2.61**	**2.23**	**2.45**	**2.30**	**2.42**	1.63	1.86	**2.31**	1.61	1.80
MgO	wt %	1.2	1.1	1.1	**1.3**	**1.6**	**1.3**	**1.7**	**1.5**	**1.6**	0.6	0.6	**1.5**	0.6	0.7
MnO	wt %	0.088	0.071	0.085	0.083	**0.100**	**0.113**	**0.109**	0.061	**0.091**	0.086	**0.097**	0.085	0.064	0.077
Ni	mg/kg	36.7	32.0	**39.0**	24	31.0	32.8	31.6	27.3	36.2	29.3	**39.8**	27.0	29.3	36.3
P_2O_5	wt %	0.17	**0.21**	**0.20**	**0.21**	**0.20**	**0.24**	**0.30**	**0.44**	**0.22**	**0.44**	**0.41**	**0.28**	**0.37**	**0.24**
Pb	mg/kg	30.0	**36.2**	**32.1**	**73**	**71.0**	**159.2**	**157.3**	**65.3**	**58.8**	**55.9**	**52.7**	**101.0**	**38.8**	**35.5**
Se	mg/kg	0.4	0.4	0.4	0.4	**0.5**	0.4	**0.5**	0.4	**0.5**	0.4	**0.5**	**0.5**	**0.5**	**0.6**
Sn	mg/kg	3.5	2.8	2.5	1.9	**7.3**	**6.9**	**10.5**	**7.4**	**6.1**	**4.0**	**4.0**	**8.0**	**3.6**	3.4
Zn	mg/kg	87.1	**98.4**	**95.0**	**96**	**101.0**	**172.1**	**166.8**	**99.9**	**109.5**	**101.6**	**116.0**	**193.0**	**93.5**	**97.9**
Samples	n	7293	133	133	396	396	276	276	680	680	275	275	637	276	276

National Background Levels

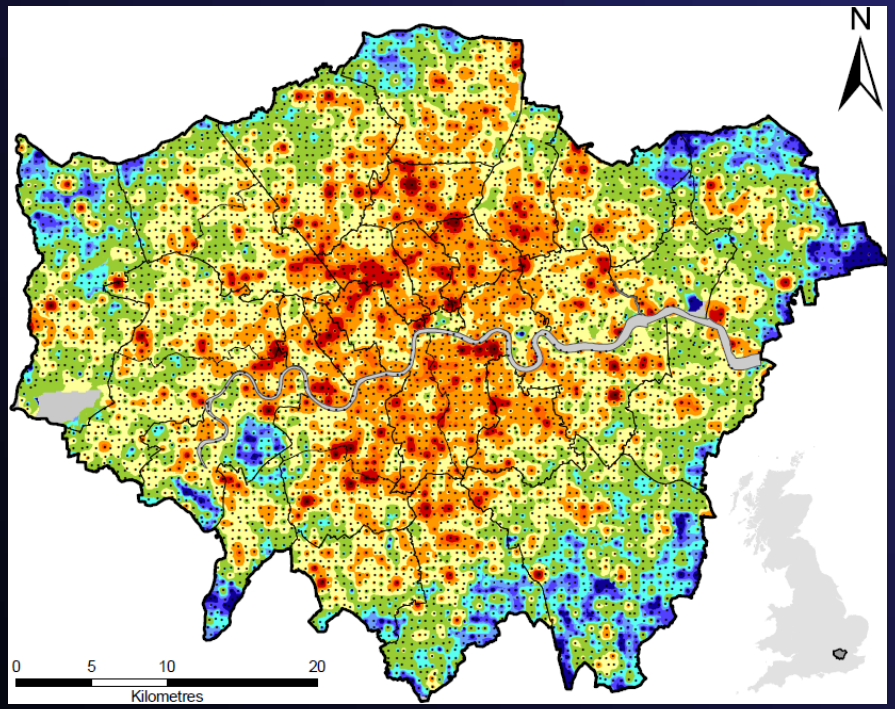
London Earth

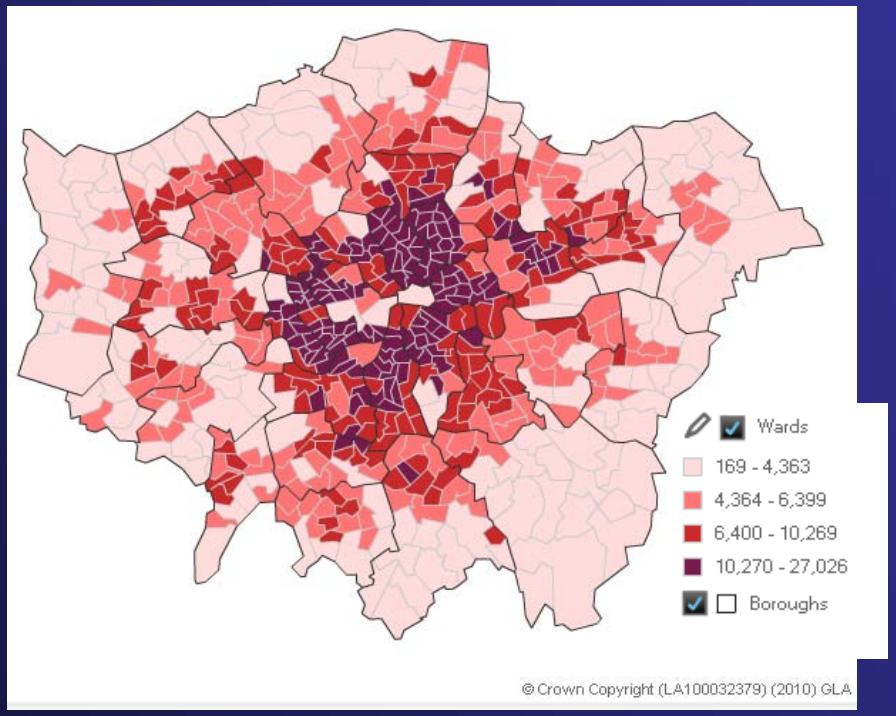
Lead (Pb) in topsoils



Black dots indicate sample locations. Lines represent boundaries of the London boroughs within the Greater London Authority.

GLA area; Topsoil Lead





Source: http://data.london.gov.uk/visualisations/atlas/

- Centrally located highs, likely to relate to use of leaded fuel
- Other sources likely to be locally important (e.g. leaded paint)
- ~ 5 times higher on average than local rural samples (n= 1900)
- Only larger parks display lower values; diffuse atmospheric source and intensity of human contact

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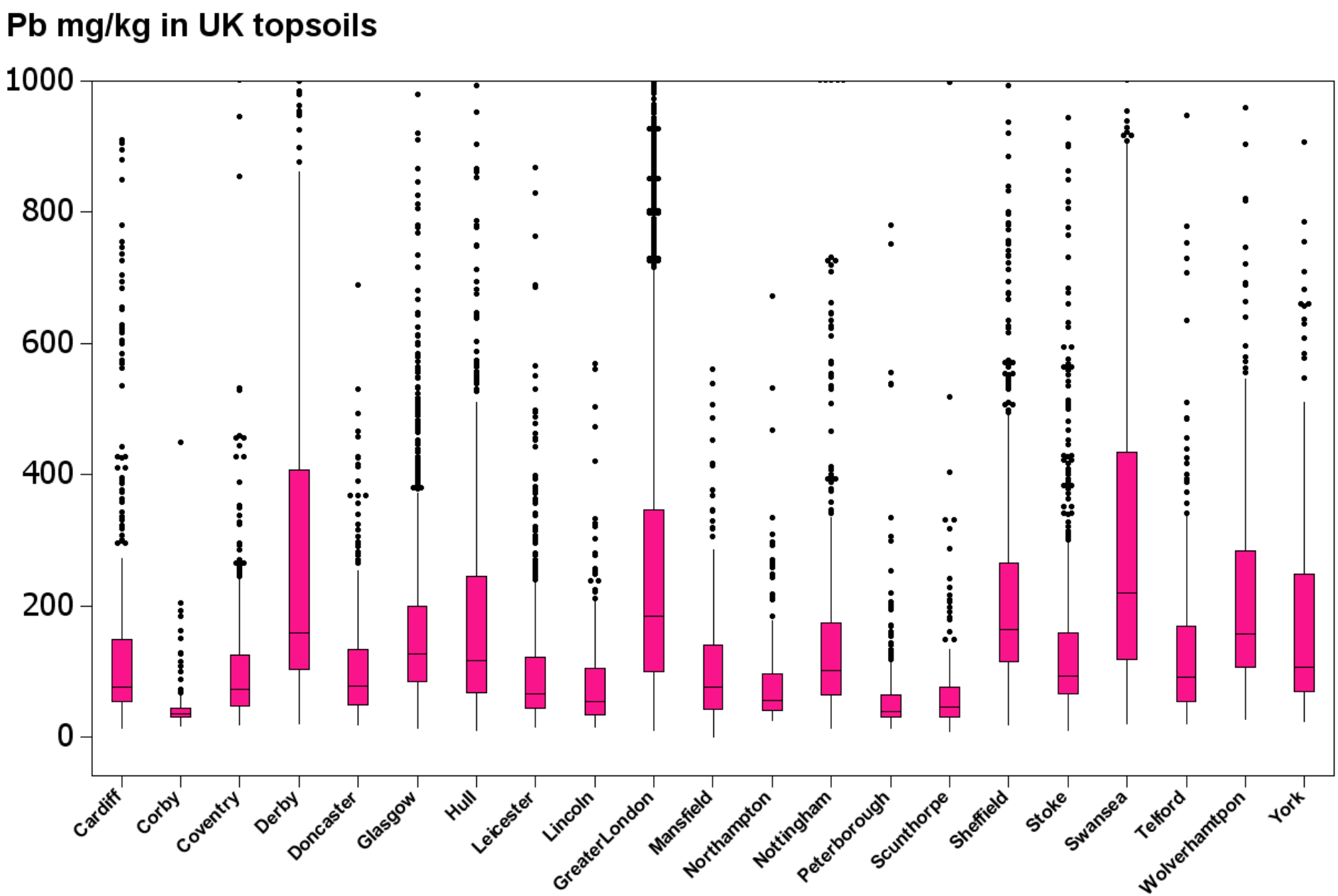
Lead; UK city intercomparison



Determining a background concentration?

-DEFRA revision of the statutory guidance
- “Normal” levels of contamination are not to be caught up in the Part 2A regime

- BUT, “normal” varies from place to place enormously; varying both with background geology and ‘urbanisation’
- Demonstrable differences between rural and urban areas
- Short scale variation, heterogeneity, particularly in urban environments
- Data source hugely important to take into account (sampling methodology, depth of sample, soil fraction, analytical technique)
- Standardised guidance on practices needed

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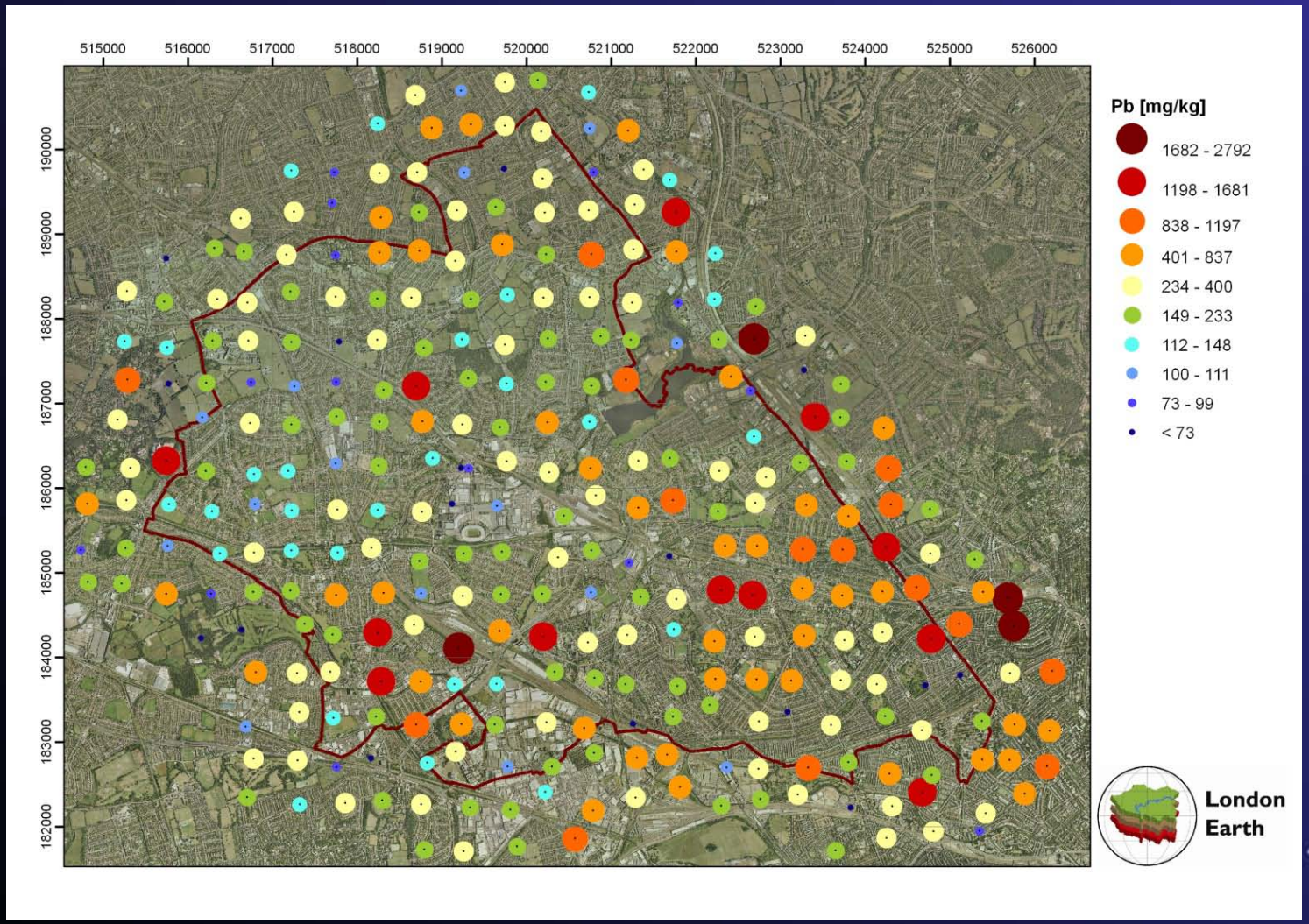
A local authority perspective on lead



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Typical make-up of the made-ground in Brent

Samples & In Situ Testing			Depth (m)	Level (m AOD)	Legend	Stratum Description
Depth (m)	Type	Results				
0.10	2					Compacted, light brown slightly organic, gravelly sandy SILT. Gravel is fine to medium subrounded to rounded flint, occasional brick and concrete, rare fine to medium fragments of coal, cobbles of tarmac and medium fragments of glass and metal (nail and wire). (TOPSOIL, MADE GROUND)
0.25	2					
0.40	2		0.40	-0.40		Compacted, light brown slightly organic, gravelly sandy SILT. Gravel is medium to coarse angular quarzite with a black staining and a slight bitumen odour (MADE GROUND)
0.60	2		0.60	-0.60		Trial pit complete at 0.60 m

Depth	Sample / Test Details	PID (ppm)	Water	STRATA				
				Legend	Depth (Thick-ness)	DESCRIPTION	COMMENTS	Instalation /Backfill
	ESK_BH55_0.1				(0.25) 0.25	MADE GROUND: Dark brown, slightly gravelly clayey topsoil with occasional medium glass and tile pieces. Gravel is medium of flint.	NVO	
					(0.15) 0.40	MADE GROUND: Medium brown sandy gravelly clay with frequent fine to medium brick and coal fragments. Gravel is medium, sub-angular.	NVO	

Both samples had Pb > 1000 mg/kg

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Typical lead levels in the Borough of Brent

Location	Pb Concentration Range (mg/kg)*
Allotments	24 - 1100
Residential gardens	14 - 2100
Industrial sites	56 - 2300

*Please note that analysis was undertaken by different laboratories

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Typical lead levels in West London boroughs

- Camden residential gardens:110-4177mg/kg (mean 1022 mg/kg)
- Kensington and Chelsea public open space: 72-1200 mg/kg
- Hounslow: samples up to 900 mg/kg are common
- Islington: 500-1000 mg/kg common

Elevated Pb not necessarily associated with sites of previous industrial use.

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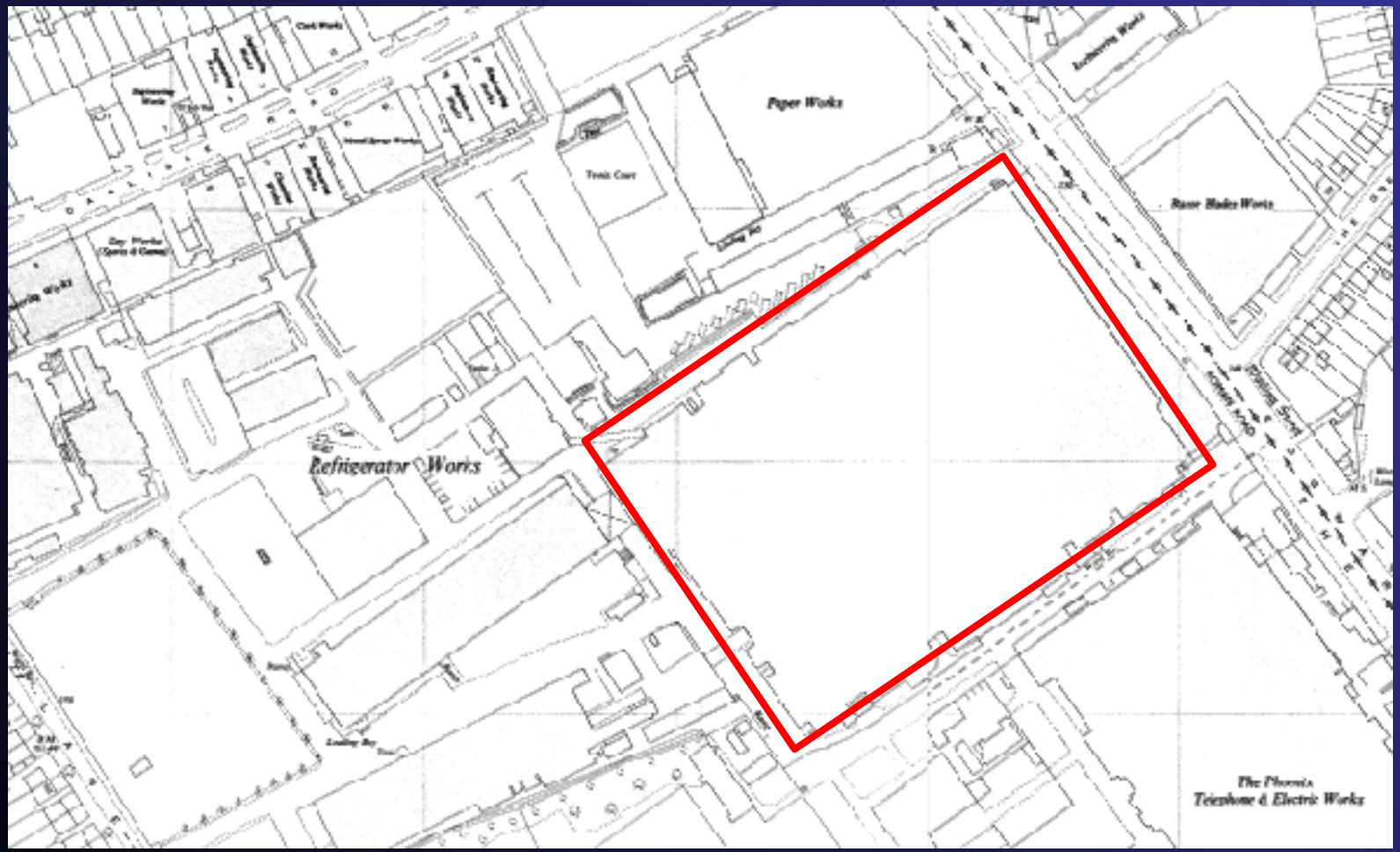
Site with industrial historic use



Buildings on site: 1935 – 2010

Site cleared for redevelopment

Pb levels: **18 - 360 mg/kg**

Mean Pb: **96.2 mg/kg**

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Site with non-industrial historic use

Allotment:1935 - 1966

Care home: 1966 - 2006

Pb levels: **54 - 1738 mg/kg**

Mean Pb: **481 mg/kg**

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A local authority perspective on lead

The Planning Regime

- Typical guideline levels used by consultants: **400 - 450 mg/kg**
- GQRA typical (not DQRA, no SSAC's)
- The typical solution if generic assessment criteria (GAC) exceeded? **Dig, dump and replace**

Questions:

- As a local authority regulator, should I be approving proposed remediation, for mean concentrations that are only slightly exceeding the GAC, and are in the region of background levels?
- Is the GAC used too conservative?
- Is it sustainable to remediate sites where the mean lead level is > GAC, but < urban background?

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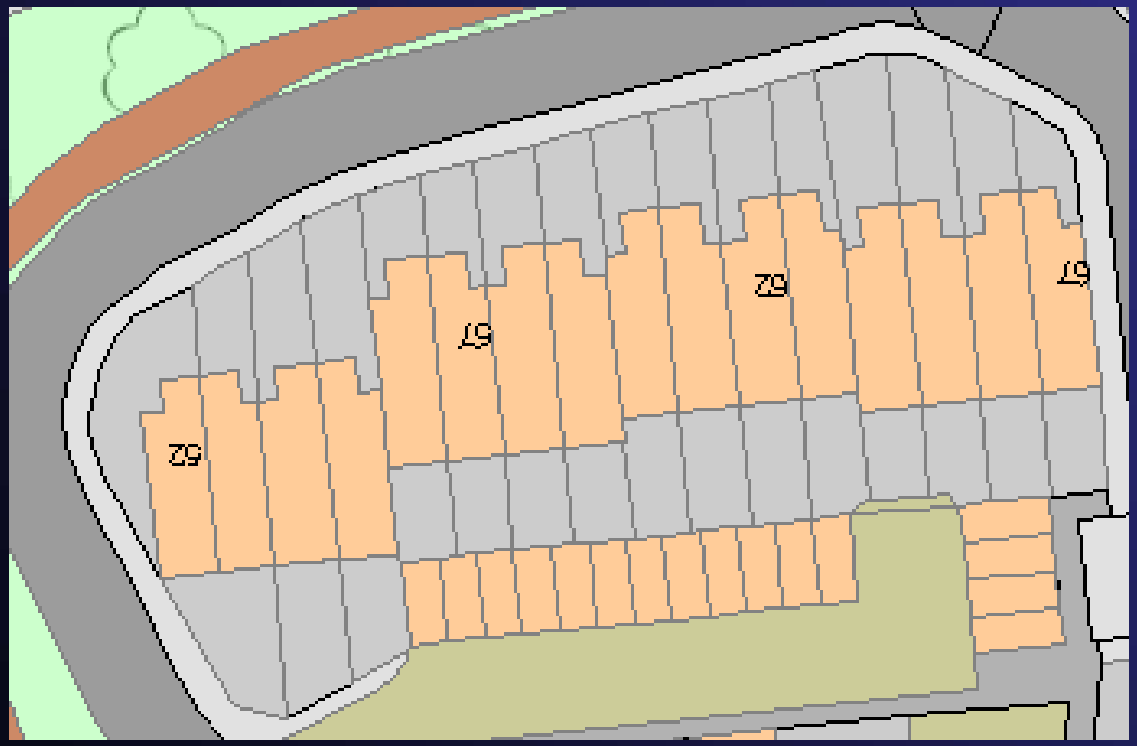
Part 2A example – Eskdale Close

- Investigated under our Contaminated Land Inspection Strategy
- 16 residential gardens



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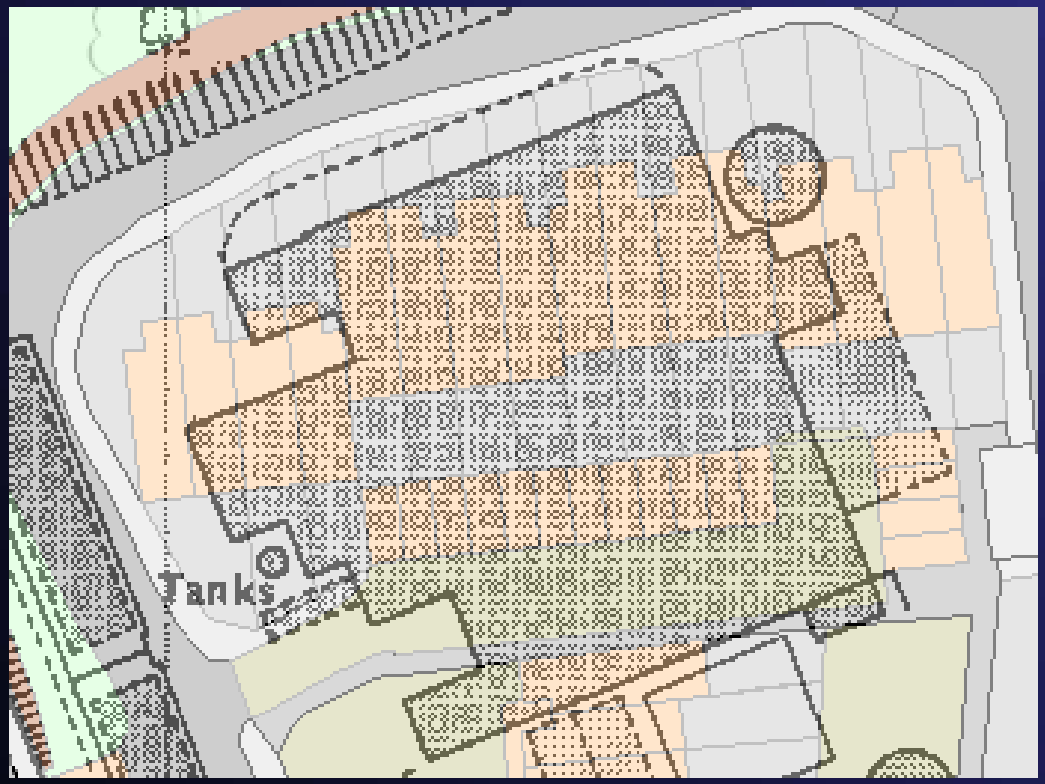
Part 2A example – Eskdale Close

- Liquid Oxygen Works built in 1943 and demolished in 1973
- Soil tested for a full suite of contaminants, only Pb was > GAC



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Garden	Min Pb (mg/kg)	Max Pb (mg/kg)	Mean Pb (mg/kg)
52	320	1000	715
53	140	780	420
54	290	1000	590
55	56	190	115
56	280	2000	1470
57	77	2100	1355.4
58	100	2300	1285
59	130	1100	610
60	93	610	358.25
61	110	540	342.5
62	200	1200	764
63	320	1400	1005
64	1100	1900	1675
65	no data		
66	1200	1700	1475
67	410	1600	1000

A local authority perspective on lead

Part 2A example – Eskdale Close

- Derivation of a **Site Specific Assessment Criteria (SSAC)**
  - bioaccessibility testing
  - site specific soil-plant concentration factors
  - SSAC of 873 mg/kg
  - still a conservative “minimal risk” level
- **Significant Possibility of Significant Harm (SPOSH)**?
  - using site specific data and Health Criteria Values that are more representative of a SPOSH situation = SSAC > 2000 mg/kg
  - protective of human health?
  - appropriate given urban background levels?

- Difficulty for Local Authorities to strike the right balance between conservative, unsustainable assessment values and health protection

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Conclusions

- Lead has had a multitude of uses over 1000's of years.
- Significant quantities of lead have entered our environment through atmospheric emissions, from vehicles, the chemical industry, waste disposal and the manufacturing industry.
- Although emissions have decreased, the lead remains in the environment due to its low mobility.
- Urban levels are significantly higher than rural.
- High variability in lead concentrations in typical made ground (56-2300 mg/kg).
- Typical assessment values are below some urban background levels.
-Difficulty for LAs in Planning and Part 2A scenarios
-**Standardised guidance on determining background concentrations will be key**

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