2015 International Year of Soils

PAHs CONTAMINATION IN URBAN SOILS FROM LISBON (PORTUGAL): SPATIAL VARIABILITY AND POTENTIAL RISKS

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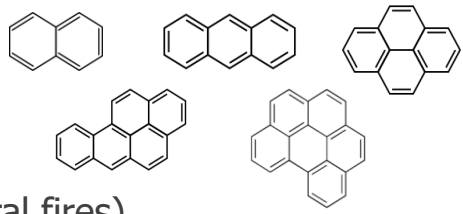
INTRODUCTION

Urban areas are strongly impacted by anthropogenic activities → Diffuse pollution

Diffuse pollution → **Soil quality** → Risk to human health and **ecosystems**

Soil services: habitat for a variety of organisms; water filtering; nutrients cycling; carbon storage; storm water retention; recreational; etc.



Polycyclic aromatic hydrocarbons (PAHs)

- Natural sources (e.g. natural fires)
- Anthropogenic sources (e.g. traffic, industry)

- \+ 100 compounds → 16 priority pollutants (US EPA)

- Hydrophobic
- Lipophilic
- Chemically stable
- Semi-volatile

→ **Persistent, mobile and ubiquitous**

Accumulate in soils and in the food chain

↓

Bonded to particles and to organic fraction

Environmental significance: carcinogenic, mutagenic or endocrine disrupting effects

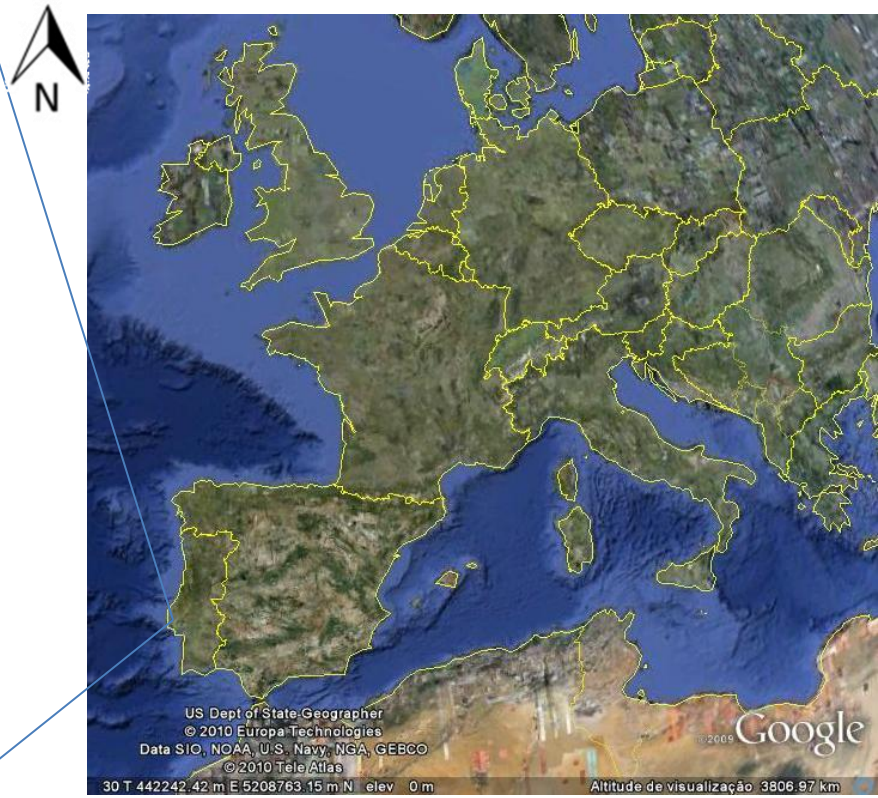
Aims

- Study the spatial variability and identify areas of potential concern regarding PAHs contamination in Lisbon urban soils

- Evaluate the potential risks to the environment based on the total levels of PAHs present in Lisbon urban soils

- Assessment of the available fraction of PAHs in selected Lisbon soil samples

Study area



- **Lisbon** urban area is the biggest of Portugal, with a population of 547,631 inhabitants and an area of **85 km²**
  - Highly industrialized area (petrochemical, textile, shipyard and siderurgy)

Sampling

- 97 samples (0-10 cm)

- composite samples
- air dried
- sieved <2mm
- frozen for PAHs analysis

- Different land uses

  Parks (PA)

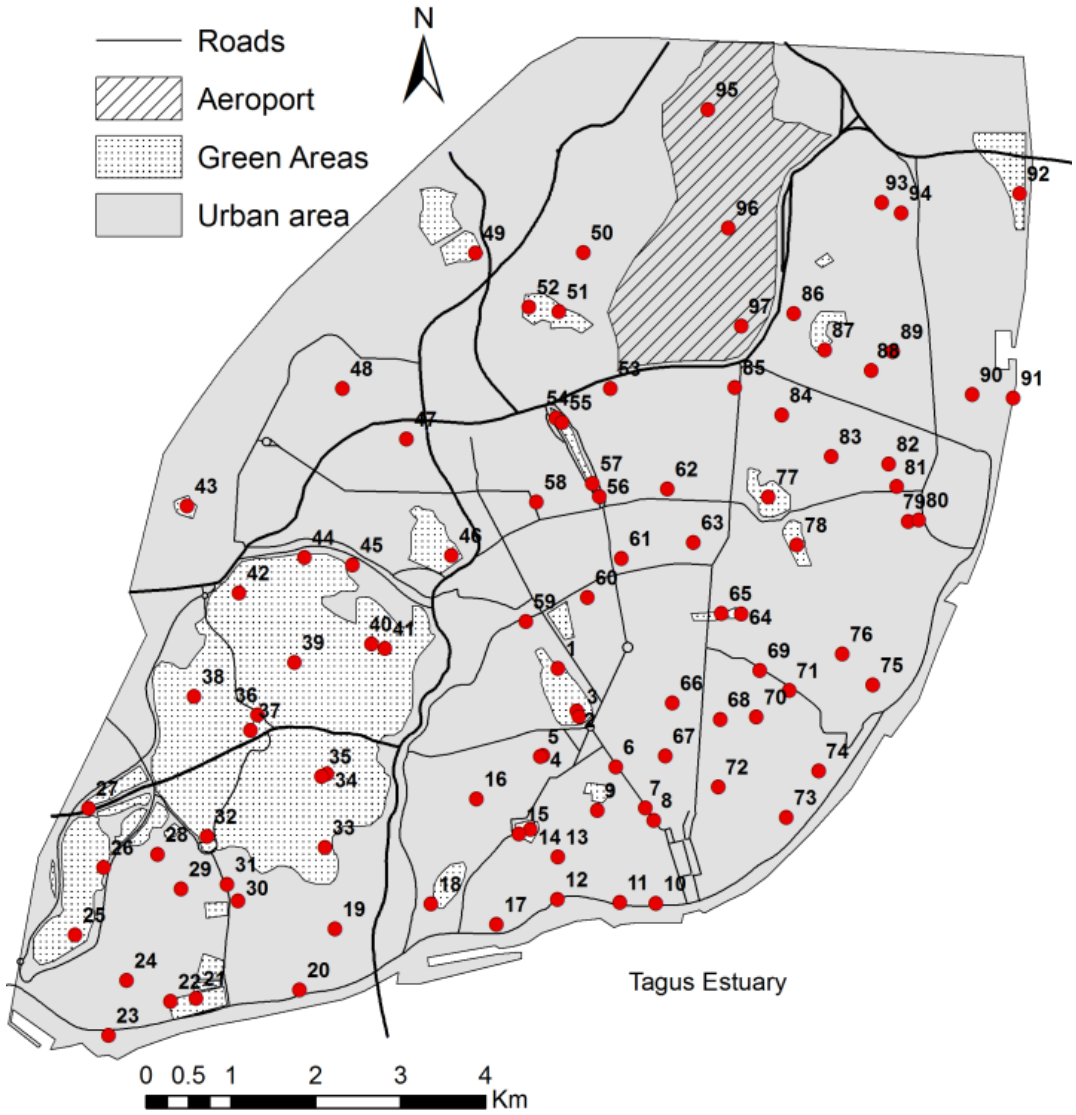
  Ornamental gardens (GD)

  Roadsides (RS)

  Playgrounds (PG)

  Schools (SC)

  Airport (AE)



Soil characterization & Chemical screening

- pH in water and $CaCl_2$ (ISO10390:1994)
- % Organic C, total C and N by elemental analysis (LECO CNHS-932; Skalar Primac SCN)
- Cation exchange capacity (ISO 13536:1995)
- Particle size: percentages of sand, silt and clay (Micromeritics® Sedigraph 5100)
- Pseudo-total content of 53 elements (ICP-MS/OES)
- **Total levels of 16 PAHs**

  Soxhlet extraction with hexane:acetone

  Clean-up by SPE (silica|alumina)

  GC/MS (EI) analysis in SIM mode; splitless injection

➢ **QA/QC**

- Analysis of certified reference material (CRM124 and CNS-300) → good agreement
- Laboratory inter-comparison exercise → good agreement
- Blanks → < detection limit
- Replicates → variability <20%
- Limit of detection → 0.10- 1.5 µg kg^{-1}

Risk assessment approach

TIER 1: TOTAL CONTENT OF PAHS

- **Comparison of total levels with guidelines**: generic; environmental protection

Hazard Quotient ➡ $HQ = \frac{\text{Soil Concentration}}{\text{Soil Quality Guidelines}}$ Hazard Index ➡ $HI = \sum HQ$

- **Environmental Risks**: EU and Dutch models

Toxic Units ➡ $TU = \frac{\text{Soil Concentration}}{\text{PNEC}}$

Potentially Affected Fraction of Species ➡ $PAF_{TMoA} = \frac{1}{1 + e^{-log(\sum HU_{TMoA})\beta_{TMoA}^{-1}}}$

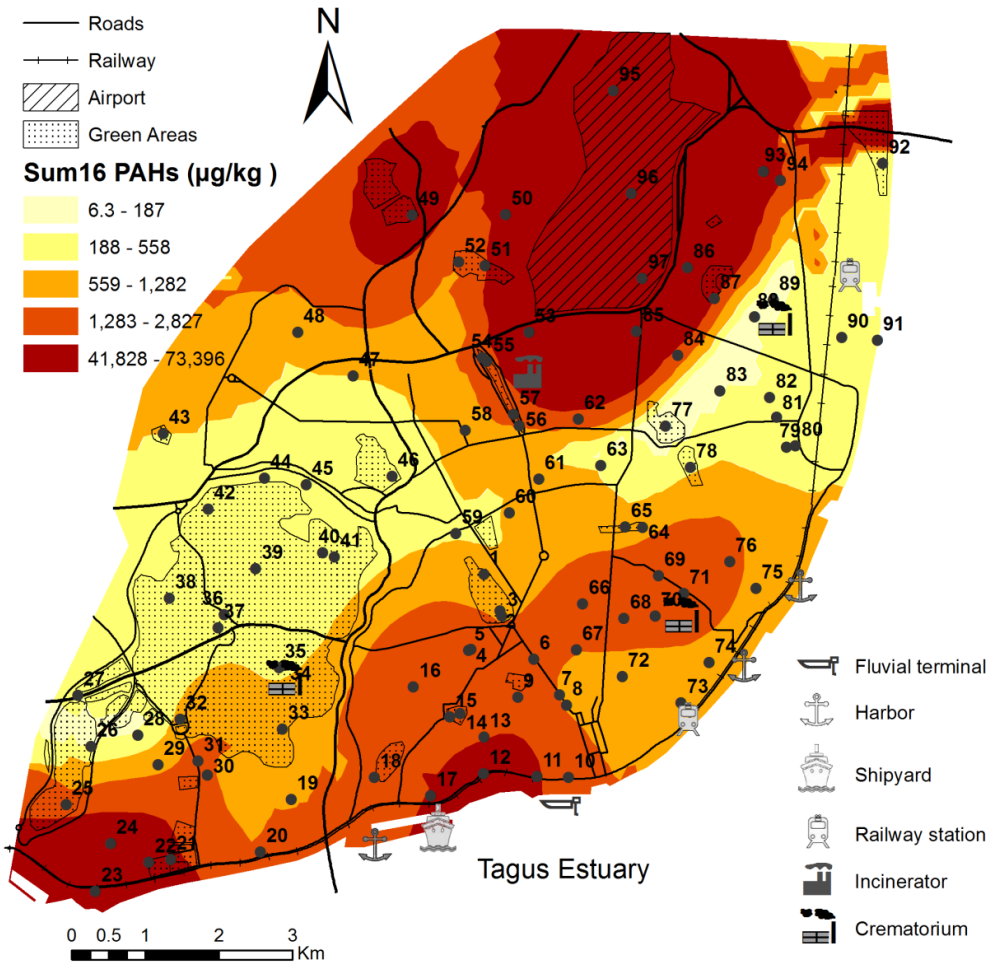
Potential risks? ➡ **More detailed risk assessment**

Total content ➡ Overestimates the risks ➡ Only a small fraction is available for uptake by organisms or can be leached to groundwater

- Water soluble fraction using Tenax-TA® (**Chemical availability**)
- Bioacumulation assays with earthworms (**Bioavailability**)

TIER 2: AVAILABLE FRACTION

Spatial distribution of ∑16PAHs



Model: spherical
Major Direction: N35°E
Geometric anisotropy
Major range (m): 3000
Minor range (m): 2141

Range: 6.3 – 73,395 µg kg^{-1}

Median: 559 µg kg^{-1}

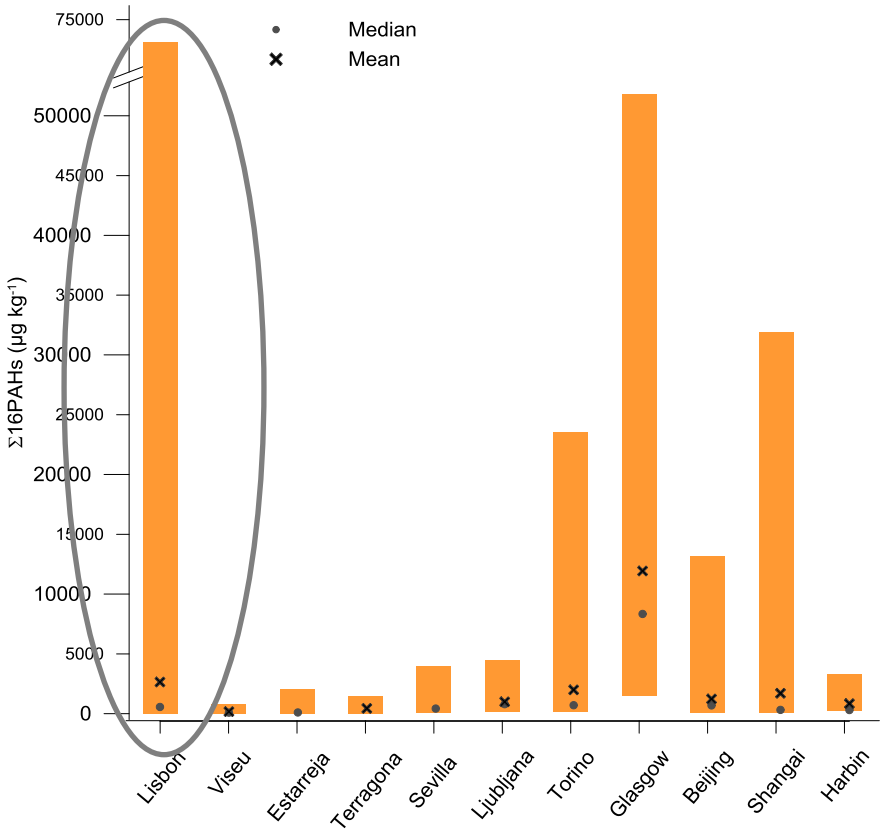
75 Percentile = 1,282 µg kg^{-1}

Upper outlier limit= 2,827 µg kg^{-1}

Airport

Harbour/Shipyard

City centre: Historical sites a long term accumulation (aged soils)

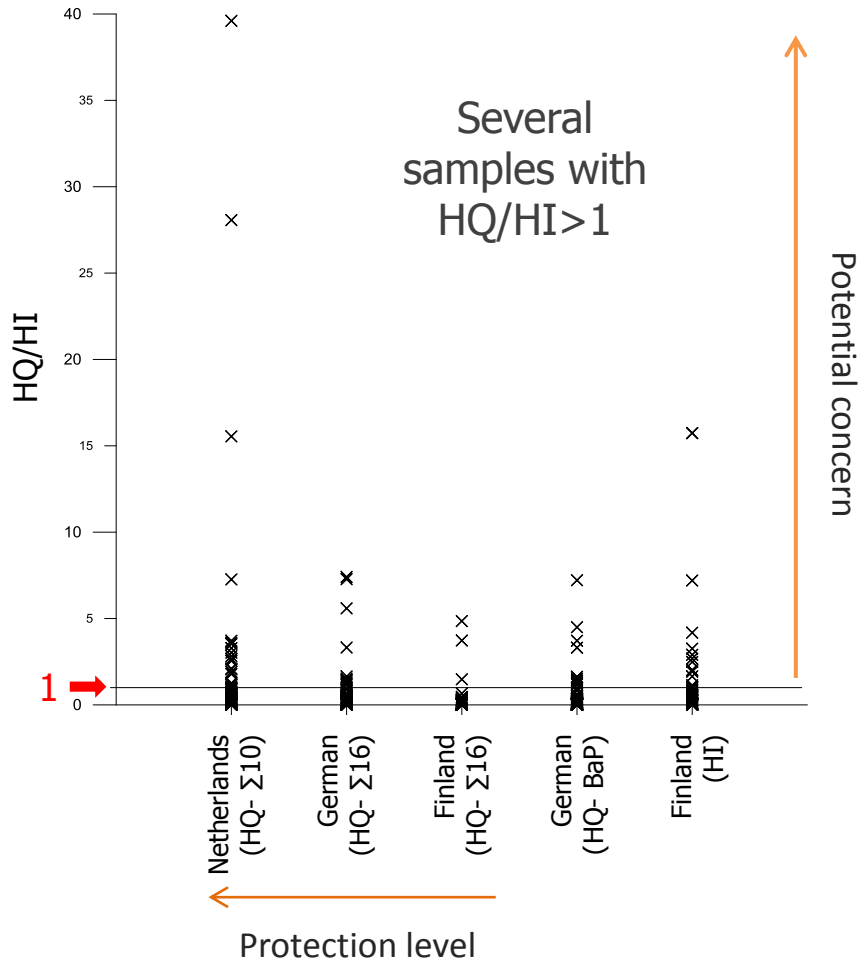


Risk assessment: Comparison with guidelines

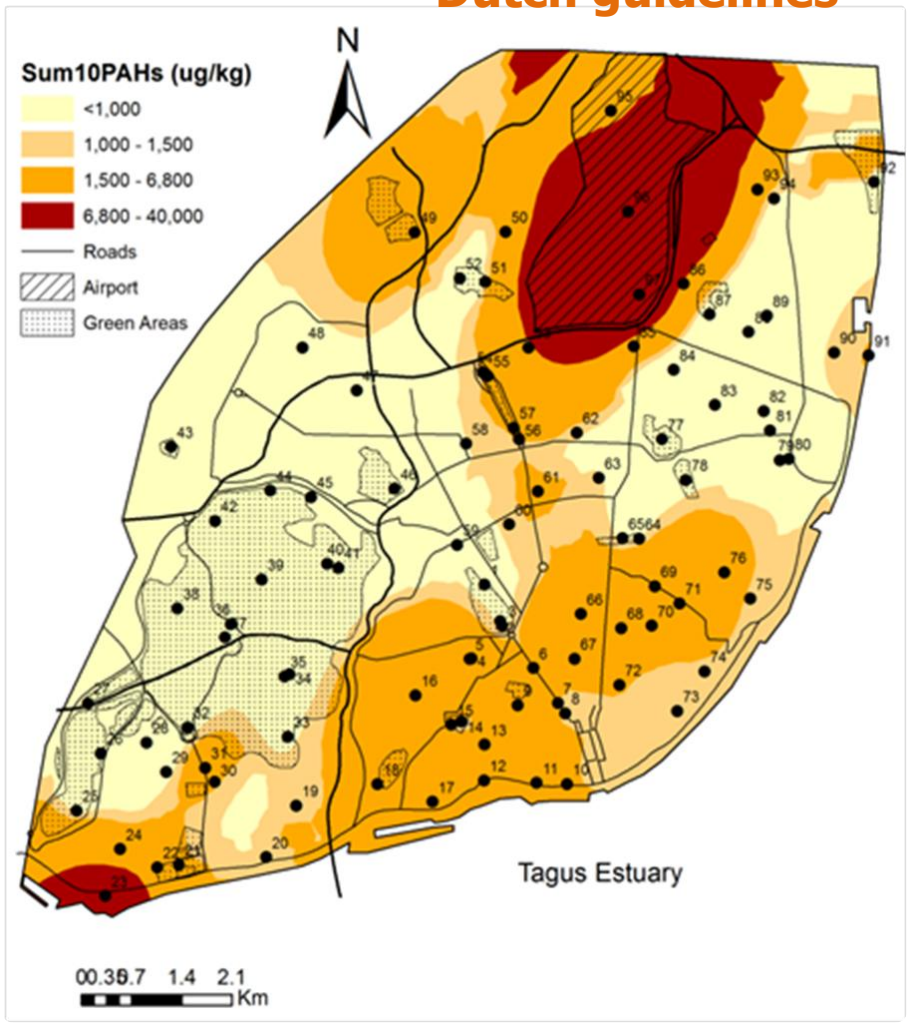
Hazard Quotient $HQ = \frac{\text{Soil Concentration}}{\text{Soil Quality Guidelines}}$

Hazard Index $HI = \sum HQ$

- Generic soil quality guidelines



Dutch guidelines



Environmental Risk Assessment

Toxic Units

Concentration addition model

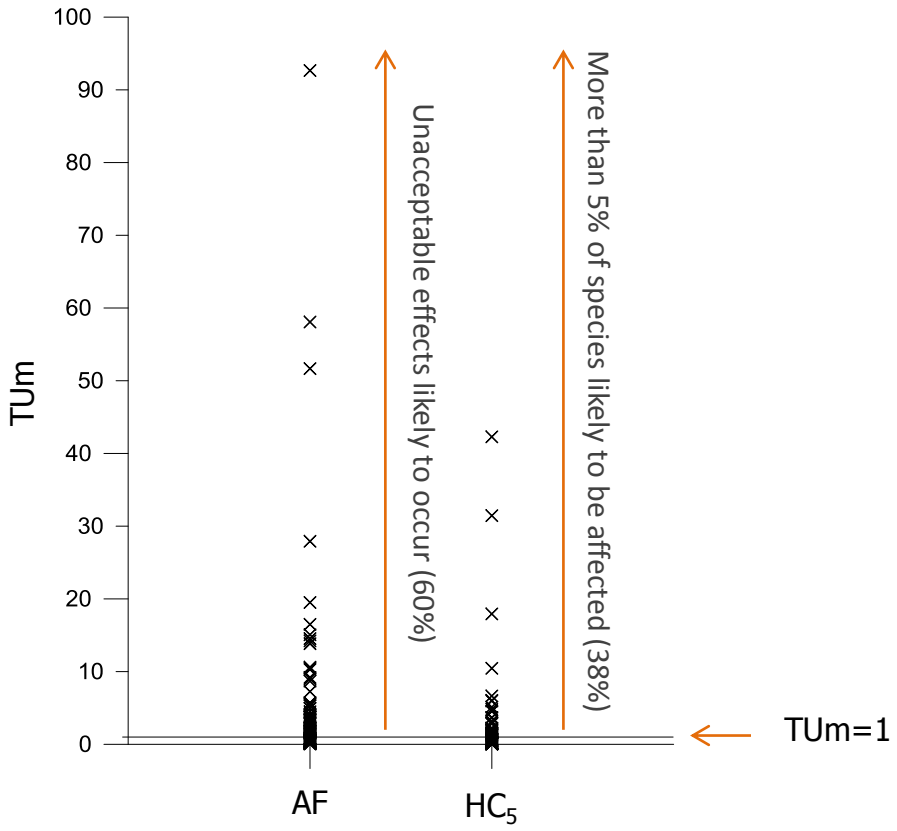
$$TU = \frac{\text{Soil Concentration}}{\text{PNEC}} \Rightarrow TUm = \sum TU$$

Assessment factors (AF) to the lowest available NOEC

Hazard Concentration 5% (HC_5) – Species Sensitive Distribution

PNEC = predicted no effect concentration

NOEC = non observed effect concentration



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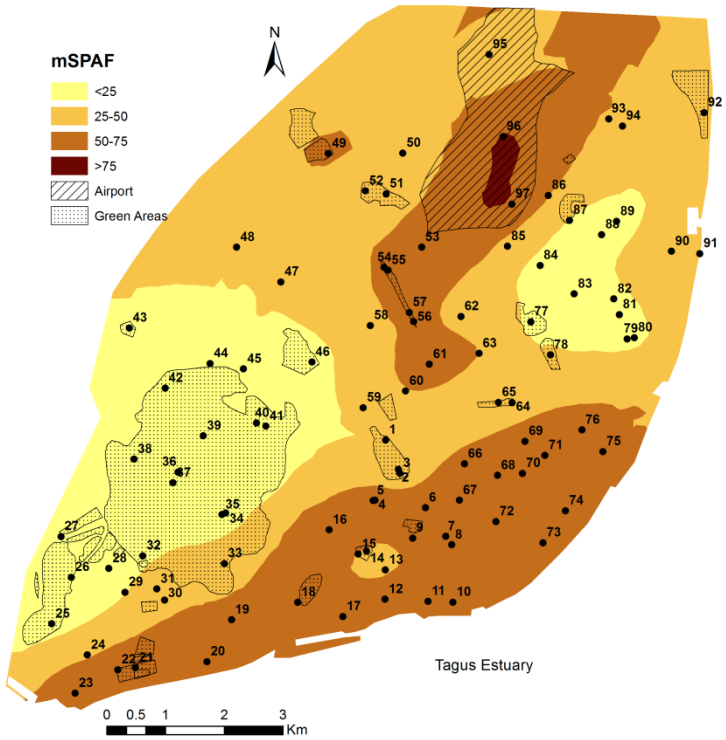
Multisubstance potentially affected fraction (mSPAF)

Concentration addition model

Hazard Concentration 5% (HC_5) – Species Sensitive Distribution

$$HU = \frac{EC_1}{HCx_1} + ... + \frac{EC_n}{HCx_n}$$

$$mSPAF = \frac{1}{1 + e^{-\log\left(\sum HU\right)\beta^{-1}}}$$



Chemical availability: water soluble fraction

- 10 samples previously identified has representing a potential hazard (different soil properties and PAHs concentrations)

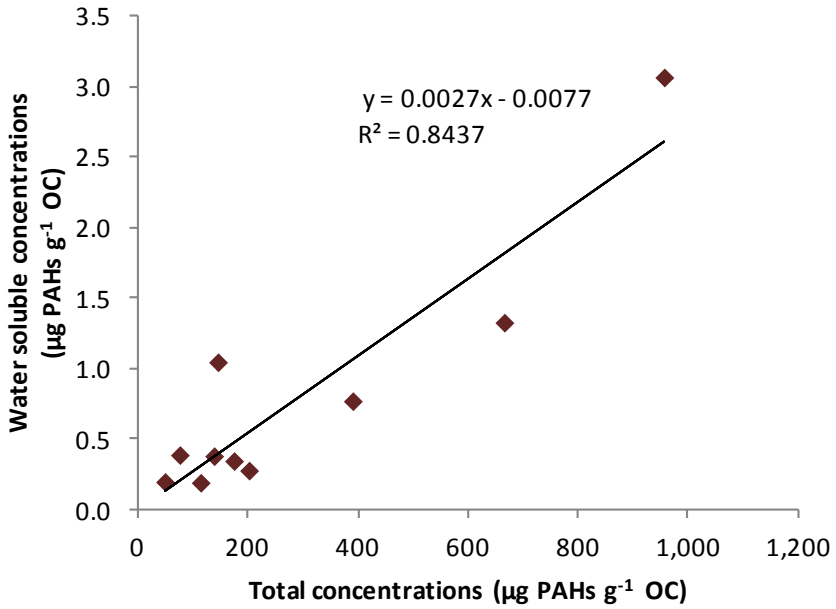
Soil + ultra pure water + **Tenax-TA** → Separation of Tenax from soil solution (6h)

Extraction of PAHs from Tenax and SPE cleanup → GC/MS analysis

The water soluble fraction represent < 1% of total concentrations

Low mobility and low potential to be uptaken from the soil solution → No risks

- No clear relationship between total concentration and total % available
  - Higher available fraction in less contaminated soils
- No clear relationship between OC and % available



Other factors may have influence on the desorption of available fraction (e.g. nature of OM, source of contamination).

Bioavailability: bioaccumulation assays

- 9 samples previously identified has representing a potential hazard (different soil properties and PAHs concentrations)

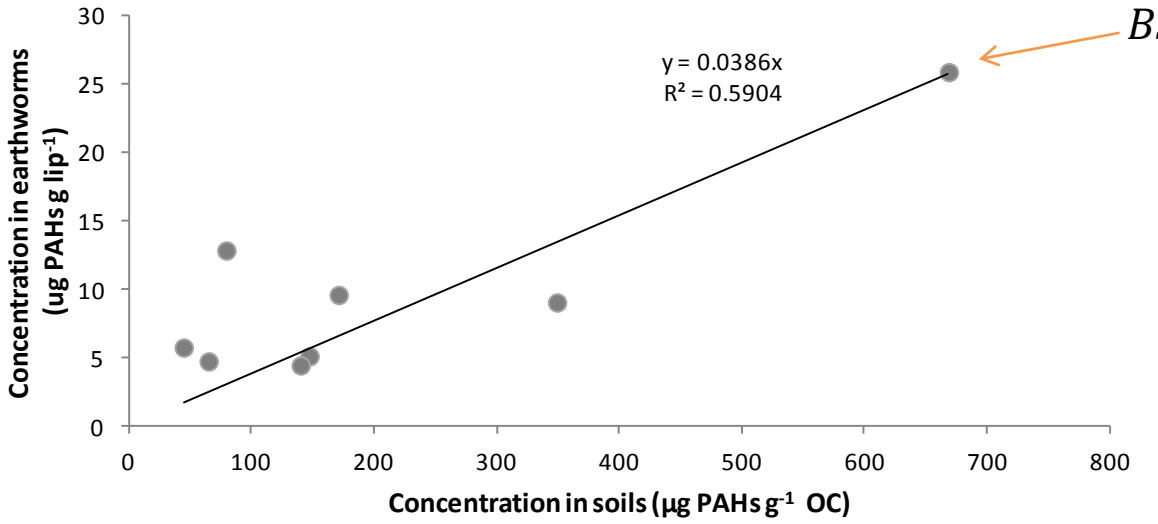
5 earthworms (*Eisenia andrei*) exposed to 250g of soil → (21 d) → Depurated and frozen

Depurated and frozen → Extraction of PAHs by methanolic saponification and cleanup by SPE → GC/MS analysis

Accumulated percentages in worms ranged between 1 and 9% of total concentrations

Biota-to-soil accumulation factor

$$BSAF = \frac{(C_{worm} \times f_{OC})}{(C_{soil} \times f_{lip})}$$



Low slope

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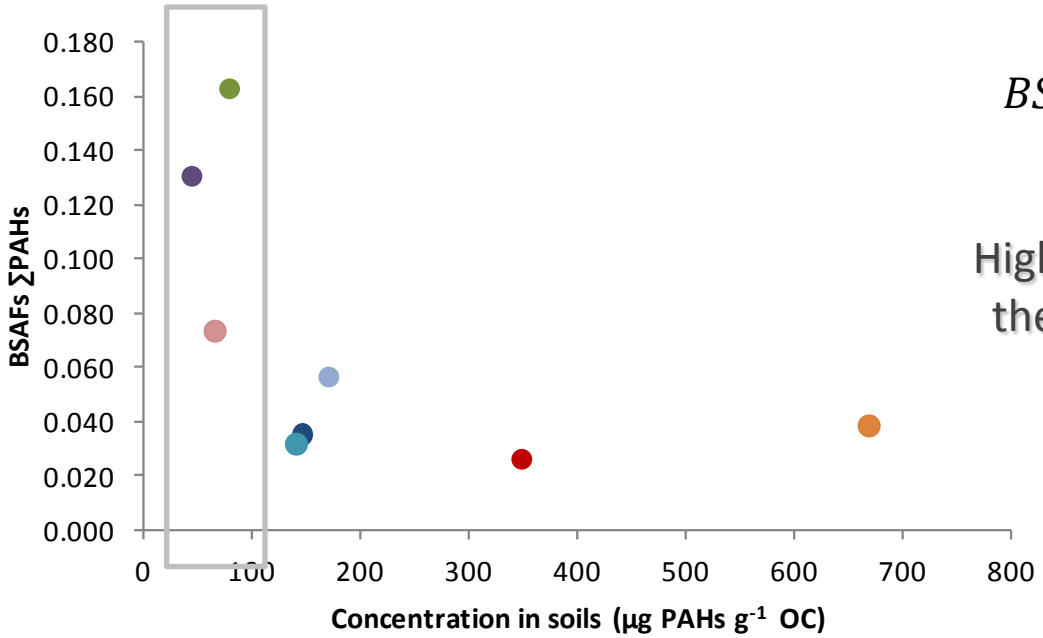
Low bioavailability

High variability

Bioavailability: bioaccumulation assays



Biota-to-soil accumulation factor

$$BSAF = \frac{(C_{worm} \times f_{OC})}{(C_{soil} \times f_{lip})}$$

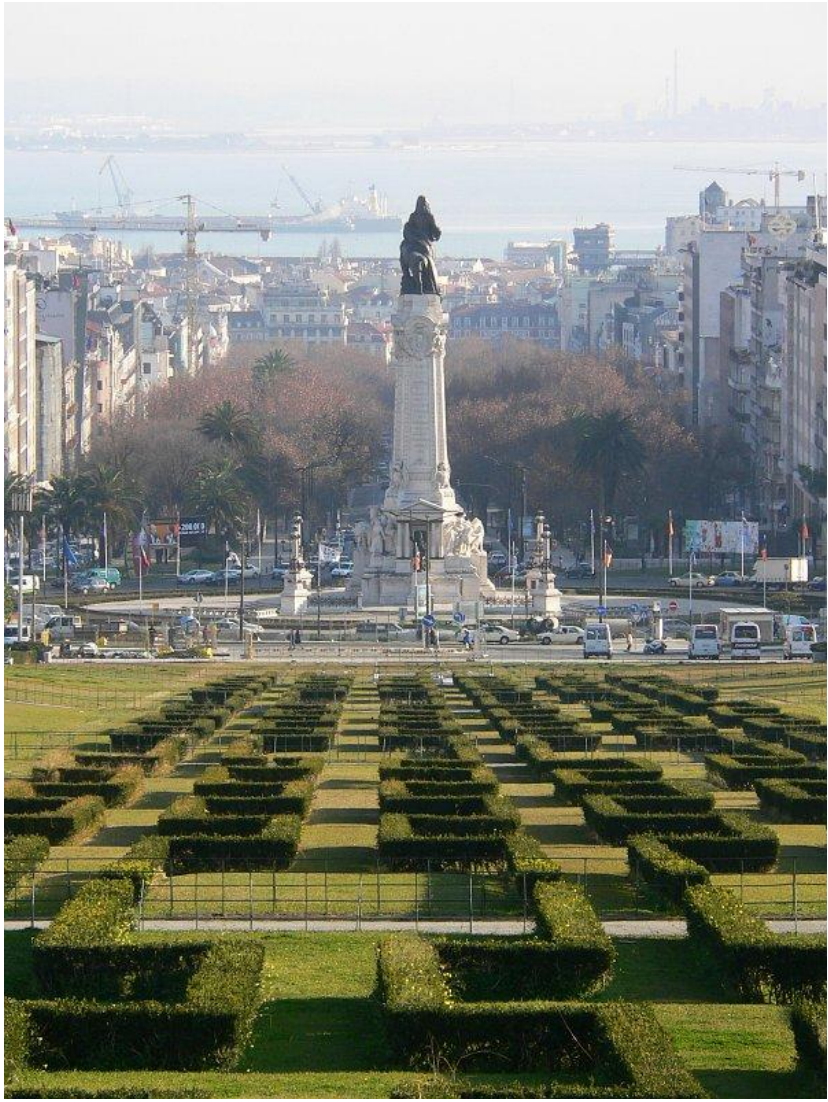
Higher BSAF values in samples with the lowest concentrations in soils

- Behavior similar to the water soluble fraction
- Sequestration; ageing of contaminants in soils due to long term accumulation
- No clear relationship between soil properties studied and bioaccumulation

Conclusions

- Great heterogeneity of PAHs concentrations in Lisbon urban soils and some "hotspots" were identified.
- In a first approach the comparison of total concentrations with guidelines allow the identification of areas of concern.
- Based on total concentrations the ecological functions of soils may be affected in some areas. However, the number of samples depend of the guideline or ecotoxicological endpoint selected.
- The use of geostatistical tools allow to create prediction maps and indentify areas of concern and where a more detailed risk assessment is needed.
- Results of the bioavailable and water soluble fractions suggest that PAHs in Lisbon soils are not available and probably levels found are a result of a long term accumulation.

Thanks for your attention



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