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Risk elements in urban agricultural spaces in greater Madrid, Spain; surveying soil quality

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1. Introduction & rationale

Land use in urban areas is transient and rapidly changing with the constant cycle of development and metabolism in the city. As such many urban soils have been augmented or deepened through past waste disposal (Davidson et al., 2006; He and Zhang, 2006) leading to the large heterogeneity in soil properties found (Hollis, 1991). In urban topsoils, physico-chemical characteristics and concentrations of heavy metals have been shown to vary considerably over relatively small geographical scales and between centres of urbanisation (Madrid et al, 2002, 2007) creating elevated levels of ‘risk elements’ (Hursthouse et al, 2004, Thums et al, 2008) as a distinguishing feature of many urban soils. In themselves, elevated concentrations of so called ‘risk elements’-those which are potentially toxic to humans, such as heavy metals-present low risk without transfer from soil to people. However, in urban agricultural spaces two exposure routes could exist, by which people could be in contact with risk elements; through direct contact (Figure 1; left) with soils and by plants grown on contaminated soils (Figure 1; right), which can accumulate heavy metals in their edible parts (leaves, fruits etc). Metabolism of some risk elements within the body are associated with toxicity symptoms ranging from mild nausea to carcinogenicity depending on exposure.

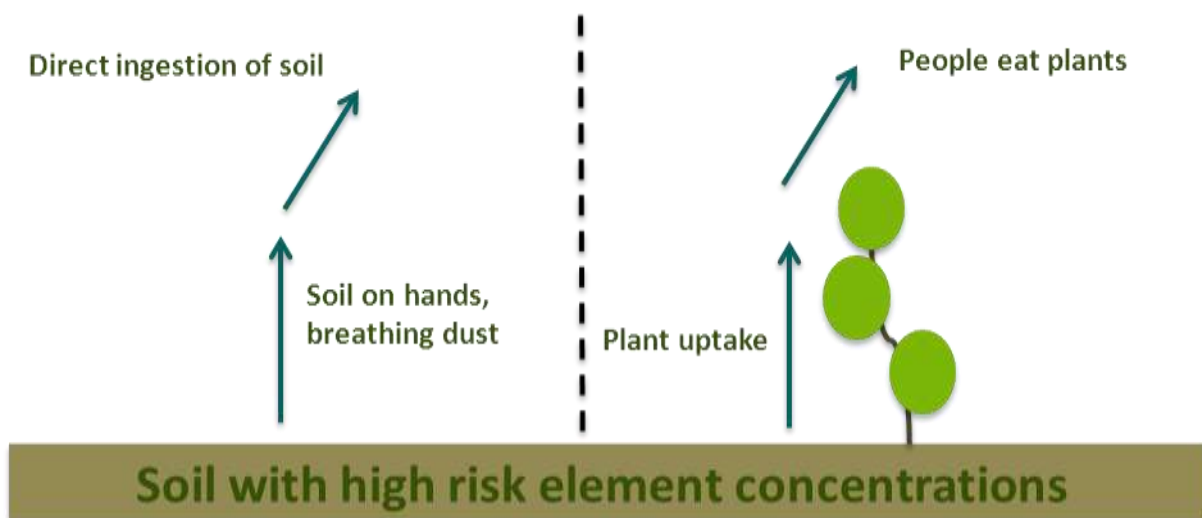


Figure 1. Example exposure routes of risk elements to humans in urban agricultural spaces

Several systematic soil surveys of urban areas have revealed concentrations of risk elements greatly variable across small geographical areas, often exceeding guidelines for safe agricultural practices. For example, Madrid et al (2007) sampled 63 soils across 3 cities and found higher Zn and Pb levels, compared to other measured elements, in 2 out of 3 cities (at up to 210 mg kg⁻¹ and 237 mg kg⁻¹ Zn and Pb respectively). Ruiz-Cortes et al. (2005) similarly measured total metal concentrations in 51 soils from 0-10 cm depth, also including urban areas of Seville, Spain, finding that Zn and Pb were present in greatest concentrations at up to 137 mg kg⁻¹ and 725 mg kg⁻¹ respectively with Cd concentrations also recorded, of 0.18 – 4.85 mg kg⁻¹. Urban agricultural practises also use many home-made composted wastes, as fertilisers, which may also introduce risk elements into the urban agricultural food system either because the source is contaminated or due to aerial deposition of risk elements. A survey of risk elements in a variety of crops from urban agriculture sites in Berlin, Germany, revealed that risk element concentration and thus risk was related to a wide variety of factors apart from the crop type grown; for example distance of the sites from roadsides, screening of the sites from roads by buildings, traffic density affect risk status, resulting in the need for a site specific approach to risk assessment (Saumel et al., 2012).

The aim of this work was to:

- 1) Identify several ‘typical’ UA spaces within Madrid city area, with special attention to those with previous industrial activity, or close to traffic emissions (sources of pollution)
- 2) Determine soil management practices (raised beds, use of existing soils, composts, manures etc)
- 3) Collect soils and composts/manures
- 4) Collect samples of the most commonly grown crops
- 5) Analyse soils and vegetation samples for risk elements, attempting to link previous land use, soil management and risk element concentrations together.

2. Study sites and methods

2.1 Study site locations

All study sites were located within the Madrid municipal area, centralised on the Atocha railway station, which was the assumed 'centre' of the city (Figure 2). In total 7 sites were surveyed, but 3 received more detailed examination and are the main focus of this report.

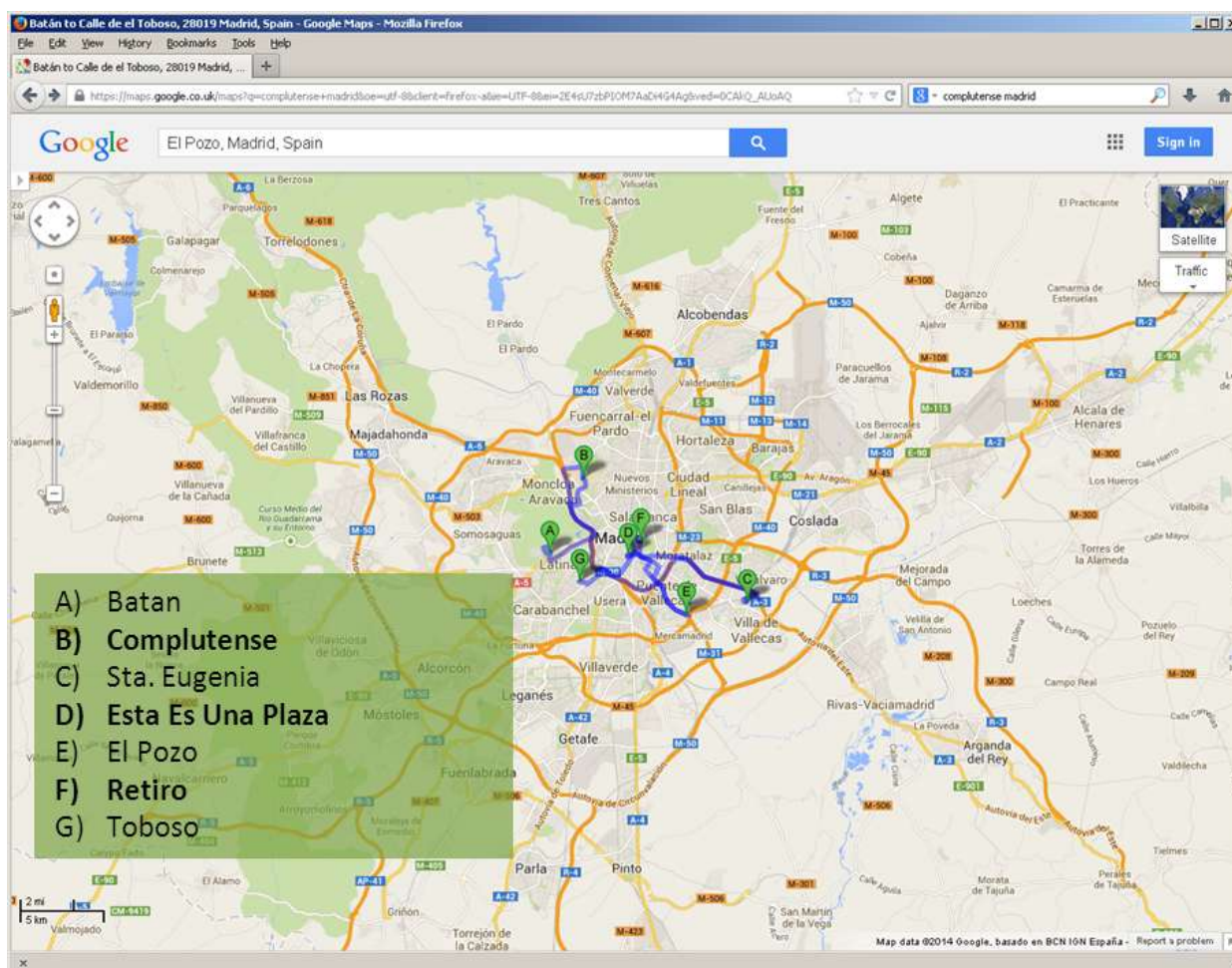


Figure 2. Locations of all surveyed study sites; those in bold text are covered in the most detail within this report.

Sites B, D and F were chosen for more detailed examination because they represent three distinctly different land uses and potential proximities to sources contamination. The range of risk elements that are expected in high concentrations, depending on the source and transport pathways of the contaminants, were thought to be most likely to be found at these sites (Table 1). Therefore, these sites represent typical scenarios of contamination of UA sites.

Table 1. Current land uses, and expected risk elements based on local contaminant sources and pathways, at study sites B, D and F.

Site	Current use	Likely pollutant sources	Expected risk elements
B. Complutense	University campus	Major motorway (aerial/runoff)	As, Pb, Zn [Pt, Pd, Sb]
D. Esta Es Una Plaza	Residential	Previous metallurgic industry (substrate)	Ag, Cu, Hg, Pb, Zn
F. Retiro	Park and gardens	Ambient (aerial)	Pb, Zn

2.2 Soils and crop collection and analysis

Before commencing sampling of soils and crops each site was examined by a walk over survey. This helped to identify possible hotspots of high concentrations of risk elements (Table 1), different soil management practices (raised beds, compost and manure addition etc.) and inform the best places to sample soils. Between 5-8 samples were taken, comprising composite bulk samples of 1kg from 3 locations within similarly managed areas of each site (for example raised beds with manure, existing soils with compost etc.). Samples were collected using a small trowel, which was cleaned between samples to avoid cross-contamination (Figure 3). Crop samples were collected by hand, with excess soil removed by shaking. Upon return to the laboratory crop material was washed in tap-water (Figure 3) and along with soils, air dried for 2 weeks at 25°C. Details of the collected samples can be found in Table 2.

Table 2. Samples inventory for each site.

Site	Soils	Wastes	Crops
B. Complutense	1) Soil borrow pit, 2) aromatics bed, 3) old amended bed, 4) freshly amended bed, 5) biochar amended bed, 6) 'bio-intensive' bed	1) Compost, 2) manure	1) Alfalfa, 2) thyme, 3) rosemary, 4) oregano, 5) beetroot, 6) red cabbage, 7) green cabbage, 8) lettuce 2013, 9) lettuce 2014, 10) broccoli, 11) chard, 12) cauliflower, 13) onion, 14) celery, 15) leek, 16) sprout
D. Esta Es Una Plaza	1) Upper terrace i, 2) upper terrace ii, 3) lower beds i, 4) lower beds ii	1) Compost, 2) bokashi	1) Tobacco, 2) lettuce i, 3) lettuce ii, 4) onion, 5) spinach, 6) spinach, 7) leek, 8) rosemary, 9) garlic
F. Retiro	1) Raised beds, 2) main beds i, 3) main beds ii, 4) main beds iii, 5) old amended bed i, 6) old amended bed ii, 7) fresh amended bed, 8) lemon tree plot	1) municipal compost, 2) horse manure, 3) home-made compost	1) Cellery, 2) garlic, 3) leek, 4) lettuce, 5) lemon tree, 6) cogollos, 7) sprouts, 8) spring onion, 9) onion, 10) spinach, 11) rosemary, 12) raddish, 13) red cabbage
Total	18	7	38

For analysis dried soil samples were lightly ground using a pestle and mortar, before sieving to pass a 2mm grate. Plant material was milled with a stainless steel blade. Trace element total concentrations were determined on dried sub-samples (approx. 3g) of soils using portable X-ray fluorescence (PXRF). Samples were held in a 25-mm diameter plastic cup with a 4- μm thick polypropylene window (TF-240 film, Fluxana, Germany) and analysed using a Bruker S-1 Turbo^{SD} PXRF instrument (Bruker Nano GmbH, Germany). The instrument was used in bench-top mode and analyses carried out using the manufacture's soil programme. A certified reference Chinese mineral soil (GBW07402) was included periodically in analyses to verify instrument accuracy. Pseudo-total trace metals and As determination for crops was by microwave digestion of 0.2 g samples in concentrated 14 M, GPR grade HNO_3 , analysed using ICP-MS. Certified reference material (CMI 7004) was used to verify accuracy, with recoveries consistently greater than 75%.



Figure 3. Soil sampling and drying in progress (inset; washing crops to remove adhered soil).

3. Results & discussion

3.1 Concentrations of risk elements in soils

Although analysis of the full range of risk elements had not been carried out at the time of writing (March/April 2014), preliminary data shows that soils collected from site D. (previous metallurgic industry) contained the highest concentration of Cu, Pb and Zn amongst the surveyed sites (Table 3) and higher values (especially for mean Pb) than soils collected from topsoils across EU member states, from roadside verges and from various locations in Madrid city limit. This is likely to be as a direct result of the previous industrial use at the site, and unlikely to be a result of leaded fuel usage and aerial deposition of Pb. At the other surveyed sites, for example site B. (Complutense), the sampled plot was approx. 20m from a major road. In this case, and as found by other authors (Werkenthin et al., 2014) it could be expected that a high concentration of Pb in soil is the result of historically prolonged soil exposure to road dusts and runoff waters containing Pb, Sb and other elements. In this case Pb isotope analysis could confirm the provenance of the Pb source.

Table 3. Mean concentrations of selected risk elements in surveyed sites, compared to literature values for various previous soil surveys.

Site/soils	Mean soil Cu concentration (mg kg ⁻¹)	Mean soil Pb concentration (mg kg ⁻¹)	Mean soil Zn concentration (mg kg ⁻¹)
D. Esta Es Una Plaza	52	353	156
Others	9.5-26	12-99	66-107
<i>EU topsoil concentrations^a</i>	14	16	52
<i>EU roadside topsoils^b</i>	40	90	180
<i>Madrid survey^c</i>	72	161	210

^a Lado et al., 2008; 1588 samples across 26 EU countries

^b Werkenthin et al., 2014; 57 samples

^c Miguel et al., 1998; 55 samples within Madrid municipal area

3.2 Concentration of risk elements in crops

Measured Cu, Pb and Zn concentrations in crops varied but reflected a general tendency that aromatics accumulated an order of magnitude greater concentration of Pb than leafy or root species at site D. (high soil Pb; table 4). Across the other sites the maximum accumulation of Cu, Pb and Zn was generally highest for aromatics (<51 mg kg⁻¹ dry weight), probably due to their perennial growth. Until full analysis is carried out it is difficult to say if this trend will be reflected across the other sites, but it is likely.

Table 4. Mean concentrations of selected risk elements in surveyed crops, grouped by edible part.

Edible portion	Range Cu concentration (mg kg⁻¹)	Range Pb concentration (mg kg⁻¹)	Range Zn concentration (mg kg⁻¹)
Leaves	9-15	0.4-1.3	77-98
Root	4.3	0.6	49
Aromatic herbs	8.5-21.5	1.5-10.8	27-45

Other authors have noted variable trends in metal accumulation in crops grown on roadside soils depending on traffic density, element, species and whether existing soils were used or soil replacement occurred (Wiseman et al., 2013). This has implications in the current study related to the various incorporations of amendments to the study site soils. Again, full analysis will reveal these intricacies.

4. Conclusions & future directions

There is no doubt that increased risks of exposure to contamination can occur at urban agricultural sites, depending on site management, proximity to contaminant sources and historic land use. The next stages of this work will:

- 1) Carry out full risk element analysis, including Pt group elements
- 2) Correlate the proximity, historic uses and soil management of the sites with risk element prevalence
- 3) Expand the scope of this work to invite all COST action members to submit samples for risk element analysis, from their plots.

Following stages 1 and 2 a publication will be prepared for submission a journal such as 'Journal of Environmental Management'. Stage 3 may contribute to the COST action atlas project and to another publication.

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