Solid-phase distribution and human oral bioaccessibility of Pb and Zn in outdoor dusts of Estarreja, Portugal

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•The study area is in the scope of OHMI Estarreja that was created in 2010 by the CNRS.

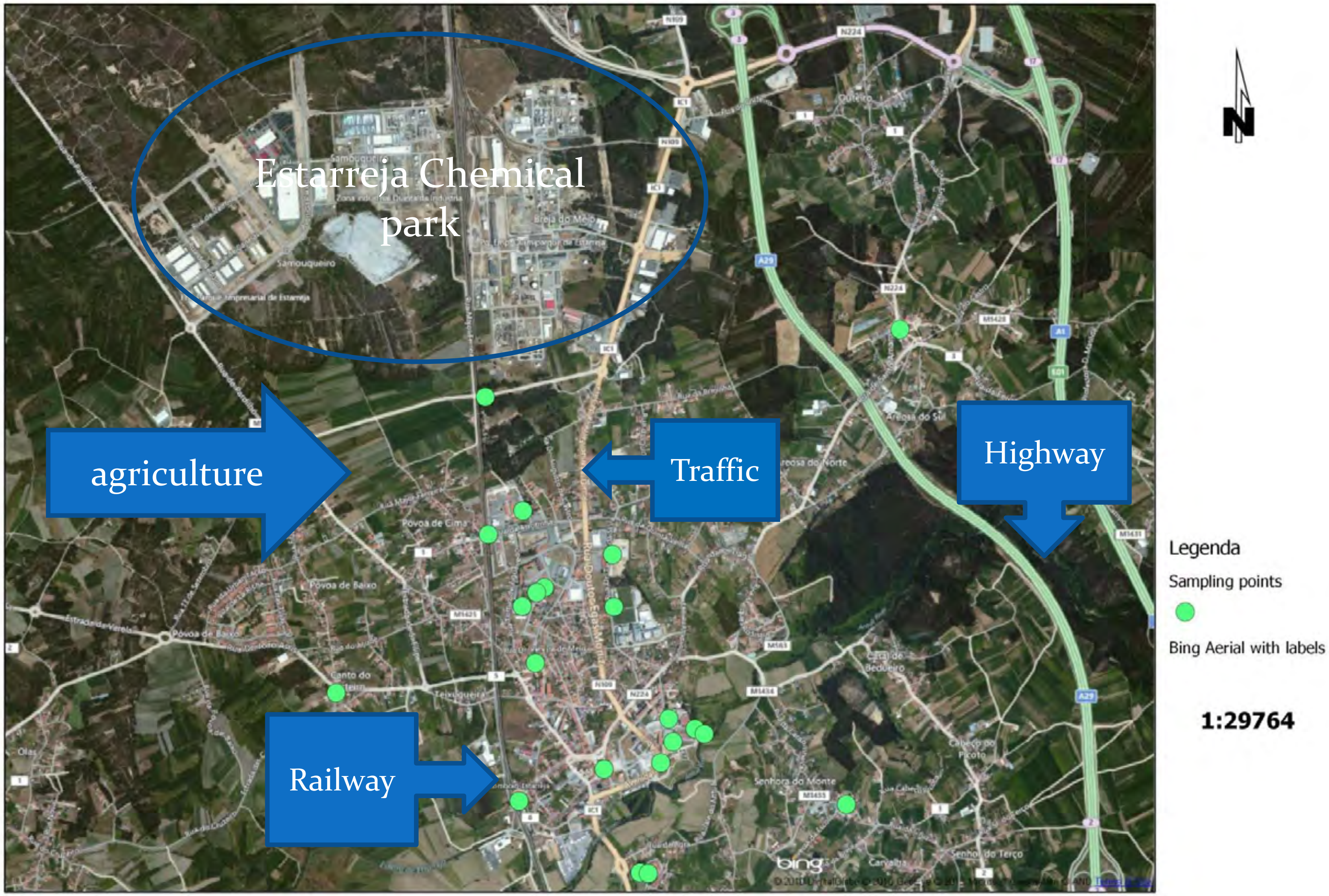
•As the OHM-BMP, the OHMI Estarreja it is an urban/industrial site; these OHM have some similarities but also significant differences;

•However their main aim is to study the motley effects of industrial activity in the environment and the local community.

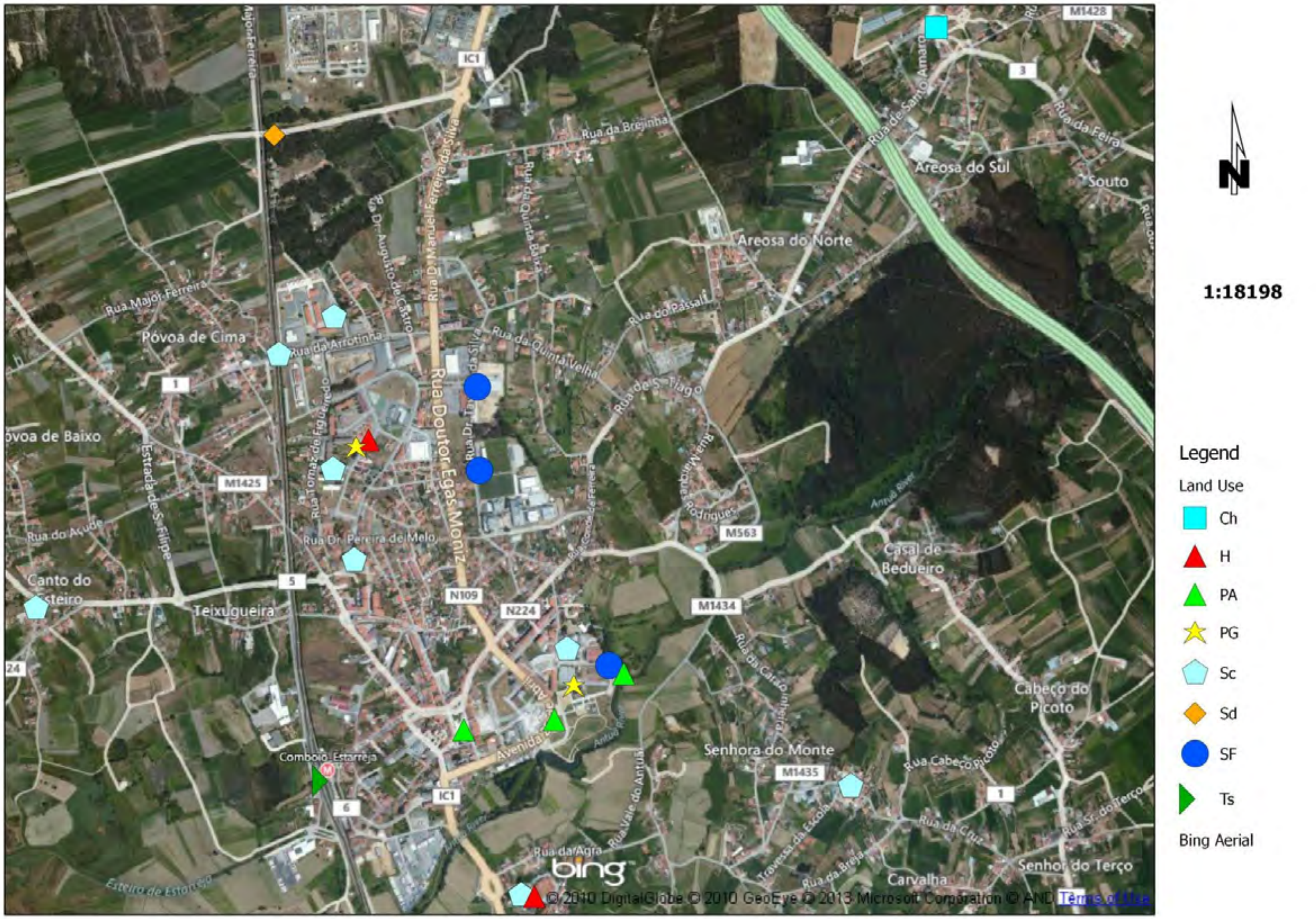
Aims:

- Sampling dust in an urban area close to a chemical complex;
- Determining near-total concentrations of Pb and Zn;
- Estimating oral human bioaccessibility of Pb and Zn;
- Investigating the solid-phase distribution of Pb and Zn.

Sampling – surface dust



Selected sites



Ch – church; H – health center; PA – public area; PG – playground; Sc – School; Sd – street dust; SF – sport facilities; Ts – train station.

Selected sites

Analysis

- Total concentration of 67 elements were analyzed by ICP-MS at a commercial laboratory.
- Oral bioaccessibility of Pb and Zn were determined using the Unified BARGE Method (UBM).
- Pb and Zn solid phases distribution studies were carried out using the newly modified sequential Extraction proposed by Cardoso Fonseca (1982).

Unified BARGE Method - UBM

Saliva gastric, bile and duodenal solutions

2 x 0.6 g sub-samples

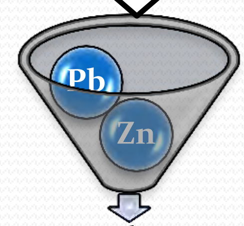
Saliva and gastric fluids were added to 2 samples, the pH was fixed at 1.2±0.05

End over end extraction at 37ºC for 1h (represents the stomach)

Bile and duodenal fluids were added to 2nd sample, the pH was adjusted to 6.3±0.5

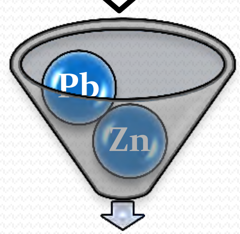
End over end extraction at 37ºC for 4h (represents the small intestine)

Sample centrifuged at 4500g for 15 min, 1 ml supernatant removed and diluted with 9 ml of 0.1 M HNO3



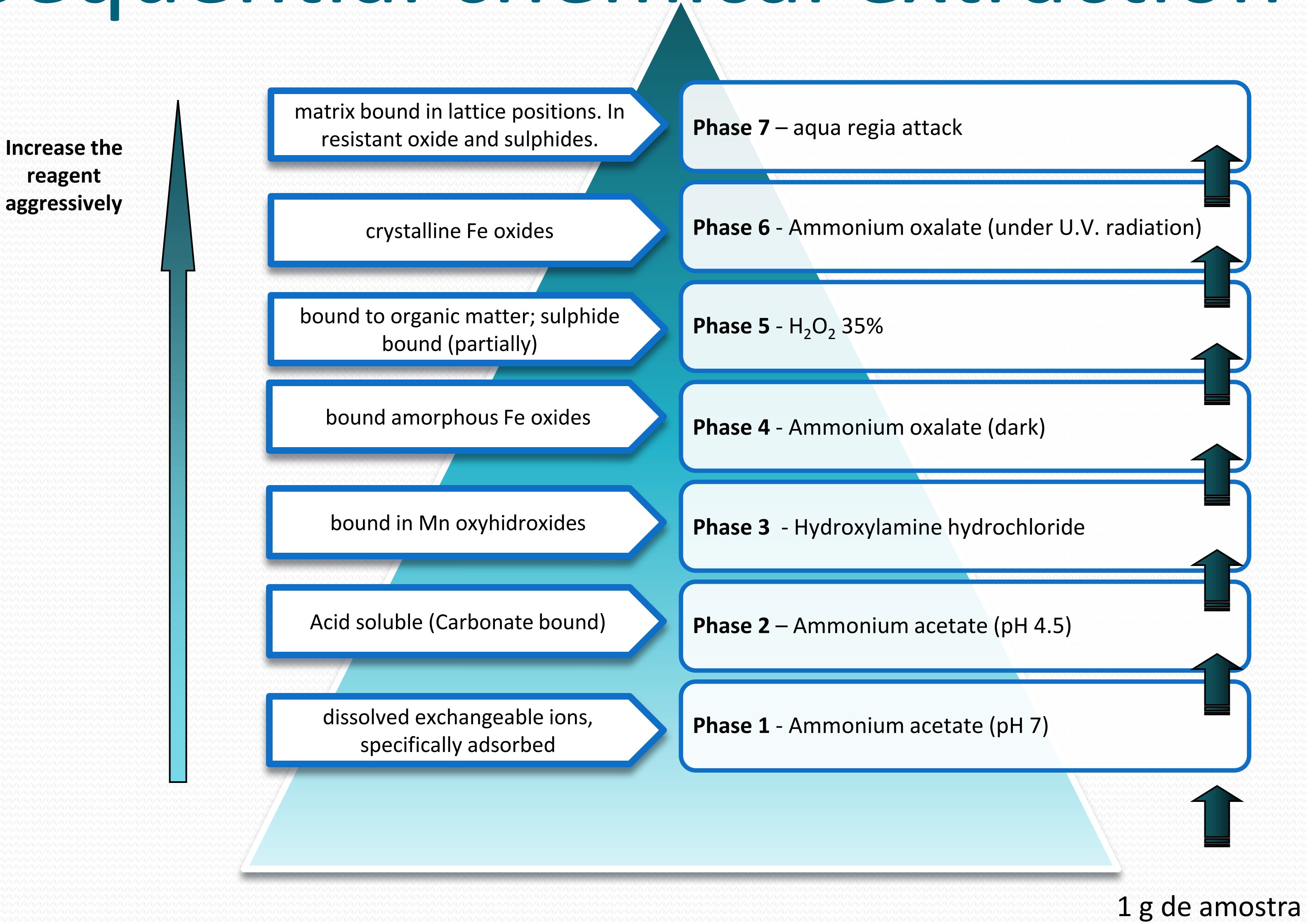
GI Phase

1 sample centrifuged at 4500g for 15 min, 1 ml supernatant removed and diluted with 9 ml of 0.1 M HNO3



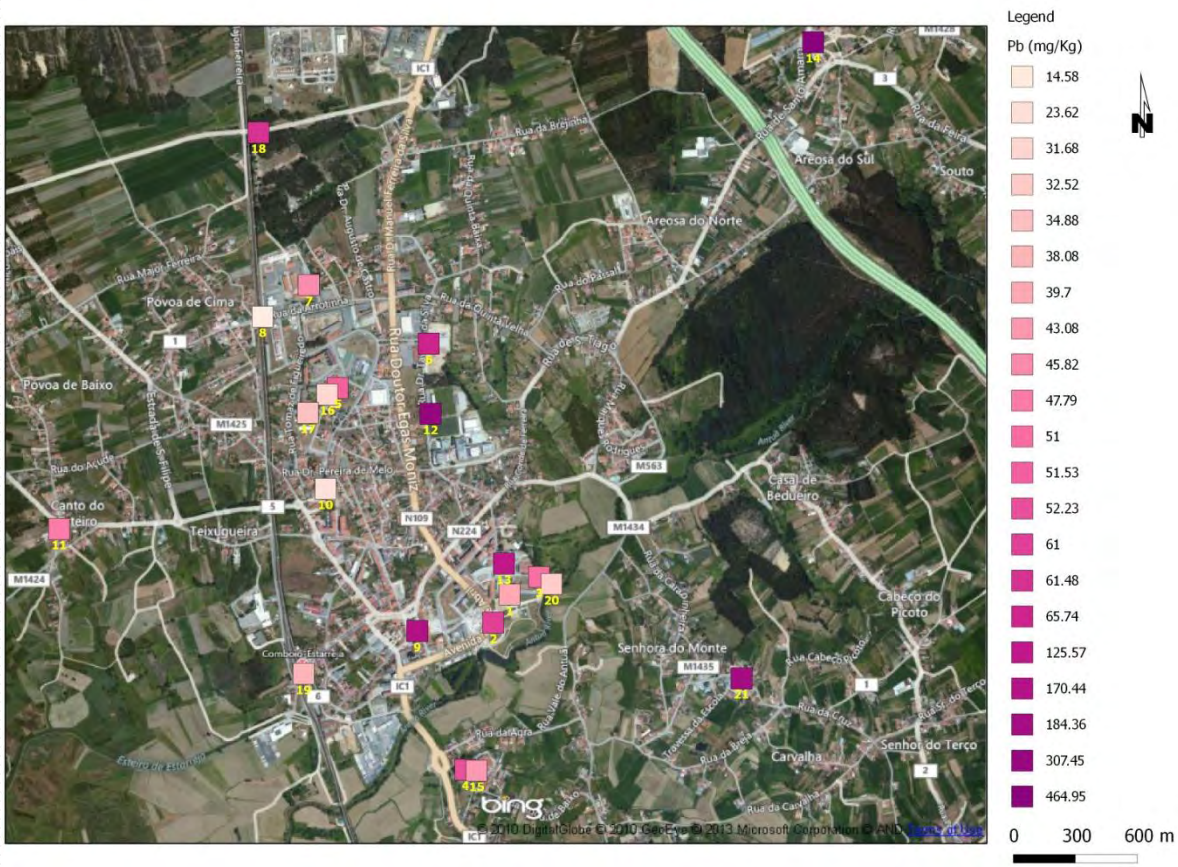
G Phase

Sequential chemical extraction



Each reagent or mixture being able to dissolve in a selective way a particular mineralogical constituent. From phase 1 to phase 7 the used solutions have increasing extracting strength.

Results – Near total Pb concentration

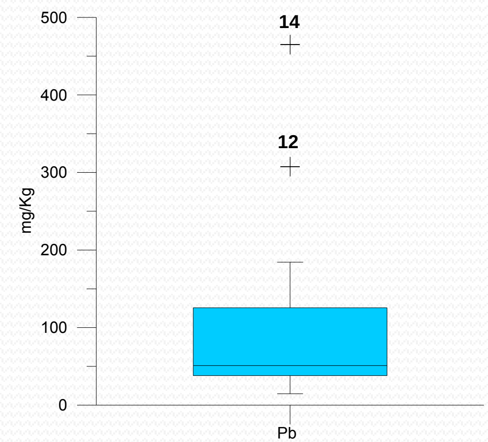


- Ranges from 15-465 mg/Kg;
- Median= 51.0 mg/Kg

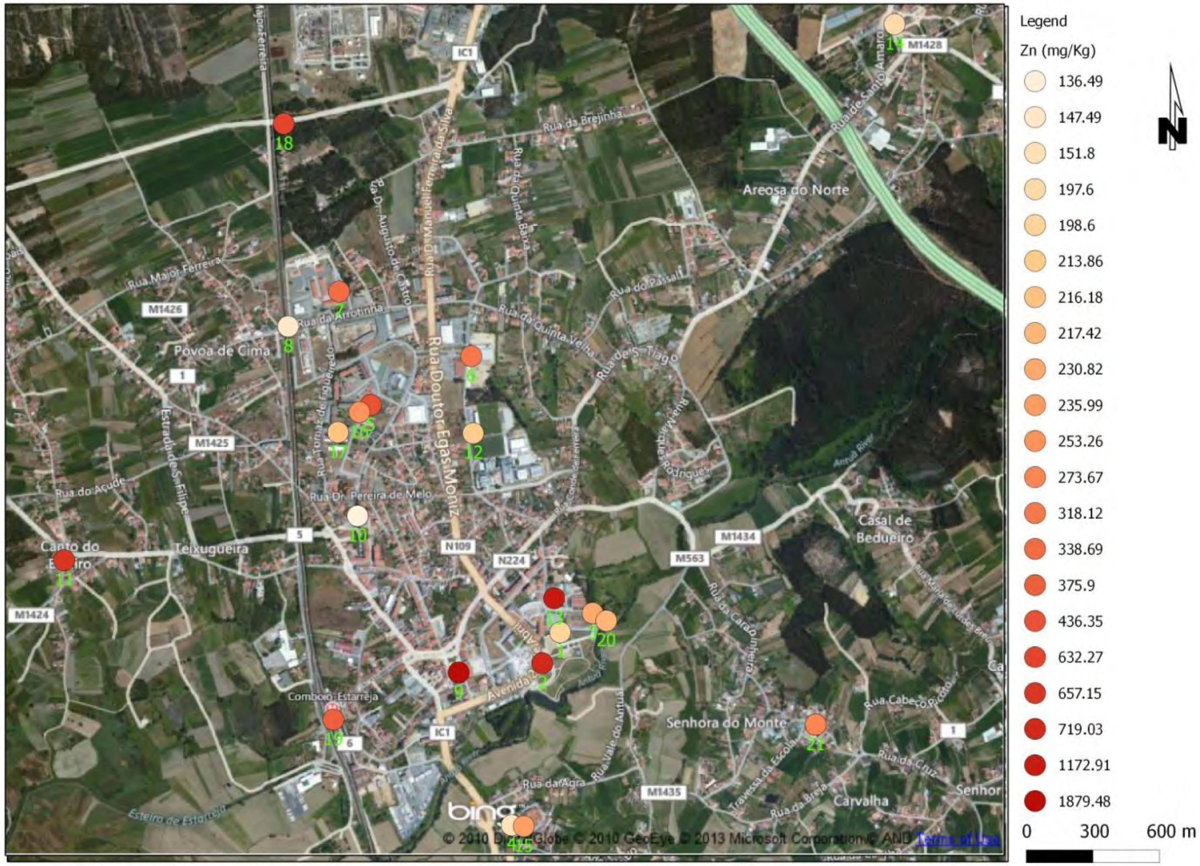
•The spatial distribution is irregular suggesting anthropogenic point-sources;

•In Europe, the lead standards for residential soils range from 40 to 150 mg/Kg. If we consider that a hazard exists when the Pb above 150 mg/Kg, only 2 samples represent a probable risk.

•Comparing average concentrations with other cities, the mean Pb concentration of Estarreja is not elevated (Newcastle – 992mg/kg – Okarie et al., 2012; Guangzhou, China- 240 mg/Kg – Duzgoren-Aydin et al., 2006; Manchester – 265 mg/kg – Robertson et al., 2003).

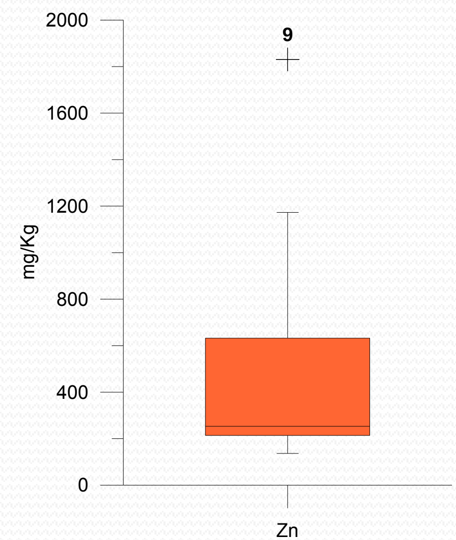


Results – Near total Zn concentration



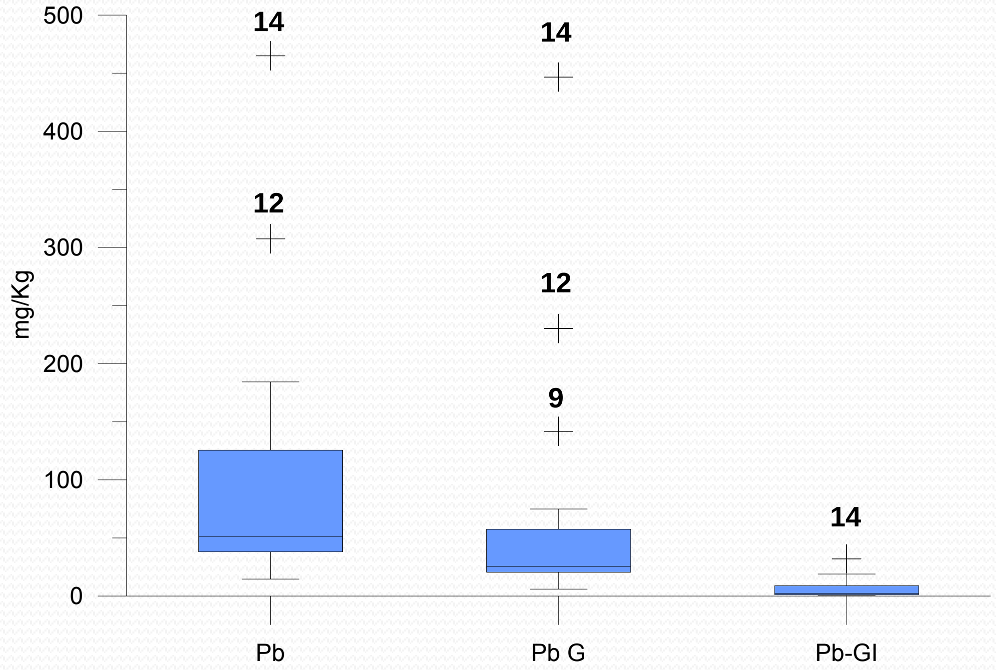
- Ranges from 136.5-1879.5 mg/Kg;
- Median= 253.3mg/Kg

•The spatial distribution is irregular, the concentrations of Zn are site-specific suggesting anthropogenic point-sources.



•Comparing average concentrations with other cities, the mean of Zn concentrations is similar with main cities (Newcastle – 421mg/kg – Okarie et al., 2012; Manchester – 653 mg/kg – Robertson et al., 2003; Guangzhou, China- 586 mg/Kg – Duzgoren-Aydin et al., 2006.

Results – Bioaccessible Pb concentration



•Bioaccessible concentrations (G-phase): 5.9-446.6 mg/kg, median= 25 mg/ kg

•Gastric extraction shows a higher bioaccessibility than gastro-intestinal extraction (enzymes addition and higher pH, complexation and precipitation of Pb)

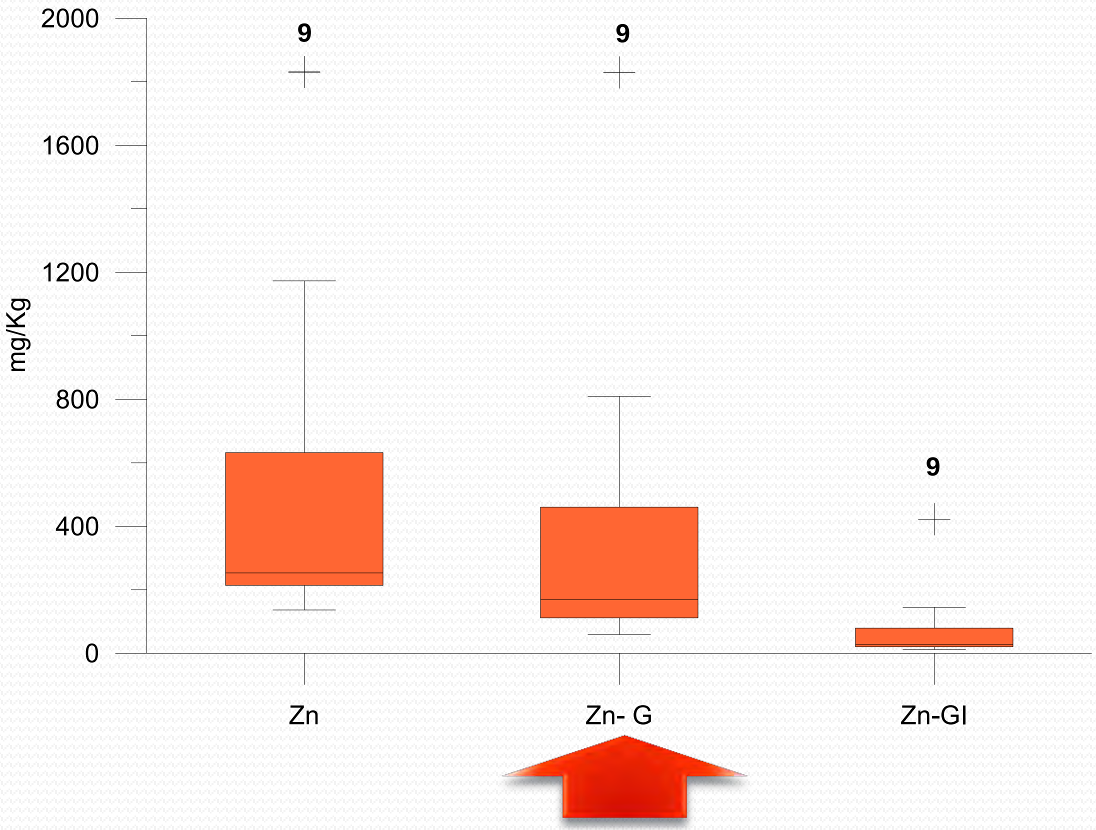
•The gastro bioaccessibility proved to be a good estimate of the overall Pb bioavailability [Casteel, 2007; US-EPA, 2007]

•only the gastro-saliva results will be presented here.

Casteel, S.W.; Weis, C.P.; Henningsen, G.M.; Brattin, W.J. Estimation of relative bioavailability of Pb in soil and soil-like materials using young swine. Environ. Health. Perp. 2007, *114 (8), 1162–1171.*

US-EPA. Estimation of relative bioavailability of Pb in soil and soil-like materials using in vivo and in vitro methods. OSWER 9285, 7–77, 2007.

Results – Bioaccessible Zn concentration

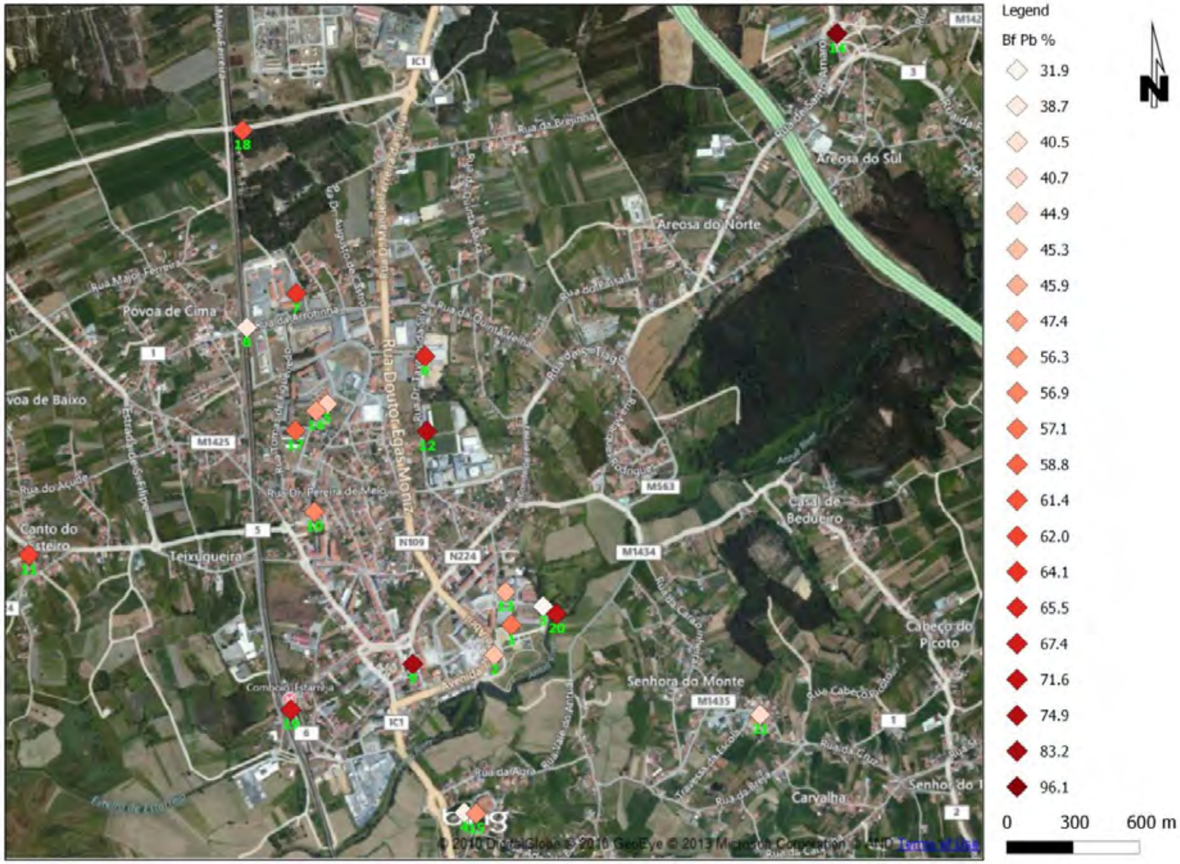


•Bioaccessible concentrations (G-phase): 59.1-1830 mg/kg, median= 168.6 mg/ kg

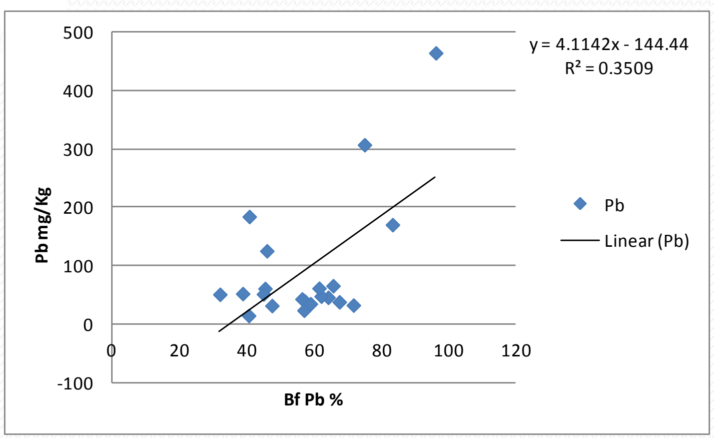
•Gastric extraction shows a higher bioaccessibility than gastro-intestinal extraction.

•only the gastro-saliva results will be presented here.

Results - Bioaccessible Fraction

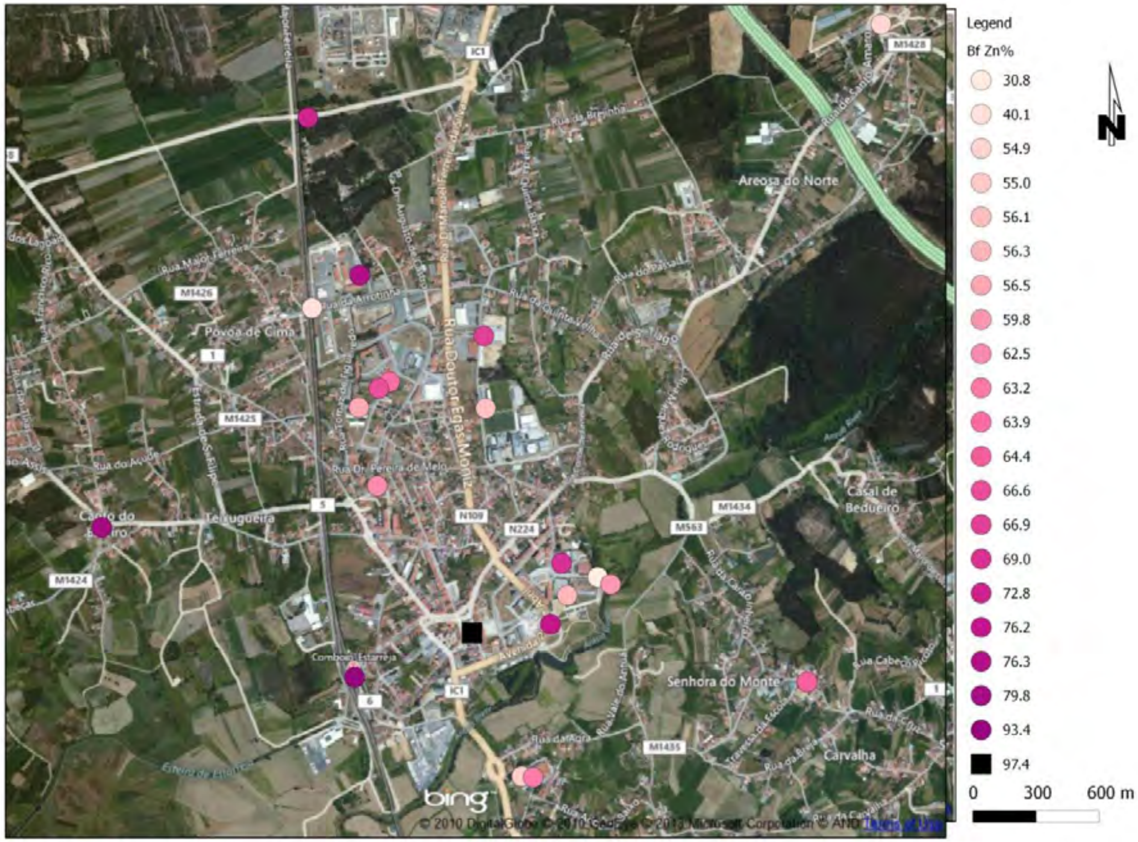


Bf Pb % = bioaccessible Pb(mg/kg)/ Total of Pb (mg/Kg) * 100

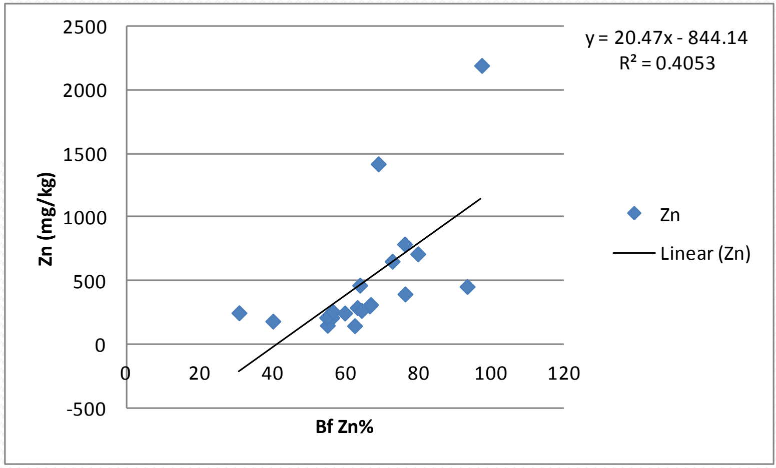


- Ranges from 31.8 – 96.1%; median= 57%
- No spatial correlation between Bf% and total Pb concentration.

Results - Bioaccessible Fraction

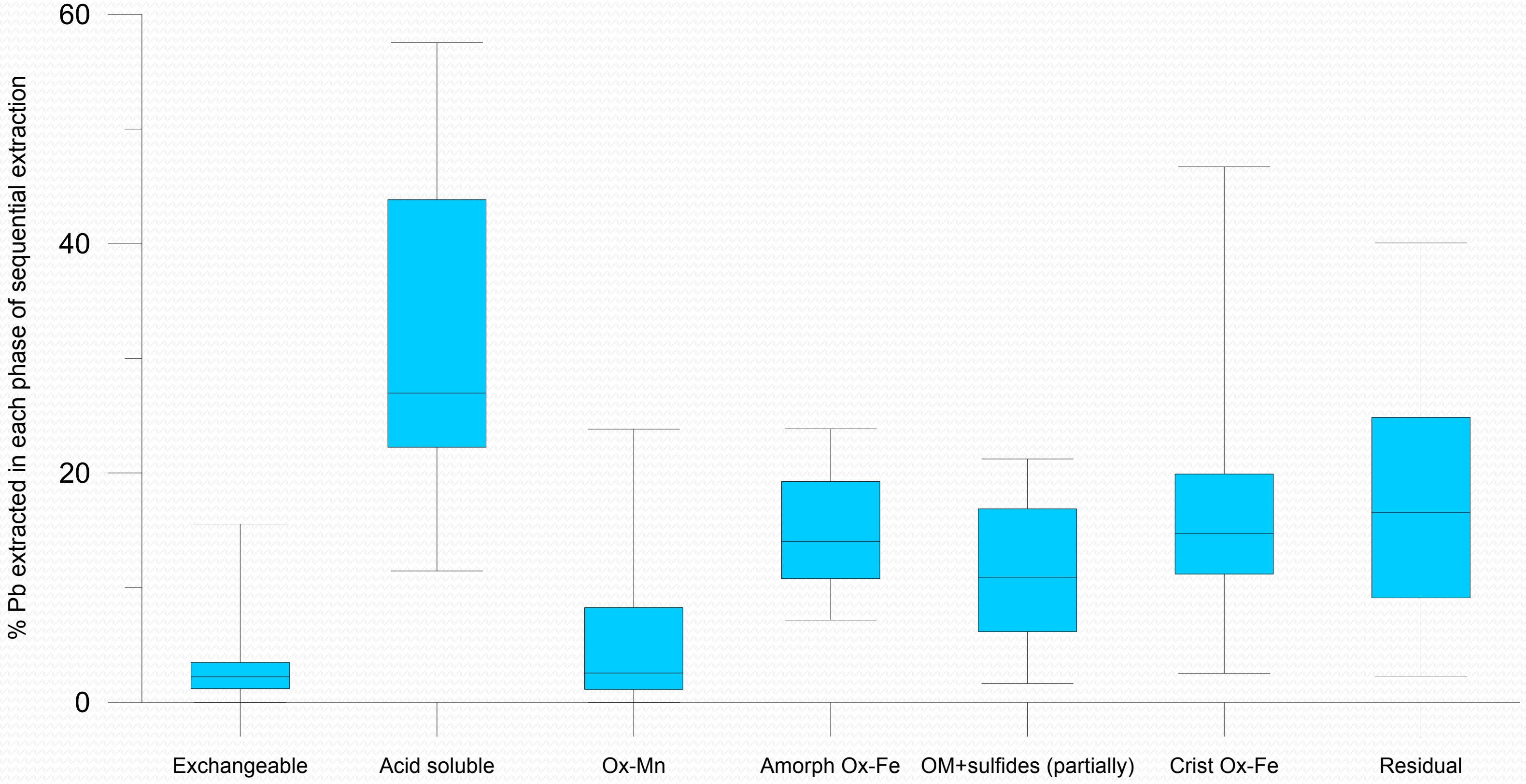


Bf Zn % = bioaccessible Zn (mg/kg)/ Total of Zn (mg/Kg) * 100



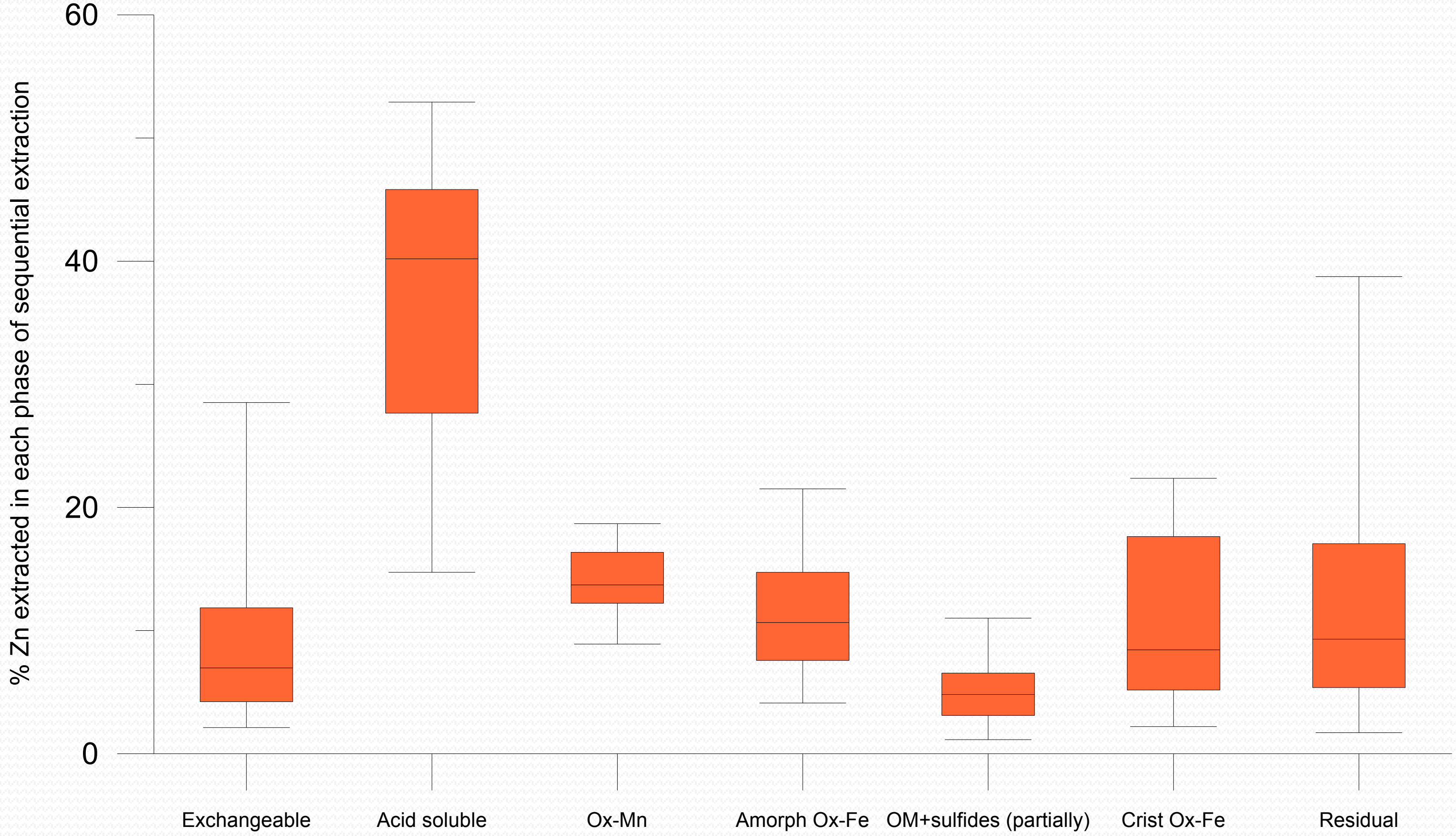
- Ranges from 30.8 – 97.4%; median=63.9%
- No spatial correlation between Bf% and total Zn concentration.

Results – Solid-phase distribution of Pb



- The major Pb-phases are, by decreasing order, **acid-soluble** phase (median = 26.95 mg/Kg), **residual** phase (median = 16.55 mg/Kg), **Crist OxFe** phase (median = 14.74 mg/Kg), **Amorphous Ox-Fe** phase (median = 14.04 mg/Kg), **OM** (median = 10.91 mg/Kg), **Ox-Mn** phase (median = 2.57 mg/Kg) and **exchangeable** phase (median = 2.23 mg/Kg).

Results – Solid-phase distribution of Zn



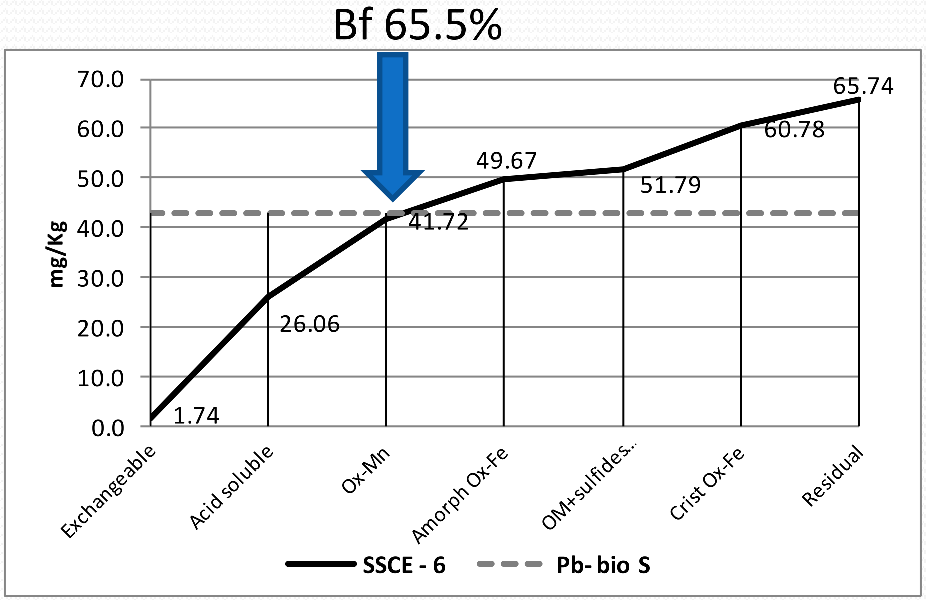
• The major Zn-phases are, by decreasing order, **acid-soluble** phase (median = 101.8 mg/Kg), **Ox-Mn** phase (median = 34.1 mg/Kg), **Crist OxFe** phase (median = 30.6 mg/Kg), **residual** phase (median = 28.04 mg/Kg), **Amorphous Ox-Fe** phase(median = 24.5 mg/Kg), **exchangeable** phase (median = 17.1 mg/Kg) and **OM** (median = 11.9 mg/Kg).

Results – Solid-phase distribution to understand the bioaccessibility estimates

Discriminate three different groups:

•Group I - bioaccessible Pb is probably in the acid soluble and Ox-Mn phases;

Group I
(samples 5, 6, 7, 8, 18, 21)



Results – Solid-phase distribution to understand the bioaccessibility estimates

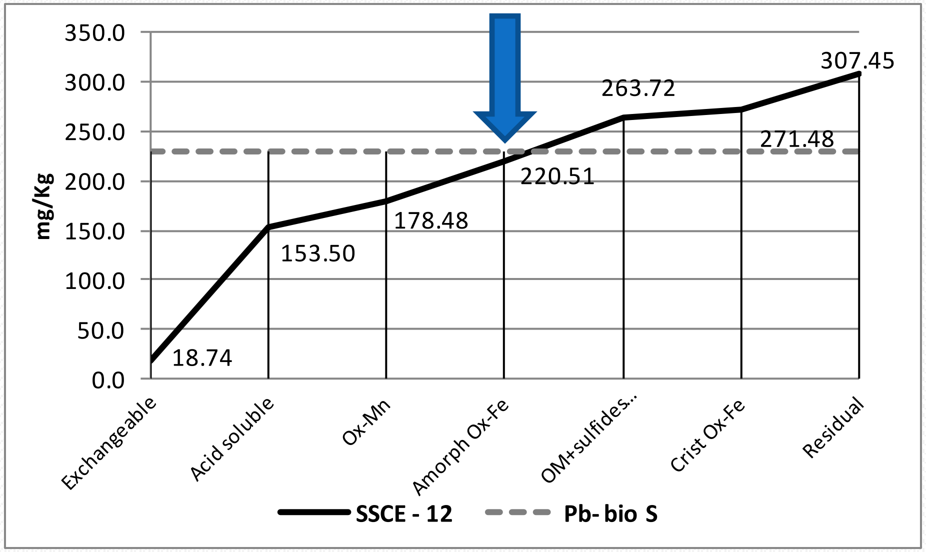
Discriminate three different groups:

•Group I - bioaccessible Pb is probably in the acid soluble and Ox-Mn phases;

•Group II - bioaccessible Pb is probably in the acid soluble and amorphous OX-Fe phases;

Group II
(samples 2, 3, 4, 12, 16)

Bf 74.0%



Results – Solid-phase distribution to understand the bioaccessibility estimates

Discriminate three different groups:

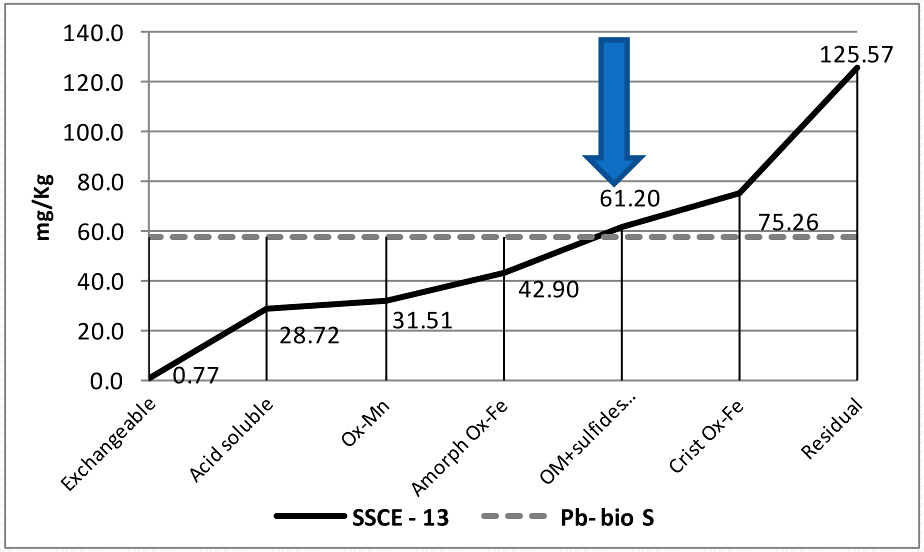
•Group I - bioaccessible Pb is probably in the acid soluble and Ox-Mn phases;

•Group II - bioaccessible Pb is probably in the acid soluble and amorphous OX-Fe phases;

•Group III - bioaccessible Pb is probably in the acid soluble, amorphous OX-Fe and OM phases ;

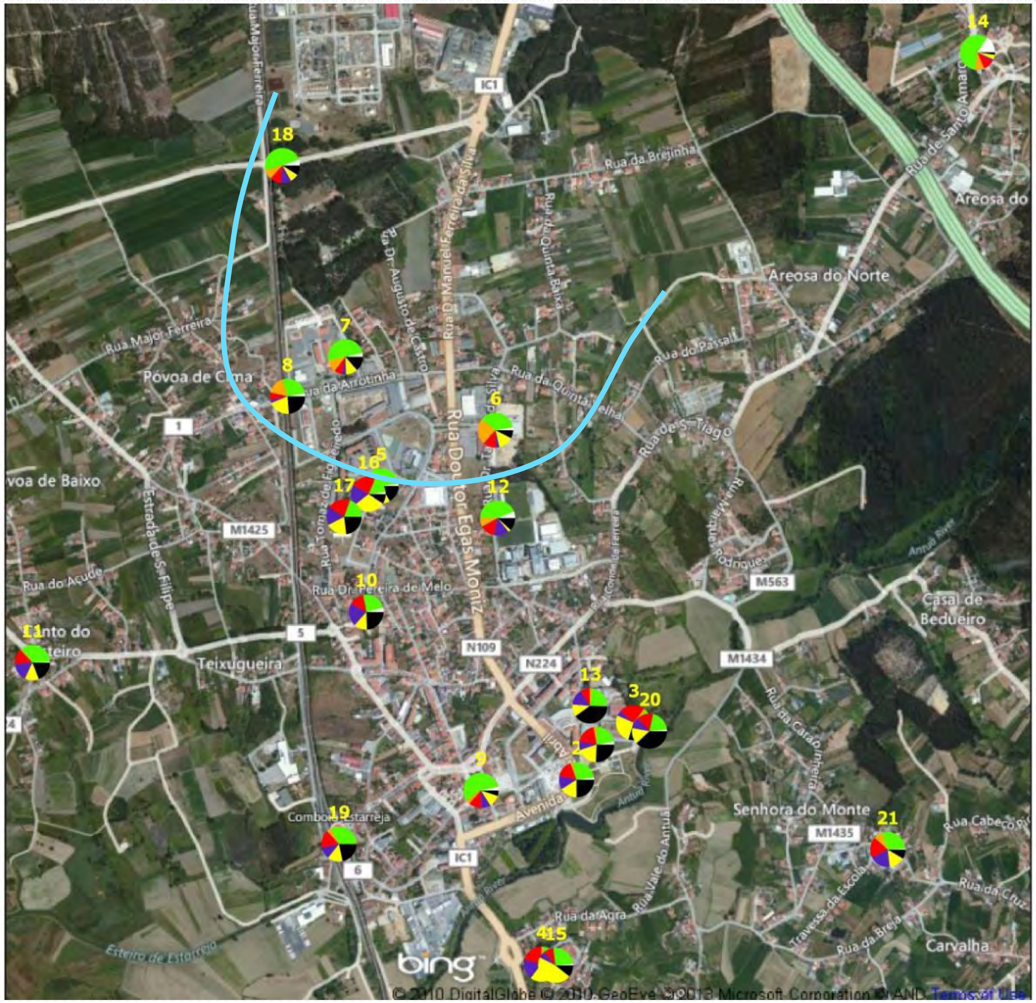
Group III
(samples 1, 9, 10, 11, 13, 14, 15, 17, 19, 20)

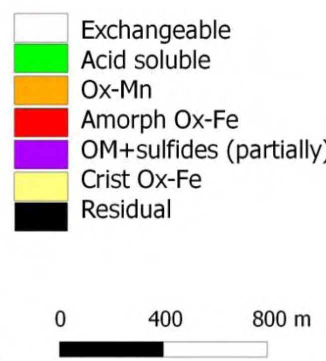
Bf 45.9%



Results – Spatial distribution of Group I

- **Group I - bioaccessible Pb in the acid soluble and Ox-Mn phases;**





Sample 5: 43%
Sample 6: 63%
Sample 7: 65%
Sample 8: 47%
Sample 18: 63%

Important metal fractions are in soluble dust phases – indicates an important anthropogenic input

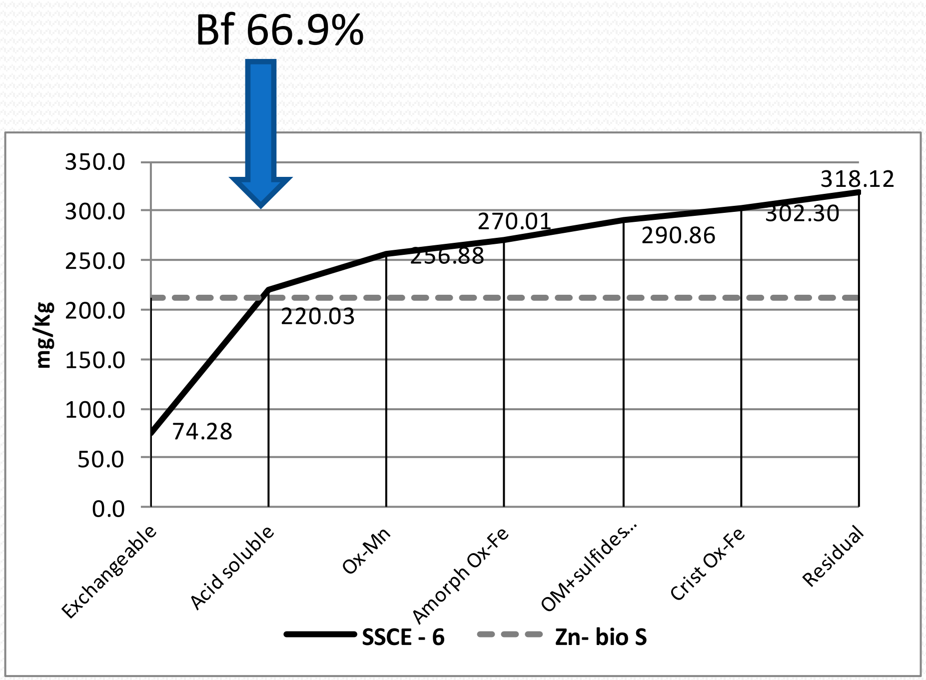
- Pb was mainly extracted in the acid-soluble phase for samples located within 1.5 km ranges from the chemical complex;

Results – Solid-phase distribution to understand the bioaccessibility estimates

Discriminate four different groups:

•Group I - bioaccessible Zn is probably in the exchangeable and acid soluble phases;

Group I
(samples 6, 18)



Results – Solid-phase distribution to understand the bioaccessibility estimates

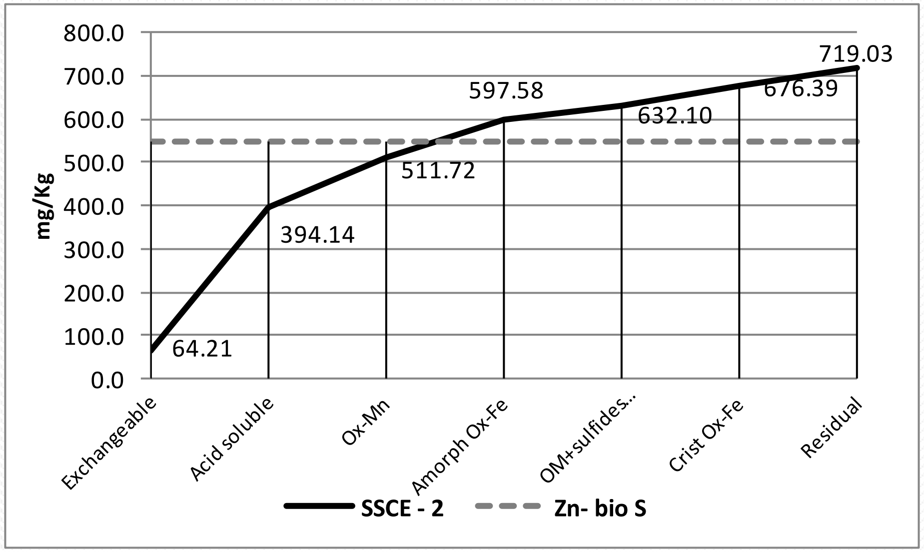
Discriminate four different groups:

•Group I - bioaccessible Zn is probably in the exchangeable and acid soluble phases;

•Group II - bioaccessible Zn is probably in the acid soluble and Ox –Mn phases.

Bf 76.2%

Group II (samples 2, 3, 4, 5, 7, 8, 11, 16 and 21)



Results – Zn solid-phase distribution to understand the bioaccessibility estimates

Discriminate four different groups:

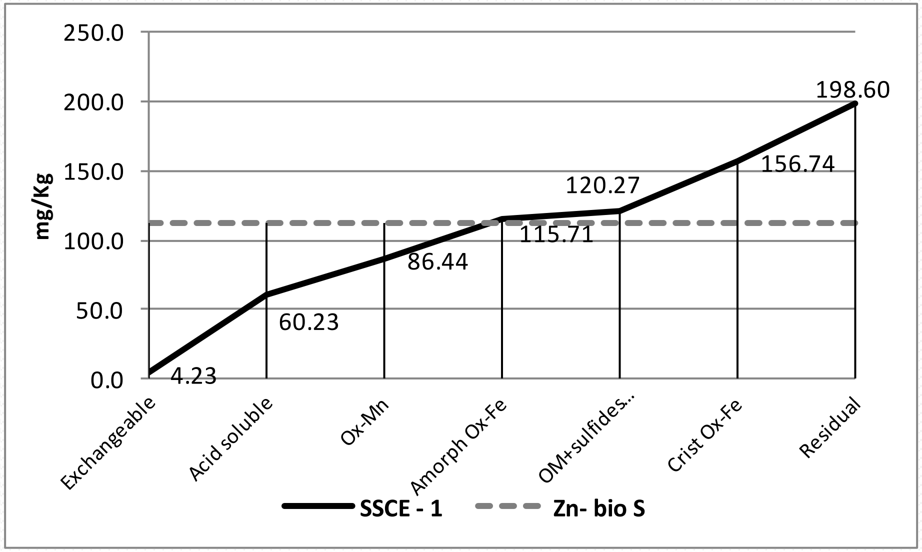
•Group I - bioaccessible Zn is probably in the acid soluble phase;

•Group II - bioaccessible Zn is probably in the acid soluble and Ox -Mn phases;

•Group III - bioaccessible Zn is probably in the acid soluble, Ox -Mn and amorphous OX-Fe phases;

Bf 56.2%

Group III (samples 1, 10, 12, 13, 14, 15, and 17)



Results – Zn solid-phase distribution to understand the bioaccessibility estimates

Discriminate four different groups:

•Group I - bioaccessible Zn is probably in the exchangeable and acid soluble phases;

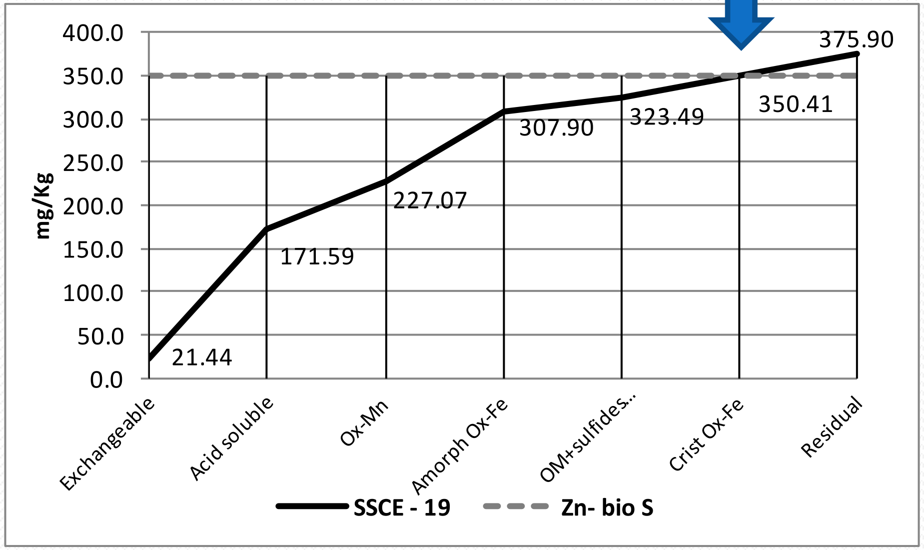
•Group II - bioaccessible Zn is probably in the acid soluble and Ox -Mn phases;

•Group III - bioaccessible Zn is probably in the acid soluble, Ox -Mn and amorphous OX-Fe phases;

•Group IV - bioaccessible Zn is probably in the acid soluble, amorphous OX-Fe and Crist OX-Fe phases;

Bf 93.4%

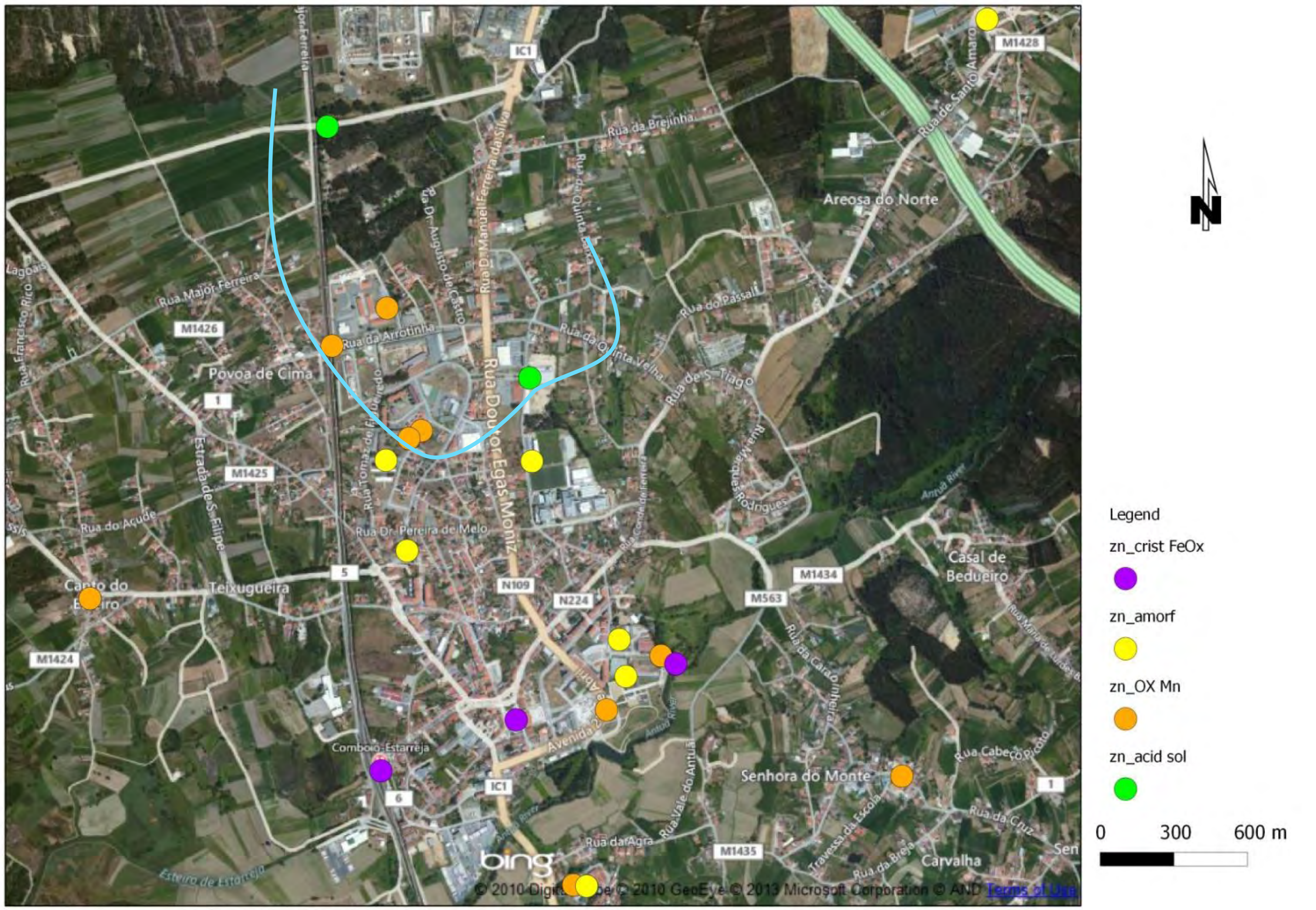
Group IV
(samples 9, 19 and 20)



Results – Spatial distribution of Group I +Group II

- **Group I - bioaccessible Zn in the exchangeable and acid soluble phases**
- **Group II - bioaccessible Zn in the acid soluble and Ox-Mn phases;**

Sample 5: 51%
Sample 6: 69%
Sample 7: 68%
Sample 8: 29%
Sample 16: 47%
Sample 18: 69%



Important metal fractions are in soluble dust phases – indicates an important anthropogenic input

- Zn was mainly extracted in the exchangeable and acid soluble phases for samples located within 1.5 km ranges from the chemical complex;

Conclusions

- Pb concentrations in the dust of Estarreja are not elevated but the element is mainly in bioaccessible forms;
- The relation between Pb bioaccessibility and its solid-phase distribution divides the samples in 3 different groups; However the major bioaccessible fraction seems to be associated to the more labile dust phases (acid soluble phase);
- Zn concentrations in the dust of Estarreja are elevated and the element is mainly in bioaccessible forms;
- The relation between Zn bioaccessibility and its solid-phase distribution divides the samples in 4 different groups; It is interesting noticing that important fractions bioaccessible Zn are associated to easily soluble phases (exchangeable phase) but also to less mobile mineral phases such as crystalline Fe Ox;
- Samples in the vicinity of the CCE show important metal bioaccessible fractions in soluble dust phases, suggesting important anthropogenic sources for the elements

Acknowledgments

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Obrigada!