



*The human impact on the natural environment of Estarreja: **past, present, future***

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Baixo Vouga Lagunar

The **Baixo Vouga Lagunar (BVL)** wetland is a typical “bocage” landscape, based on traditional forms of agriculture and a particular biodiversity.

- ❖ Ria de Aveiro is a humid and sensible zone and with high economic relevance;
- ❖ Natural habitat of aquatic and terrestrial specie;
- ❖ Special Protection Area and Nature Net 2000



Nature with brackish and fresh water systems



Industry

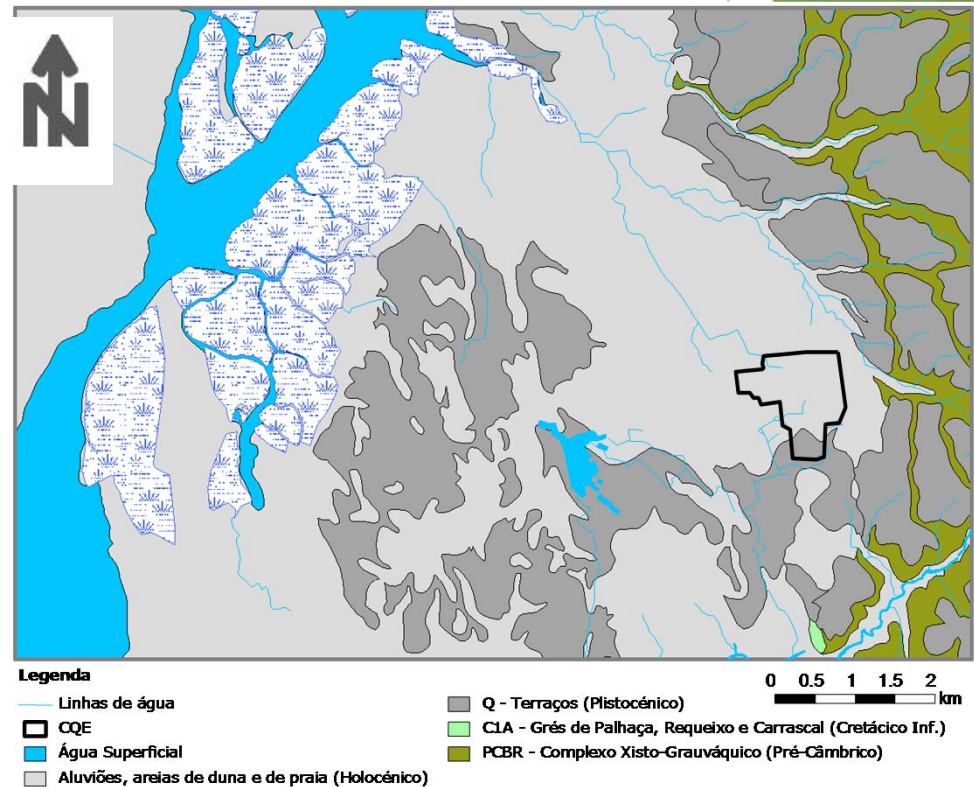


Agriculture

Geological settings of “Baixo Vouga Lagunar”

The main geological units are:

- detritic sedimentary deposits (siliceous sediments), with high permeability, hosting the superficial aquifer;
- Bedrock is composed by sandstones and schists.



Extracted from Branco C. (2008).

Estarreja Chemical Industry

- By the end of 1930s: production of Cl_2 and NaOH ;
- After the 2nd World War: production of ammonium (for fertilizers);
- 1952: production of ammonium sulphate and sulphuric acid (by pyrite ustulation);
- 1956: production of Cl and Na ;
- 1959: production of Cl and Na by electrolytic process using Hg cathodes;
- 1963: start the production of PVC and VCM using Hg catalysers;
- 1970: production of fertilizers and aromatic compounds (mononitrobenzene and aniline);



Estarreja Chemical Industry

- 1980 decade: new industrial unit for the production of polyurethanes;
- 1990 decade: new method for aniline production using less amount and with low concentration of sulphuric acid;
- End of 1990s: production of sulfanilic acid and cyclohexylamine; the Hg cells were replaced by membrane cells.



Estarreja Chemical Industry

- Almost all the chemicals produced in the past continues to be produced nowadays, however the manufacture technologies have been experiencing appreciable improvements becoming more environmentally sustainable;
- Industrial activity continues to be an important employer in this region. This leads to the growth of the city and population, approaching from the industrial pole and occupying the farm lands.



Environmental Legacy (85 years of industrial activities)

- Liquids effluents: Cl, Hg, SO₄, NO₃, NO₂, nitrofenols, MNB, aniline, vinyl chloride, methanol;



- In the past, these effluents were discharged directly to the Aveiro lagoon through sewage outlets;
- Nowadays, these effluents are transfer to wastewater treatment stations, where physical and chemical treatments are conducted.

- Solid wastes: 100 000 tones of muds, mainly composed by Hg, NaCl, CaSO₄, CaCO₃, Mg(OH)₂, Ca(OH)₂, Fe, NaOH; 150 000 tones of pyrite residues enriched in As, Hg, Zn, Cu, V, Fe; and 320 000 tones of muds of Ca(OH)₂.



- In the past these wastes were deposited in the soils without any kind of impermeabilization;
- Nowadays, these wastes are deposited in confined landfills.

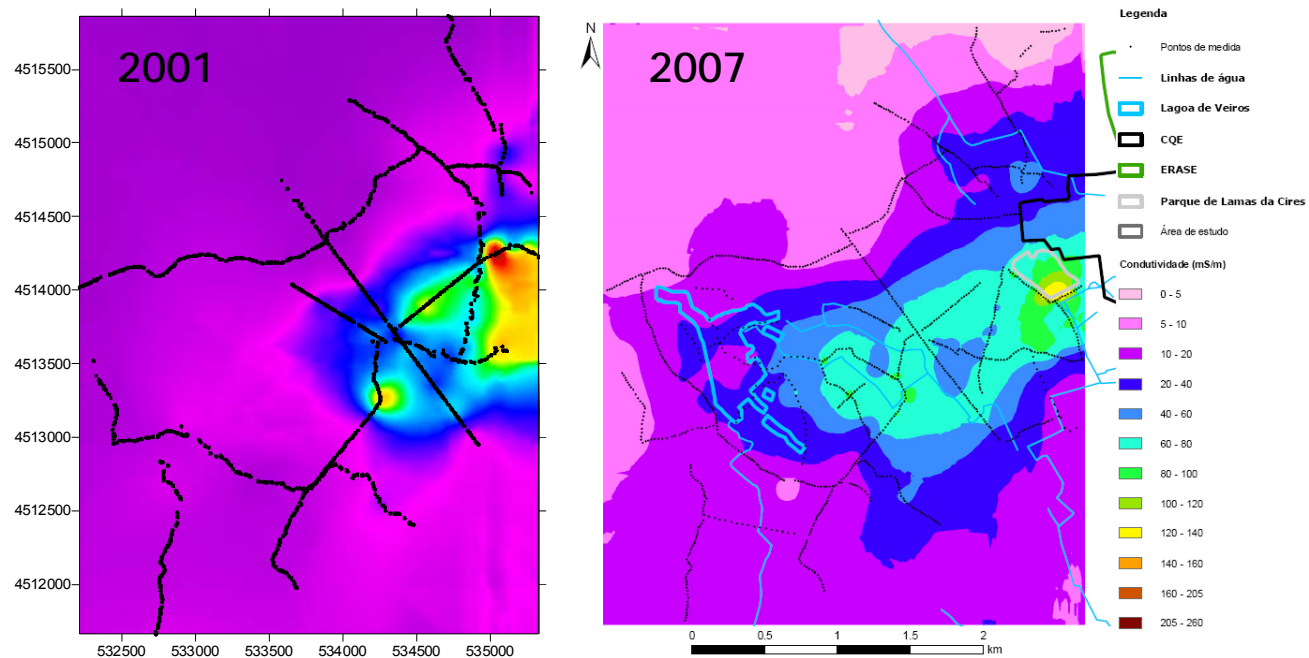


State of the Art: 30 years of environmental studies

- The first studies in this region were dedicated to the inorganic contamination (mainly Hg) in sediments (Hall et al., 1985; 1987; 1988) and later extended to other heavy metals and encompassing other natural compartments as soils and waters (e.g.: Fonseca et al., 1992; Inácio, 1993; Inácio et al., 1998; Costa et al., 2001);
- Changes in production technologies (1990s), mainly related with Hg cells substitution and at the same time the increasing production of materials using organic compounds (e.g.: PVC), led to an increase of studies dedicated to organic contaminants (Leitão, 1996; Ordens, 2007; Cachada et al., 2008; Neves, 2015);
- Also, the risk perception of the population, the increase number of diseases in the region and the scientific studies led the Authorities and Industries to: elaborated environmental impact studies; the construction of a landfill for the solid waste deposition; the effluent treatments and the implementation of more ecofriendly production technologies.

Main results obtained from previous studies

- The spatial distribution of As, Cu, Hg and Zn shows a typical anthropogenic pattern, with the highest values near the factories and sewage outlets. Values decrease to background with the distance from the sources (Inácio et al., 2011).



Contamination plume (electric conductivity geophysical method) (Ordens, 2006)

Main results obtained from previous studies

- The superficial aquifer in this region is contaminated mainly by Cl, SO₄, NO₃, heavy metals and organic compounds (Ferreira, 1989; Barradas, 1990; Leitão, 1996; Ordens, 2006).

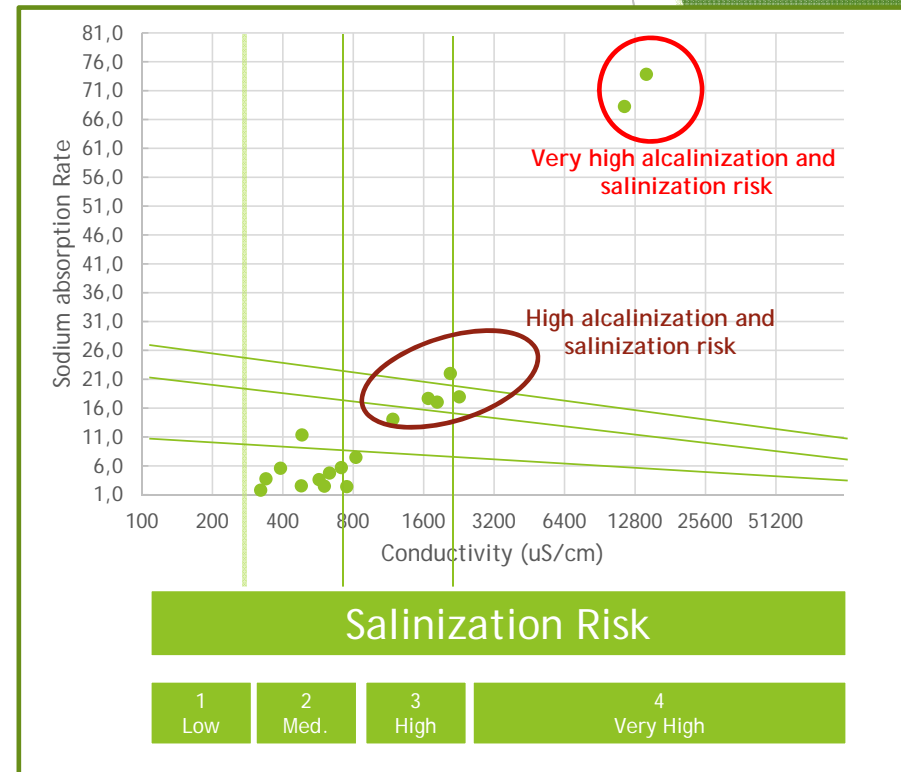
- Although the contamination of groundwater is still present nowadays, the improvement of the industrial production methods, the confinement of the solid wastes, and the treatment of liquid effluents resulted in a reduction of contamination.
- Nevertheless these waters continues to exceed the maximum admissible levels for human consume (Dec. Lei 236/98). Although can be used for irrigation.



13	2006	2007	2009	2014
As (µg/l)	3640	1138	797	300
Hg (µg/l)	30	17	2	-
Sb (µg/l)	-	25	27	<10

Results - The salinization risk (ongoing studies)

- All samples show salinization risk from medium to very high;
- The use of these waters for irrigation represents a serious problem for agriculture and can promote the desertification of soils.



Volatile Organic Contaminants (VOCs) (ongoing studies)

Environmental behaviour and effects

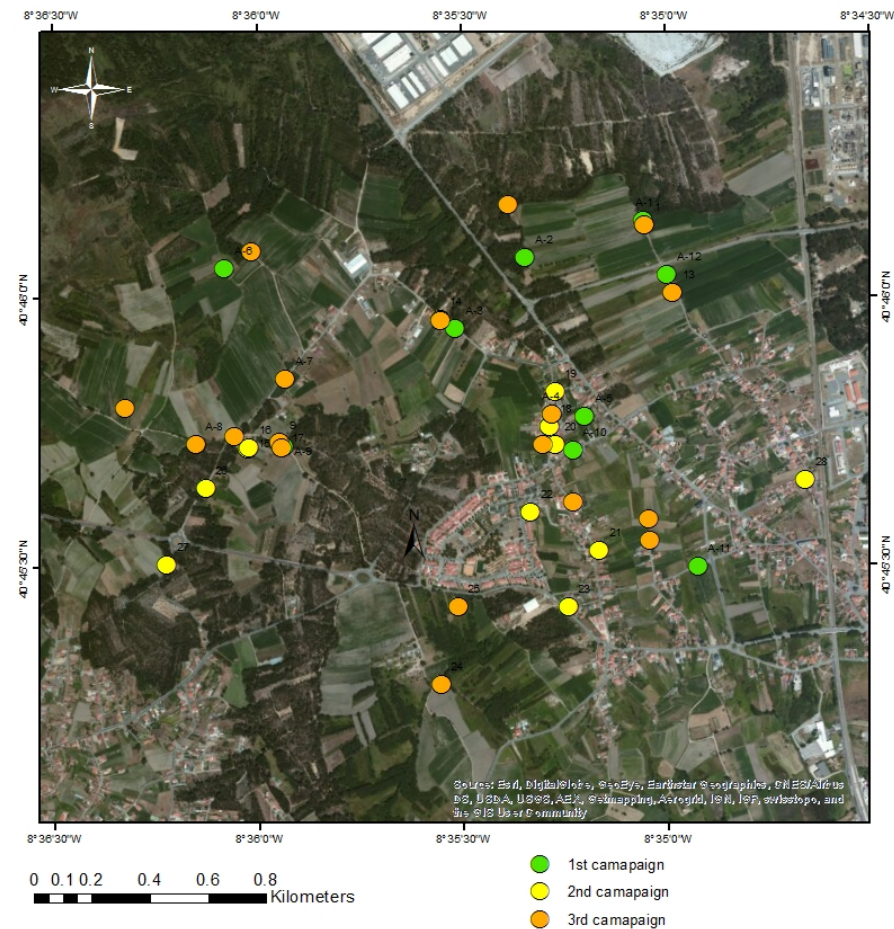
- VOCs, due to their low reactivity, are relatively persistent in groundwater, and they may be transported for long distances.
- Harmful environmental effects (crop, vegetation and materials damage, reduced visibility) when they chemically interact with oxides of nitrogen and sunlight to form ground-level ozone.

Human health problems

- Some VOCs may have short- and long-term adverse health effects; many are known as human carcinogens.
 - Ingestion: can cause damage to the central nervous system, the kidneys, or the liver.
 - Inhalation: can damage the tissue of the lungs, and they may also cause irritation if they come into contact with the skin. VOCs vaporize at a much faster rate than water, causing serious health threats.

Results - VOCs in water

- Analyses of 63 VOCs by GC-MS using solid phase microextraction (SPME);
- Three sampling campaigns:
 - 1st (July 2013): 12 samples
 - 2nd (June 2014): 18 samples
 - 3rd (June 2015): 19 samples (ongoing)

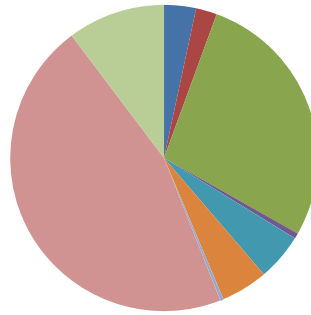


Results - VOCs in water (2013)

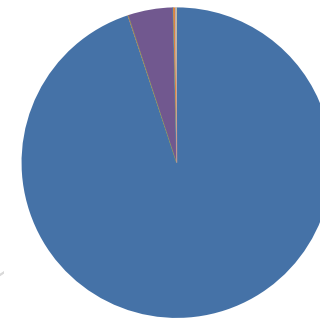
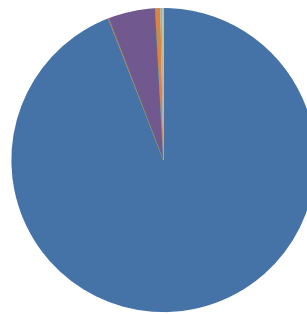
- 1st sampling campaign
- 37 VOCs were below detection limit;
- 26 VOCs were detected in groundwater samples

Guidelines for Canadian Drinking Water Quality:

- 2 samples above the maximum acceptable concentration (MAC) for benzene in drinking water (5 µg/L).



- benzene
- chlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethane
- 1,1-dichloroethene
- trichloroethene
- tetrachloroethene
- vinyl chloride
- Others



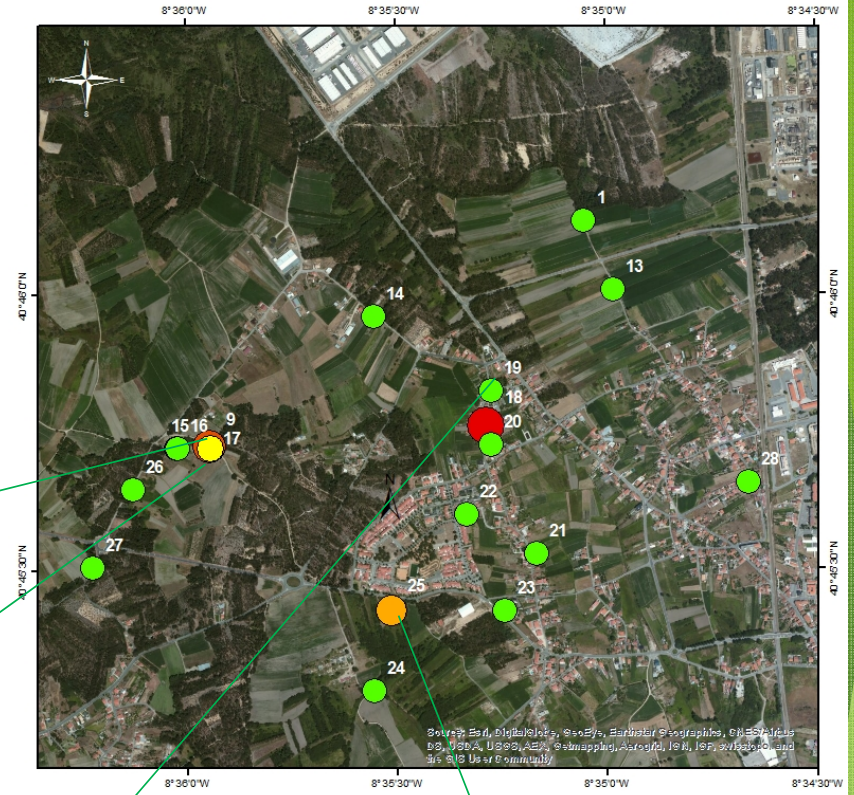
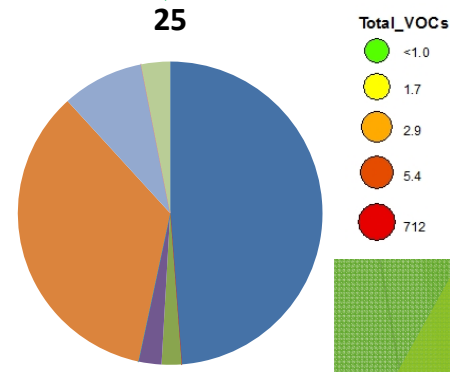
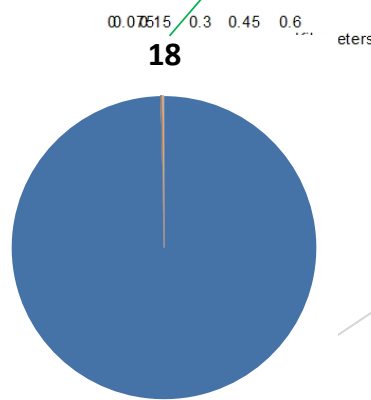
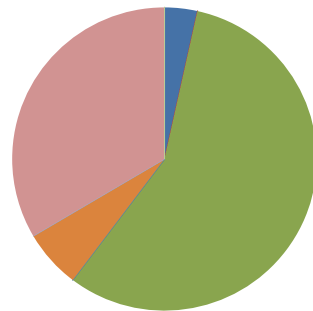
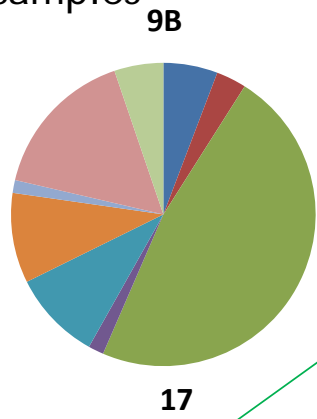
Results - VOCs in water (2014)

- 2nd sampling campaign
- 45 VOCs were below detection limit;
- 18 VOCs were detected in groundwater samples

Guidelines for Canadian Drinking Water Quality:

1 sample above the maximum acceptable concentration (MAC) for benzene in drinking water (5 µg/L).

- benzene
- chlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethane
- 1,1-dichloroethene
- trichloroethene
- tetrachloroethene
- vinyl chloride
- Others



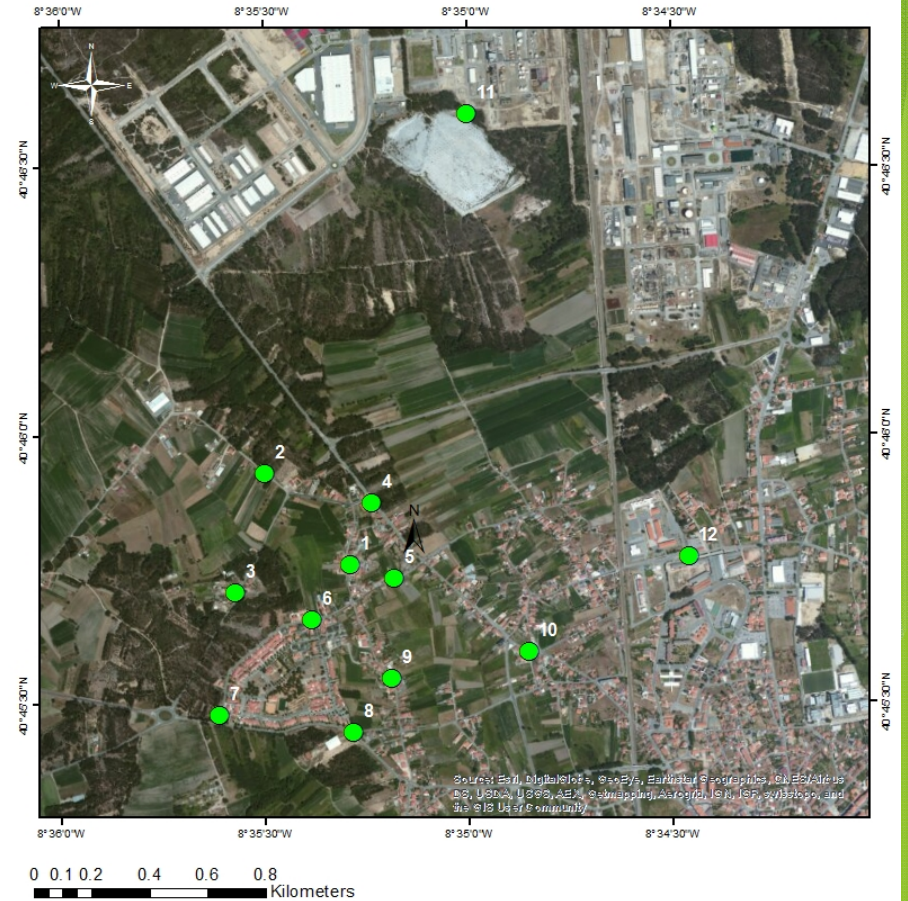
Results - VOCs in the atmosphere (2015)

Methodology

Radiello® Passive Air Sampling



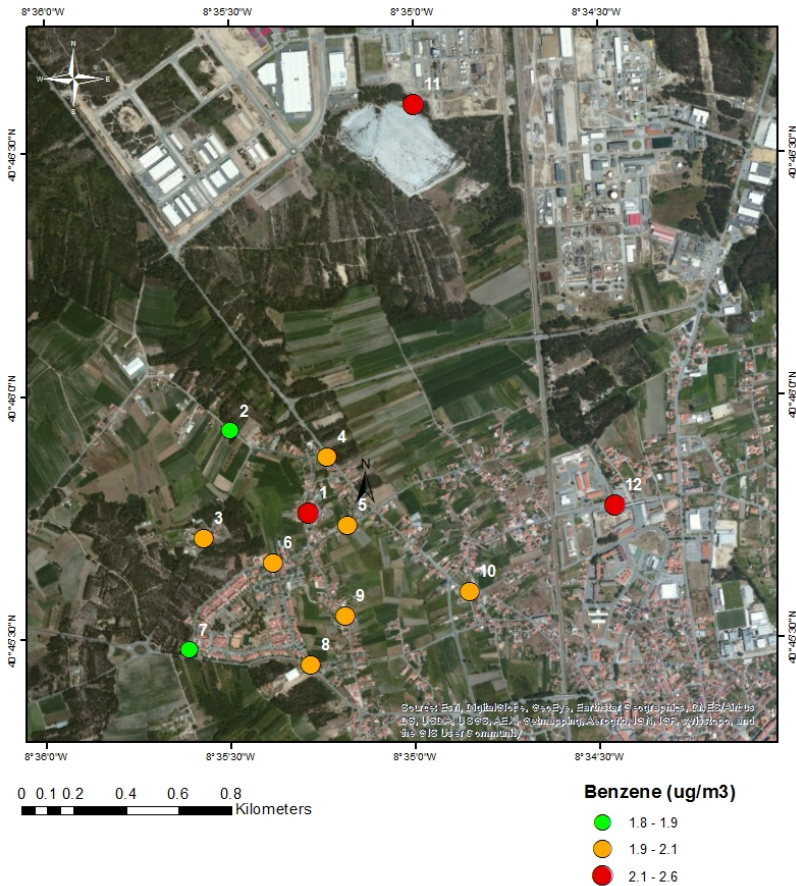
- 14 days exposure
- 21 VOCs analyzed by GC-MS
- 12 samples



Results - VOCs in the atmosphere (2015)

13 of the 21 compounds analyzed were detected

Similar levels within the sampling area (e.g. of benzene)

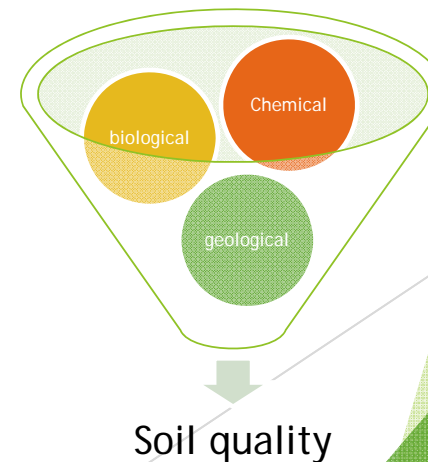
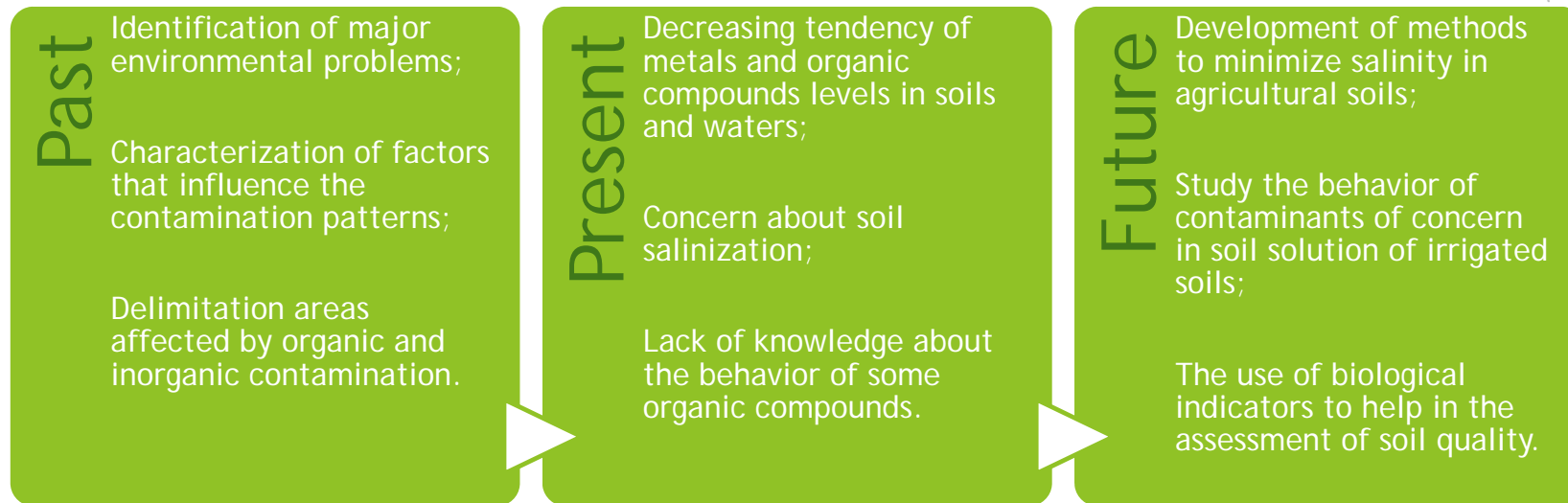


City	Levels
Ilhavo	≤ 1.7
Oporto	2-3.5
Lisbon	3.8
Madrid	4.5
Brussels	2.5
Dublin	1.1
Estarreja	1.8-2.6

- ✓ chloroform
- ✓ carbon tetrachloride
- ✓ benzene
- ✓ 1,2- dichloroethane
- ✓ toluene
- ✓ tetrachloroethene
- ✓ chlorobenzene
- ✓ m+p-xylene
- ✓ ethylbenzene
- ✓ o-xylene
- ✓ 1,2,4- trimethylbenzene
- ✓ naphtalene

- For benzene the risk is higher than $10E^{-5}$ in all samples
- For chloroform the risk is higher than $10E^{-6}$ in 10 samples
- For carbon tetrachloride the risk higher than $10E^{-6}$ in all samples

Future projects



Thank you for your attention



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