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## A contribution to the Environmental Risk Assessment of Estarreja Chemical Complex

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## Introduction

Estarreja is notorious for its Chemical complex (ECC). Even though there have been many works denoting the presence of contamination caused by inappropriate discharges through ditches and sewage conducts in the past, there is still work to be done when it comes to relating the contamination and its impact on the environment. Previous works (Moreira et al., 2011; Inácio et al., 1998) identified the presence of contamination in the area around the ECC. Nevertheless, the real dimension of the problem is not well understood. Under the scope of the project @10years, a review of existing data was performed in order to understand the spatial distribution of contaminants, identify areas and contaminants of concern, the receptors and the ecosystem services at risk. The results of this first step showed that little is known about the potential risks to the environment. In this context, an area nearby Vala de S. Filipe (a water way used to dispose contaminated effluents into the Ria de Aveiro) was selected in order to accomplish a site-specific assessment based on two lines of evidence (chemical and ecotoxicological). Thus, in addition to a very complete chemical dataset (metal(loid)s and organic contaminants) on soil samples, a battery of ecotoxicological tests was carried (both on whole soil and soil elutriates). When concluded the assays with the best response will be selected and a simplified methodology will be proposed for application in a much wider area in the vicinity of the ECC.

## Methodology

- Composite soil samples were collected (10 cm depth), in an area surrounding the S. Filipe ditch in a total of 23 samples (Fig. 1).
- To gather basic physical-chemical data, the following parameters were determined (<2mm):
  - ⇒ pH in 1:5 (v/v) water suspension by following the ISO 10390 protocol;
  - ⇒ Electric conductivity (EC) was determined in a 1:5 water soil suspension after 24h;
  - ⇒ Organic matter (OM) content was determined by the LIO (8h at 450°C) procedure;
- The concentration of anilines and other organic and contaminants was determined by a certified laboratory (Eurofins, TerrAttes®). Inorganic contaminants were also determined by ICP-MS after acid digestion (Department of Geosciences, University of Aveiro).
- To gather ecotoxicological data, the following assays were performed in fresh soil (<4mm):
  - ⇒ Earthworms avoidance test with *E.fetida* following ISO 17512-1:2008 protocol (Fig.2);
  - ⇒ *Lemna sp.* Growth Inhibition Test following OCDE 221 protocol;
  - ⇒ Terrestrial Plant Test Seedling Emergence and Seedling Growth Test (OCDE 208) with *Zea mays* (Fig.3);

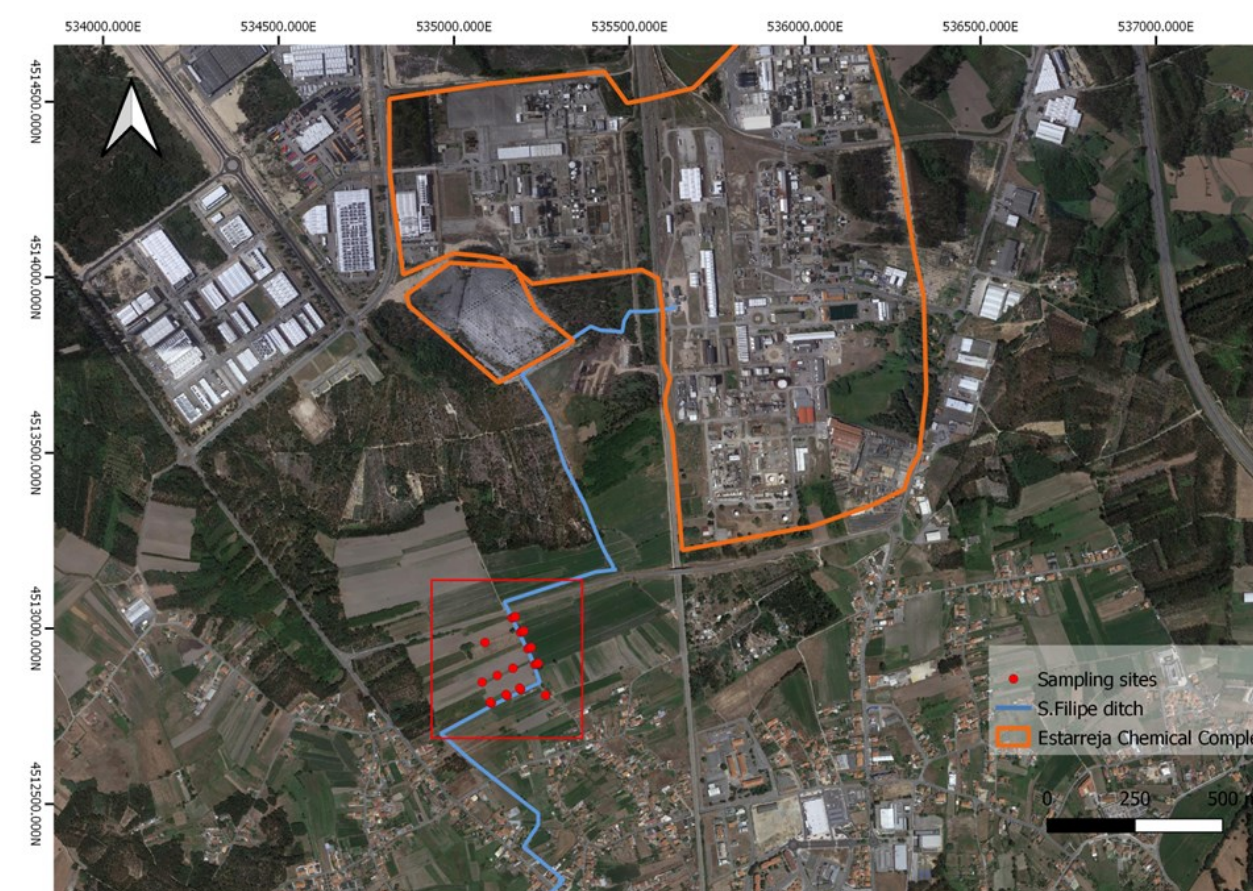


Fig 1-Map with the location of the sampling sites, the chemical complex.



Fig 2- Avoidance Test with *E.fetida*.

Fig 3- Terrestrial Plant Test Seedling Emergence and Seedling Growth Test.

## Results

- Median value for pH points to moderately acid soils but, samples present slightly alkaline properties which can be related with agricultural practices (Table 1).
- Based on the median value, these soils can be classified as containing low amounts of organic matter (Table 1).
- Organic contaminants such as PAHs, PCBs, hexachlorobenzene present but at low concentrations.
- Inorganic contaminants present at high concentrations.
- Of particular concern are the high levels of Hg, As and Pb, that in the majority of samples surpassed the guideline values recommended by Portuguese Environmental Agency (APA 2019) (Table 2).
- High avoidance percentage shows that habitat function of the soil is not being provided for soil 6,12 and 13 (Fig.3).
- The species analysed in the terrestrial plant test show that production function of soil is not being affected by the contaminants (Fig.4).
- All samples affected the growth of *lemna minor* in the growth inhibition test of aquatic plants demonstrating the possible toxicity of the samples to these organisms (Fig.5).

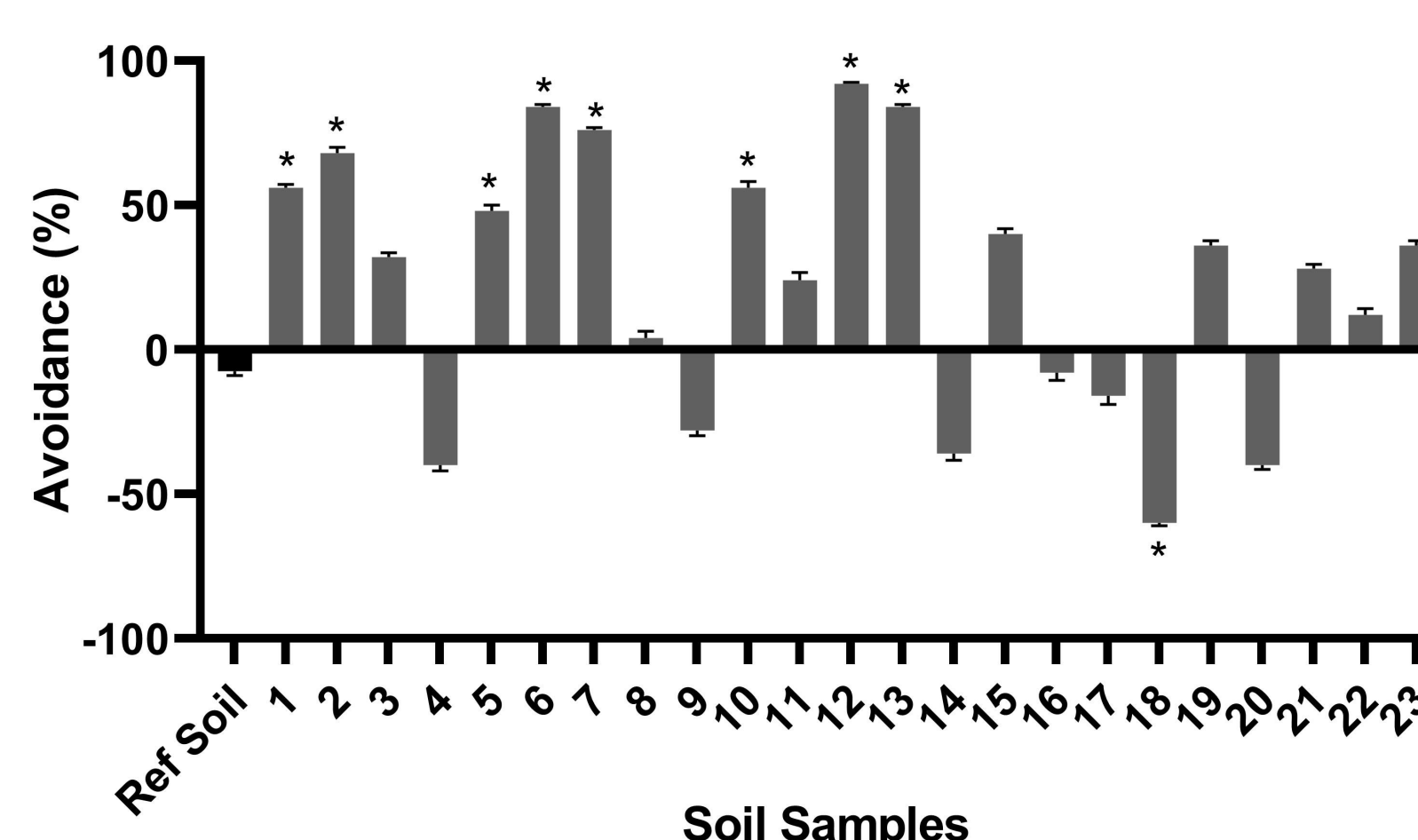


Fig 3 - Percentage avoidance of *E. fetida* after exposure to different soil samples from the surrounding area to the ECC. Results are represented by mean ± SD values. Asterisks mark significant differences compared to a reference soil (p < 0.05, Fisher's test).

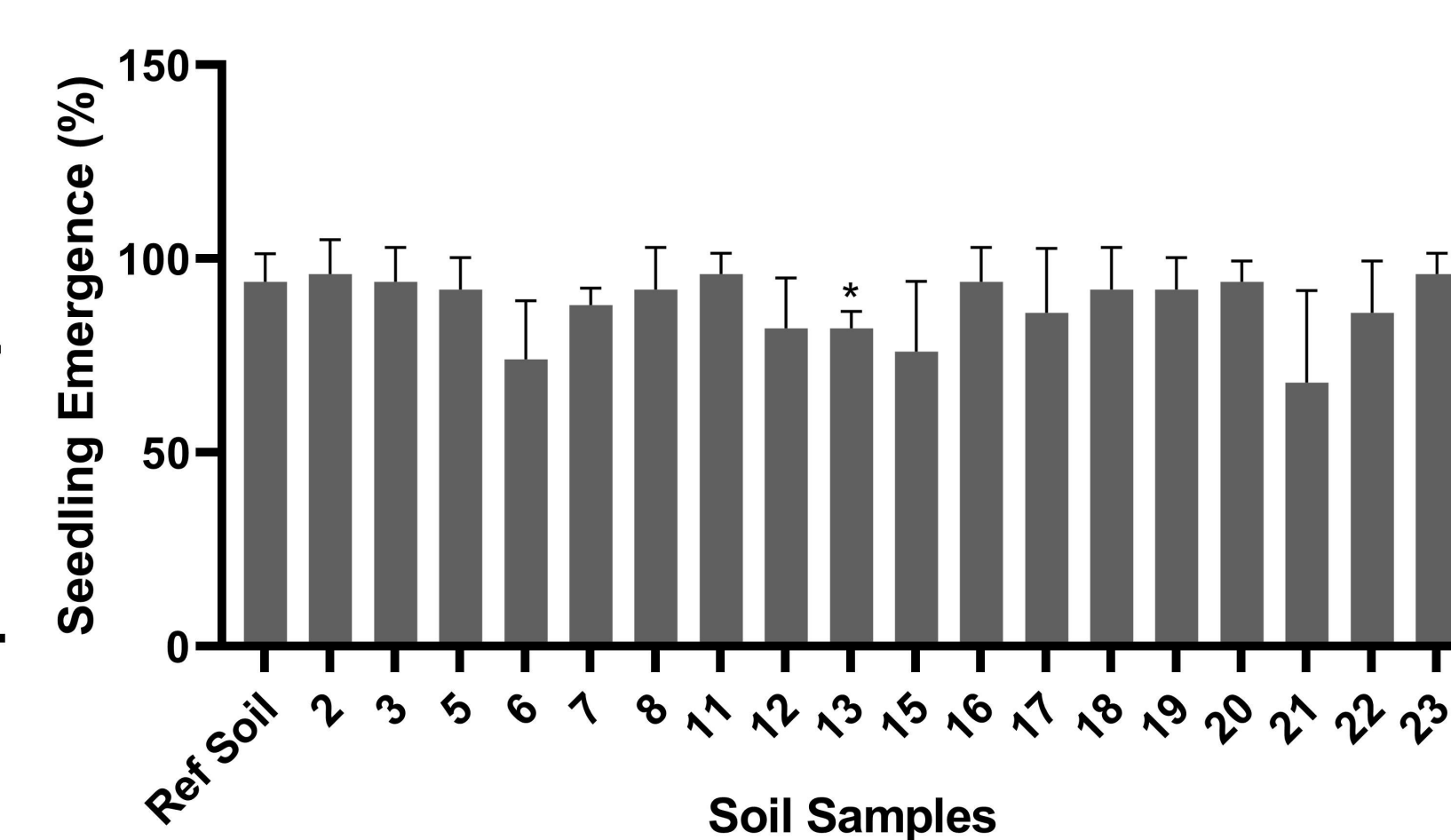


Fig 4 - Percentage seedling emergence of *Z. mays* after exposure to our soil samples. Results are represented by mean ± SD values. Asterisks mark the significant differences compared to a reference soil (p < 0.05, Dunnett's).

Table 1 - Descriptive statistics for some general soil properties of the samples collected.

|          | pH <sub>w</sub> | EC (μS/cm) | OM (%) |
|----------|-----------------|------------|--------|
| Median   | 5.67            | 238        | 3.86   |
| Mean     | 5.93            | 261        | 3.93   |
| Std. Dev | 0.75            | 150        | 0.825  |
| Min      | 4.93            | 66.1       | 2.88   |
| Max      | 7.84            | 620        | 6.10   |

Table 2 - Descriptive statistics for some contaminants of most concern, and recommended limits by APA. Values are presented in mg/kg.

|                   | As (mg/kg) | Hg (mg/kg) | Pb (mg/kg) |
|-------------------|------------|------------|------------|
| Median            | 406        | 28.0       | 107.0      |
| Mean              | 375        | 23.2       | 81.10      |
| Std. Dev          | 338        | 19.9       | 59.60      |
| Min               | 12.4       | 0.350      | 10.00      |
| Max               | 1104       | 59.0       | 175.0      |
| Recommended Limit | 11.0       | 0.250      | 45.00      |

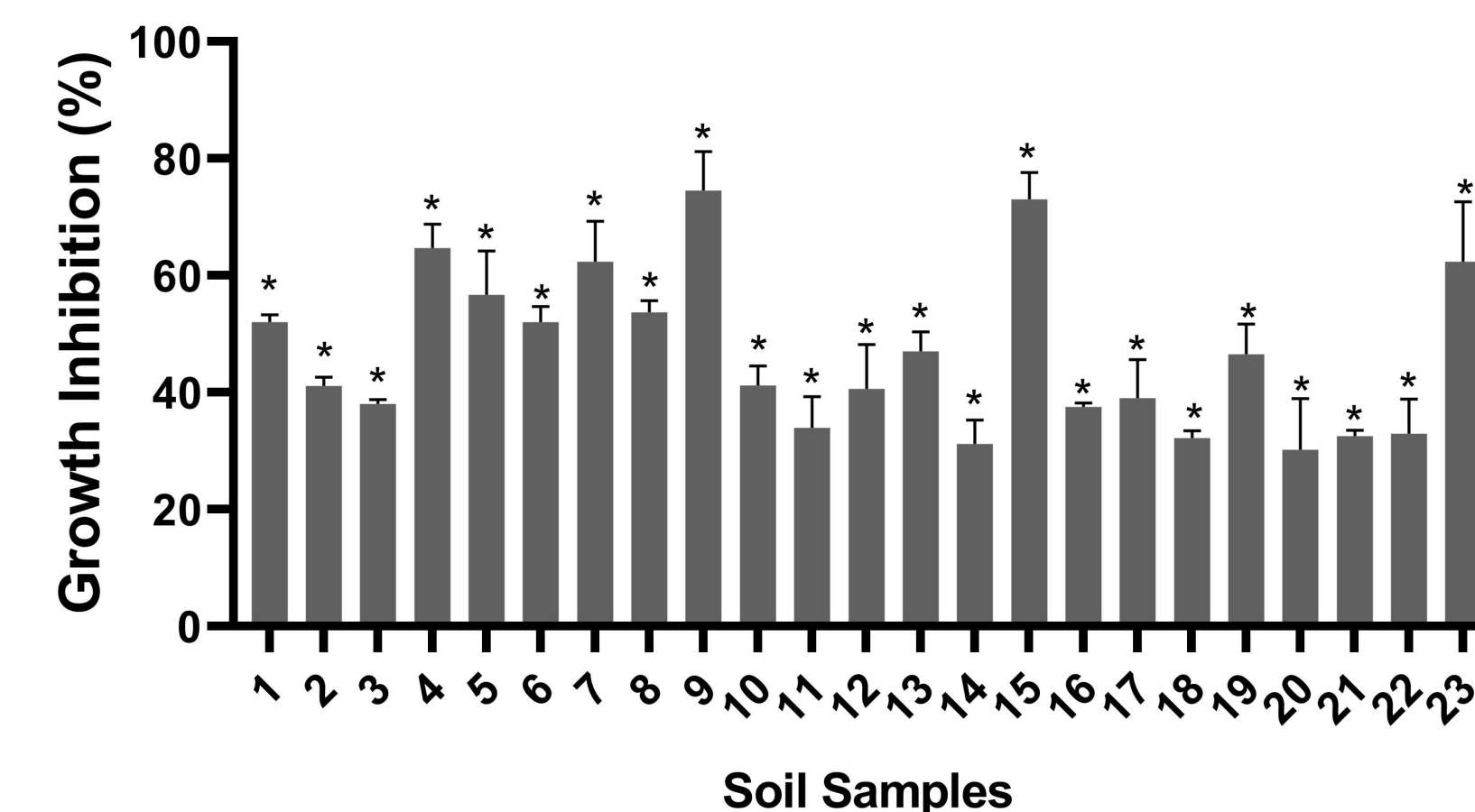


Fig 5 - Percentage of growth inhibition of *L. minor* after exposure to soil elutriates of our soil samples. Results are represented by mean ± SD values. Asterisks mark the significant differences compared to control (p < 0.05, Dunnett).

## Conclusions

Taking the presented data into account we can conclude that the contaminants are present around the ECC and, further more in concentrations that may have an environmental impact when in combination with the low pH and organic matter contents. From the ecotoxicological data we can conclude that to some species there is a clear impact, this is the case for *Lemna* and *E.Fetida*. These results may show that the contamination present in this location may put in danger the production function, such as habitat, and impact other environmental compartments as shown by the toxicity of elutriates. Lastly the data allows to conclude that the production function, may not be affected, at least for the test species. This can be due to the low sensitivity of the species or the endpoint tested, or even due to the low availability of contaminants. Thus we must test more species present in the area and apply more sensitive assays to get more definitive conclusions.

## References

- Moreira et al., (2011). Water, Air, and Soil Pollution, 377-398, 221  
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