Spatial and temporal evolution of groundwater metal contamination in an industrial area: the case study of Estarreja

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Estarreja – a city of contrasts

Estarreja has always been a region with extensive farming areas, developing parallel and competing for land with an important industrial pole - the Estarreja Chemical Complex (ECC).
The main geological units are:

- Detritic sedimentary deposits (siliceous sediments), showing high permeability and porosity, and hosting the superficial aquifer. The characteristics of this unit allows the contaminant’s dispersion, thus causing high aquifer vulnerability.

- Bedrock is composed by sandstones and schists.
The evolution of the Estarreja Chemical Industry

- By the end of 1930s: production of \( \text{Cl}_2 \) and \( \text{NaOH} \);
- After the 2\textsuperscript{nd} World War: production of ammonium (for fertilizers);
- 1952: production of ammonium sulphate and sulphuric acid (by pyrite ustulation: \textit{As, Cu, Zn, Fe, etc});
- 1956: production of \( \text{Cl}_2 \) and \( \text{Na} \);
- 1959: production of \( \text{Cl}_2 \) and \( \text{Na} \) by electrolytic process using \textit{Hg} cathodes;
- 1963: started the production of PVC and VCM using Hg catalysts;
- 1970: production of fertilizers and aromatic compounds (mononitrobenzene and aniline);
- 1980 decade: new industrial unit for the production of polyurethanes;
- 1990 decade: new method for aniline production using less amounts and low concentrations of sulphuric acid;
- End of 1990s: production of sulfanilic acid and ciclohexilamine; the Hg cells were replaced by membrane cells.
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 (more than 85 years of industrial activities)

- Liquids effluents: Cl, Hg, $\text{SO}_4$, $\text{NO}_3$, $\text{NO}_2$, nitrofenols, MNB, aniline, vinyl chloride, methanol.

- In the past, these effluents were discharged directly to the Aveiro lagoon through sewage channels;

- Nowadays, these effluents are transferred to wastewater treatment stations, where physical and chemical treatments are conducted.
Environmental Legacy (more than 85 years of industrial activities)

- 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, Fe;
- 320 000 tones of Ca(OH)₂, muds still exposed to weathering conditions.

Nowadays, these wastes are deposited in confined landfills (concluded in 2005)
Aims

- To assess the long-term (1989–2016) and spatial distribution of heavy metal concentrations in waters using geophysical and geochemical data;

- To understand the influence of the geological features in the evolution of contamination dispersion;

- Linked the contamination evolution with the changes introduced over time in the industrial practices;
Sampling and Analysis

Sampling campaigns

- 1989
  - 60 samples
  - 8 chemical elements (Fe, Cu, Pb, Zn, Mn, Cd, Co, Ni);
  - AAS analysis after samples pre-concentration through lyophilisation;

- 2006
  - 34 samples
  - 69 chemical elements
  - ICP-MS

- 2015
  - 19 samples
  - 36 chemical elements
  - ICP-OES

- 2016
  - 32 samples
  - 25 chemical elements
  - ICP-MS
Select elements: Fe, Cu, Zn, Mn, Cd, Co, Ni

Limitations in extrapolating data

Sampling and Analysis


Different sampling points
Different analytical methods
Different elements analyzed
Geochemical data: sampling map
Geochemical data: sampling map

2015

2016

Legend
- Water sampling-2015
- Pond
- sludge park
The spatial distribution of electrical conductivity show the contamination dispersion along the time.

- In 1989 the high values are close to the factories.
- In 2006 and 2016 the contamination is defined in two main areas: close to the factories (with a tendency to decreasing); and associated with the old sewage channels.
Geochemical results: pH

- High pH range
- Median near to pH=6
- Anomalous values – occurrence of high acidic waters locally
Geochemical results – Electric conductivity

- Considerable high EC values range
- Median values between 500 and 1000 μS/cm
- Anomalous values – occurrence of waters with very high EC values locally
Geochemical results: Cu in water

- Usually the levels of Cu in waters are low and below the legal limits;
- A general decrease of Cu concentrations in waters;
- Occurrence of anomalous locally Cu concentrations, but showing a general decreasing tendency.
• The levels of Mn in waters are high (mean values are high or near de drinking water limit);
• A general decrease of mean Mn concentrations in waters, below the limit for irrigation waters;
• Occurrence of anomalous locally Mn concentrations
• The levels of Zn in waters are high (above the drinking water limits);
• A general decrease of mean Zn concentrations in waters, below the limit for irrigation waters;
• Occurrence of anomalous high locally Zn concentrations
Geochemical results: Fe in water

- A general decrease of mean Fe concentrations in waters, below the limit for irrigation waters and also the drinking water limits (2015-2016);
- Occurrence of anomalous locally Fe concentrations.
• The levels of Cd in waters are in general low (above the drinking and irrigation water limits);
• A general decrease Cd levels in waters over years;
• Occurrence of anomalous high locally Cd concentrations (1989-2006).
Geochemical results: Metals – $\sum (Fe+Mn+Cu+Zn+Co+Ni+Cd)$

- In general are occurring a decrease of metals concentrations in waters over years;
- Occurrence of anomalous metal concentrations – locally effects.
Geochemical results: Evolution of metal contamination $\Sigma(\text{Fe+Mn+Cu+Zn+Co+Ni+Cd})$

- The main metallic focus are the factories and the sewage channels
Geochemical results: Evolution of metal contamination $\Sigma(Fe+Mn+Cu+Zn+Co+Ni+Cd)$

- Dispersion of the contamination from the factories
Geochemical results: Evolution of metal contamination $\Sigma(Fe+Mn+Cu+Zn+Co+Ni+Cd)$

- Dispersion of the contamination from the factories and from the sewage channels
Geochemical results: Evolution of metal contamination $\Sigma$(Fe+Mn+Cu+Zn+Co+Ni+Cd)

- Dispersion of the contamination from the factories and from the sewage channels following the main underground flux directions
Geochemical results: Main profiles of metal contamination

![Graph showing metal contamination profiles](image-url)
Concluding remarks

Despite the several limitations in the assessment of metal contamination in a period range of almost 30 years, it is possible to conclude about the following points:

• In the past exist two main focus of metal contamination: the factories and the industrial sewage channels;

• Nowadays the main metal contamination focus seems to be the old industrial sewage channels – locally contamination effects;

• 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 significant reduction of contamination;

• Nevertheless these waters continues to exceed the maximum admissible levels for human consumption, but its standards improve such they can be used for irrigation.
Concluding remarks

TO THINK ABOUT...

• Metals are not degradable agents as organic compounds, which means that in waters they can only be attenuated by:

  • Dilution (in situ)
  • Dilution (ex situ) – dispersion
  • Precipitation

• Dispersion seems to be the main process occurring, but this have the disadvantage of affect other sites;

• Precipitation also may occur, but changes in physicochemical conditions may cause the remobilization and again the entry of these metals into the aqueous system.
Thank you for your attention

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