



# COST

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Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

**Special Session: Environmental Case Studies from  
Mediterranean, Central and Eastern Europe**

**Duisburg, Germany, 4 - 6 March 2013**

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Year: 2012-2013 (*Starting Action*)

## Speaker Organization

### Logo:



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Function in the Action: **WG Member**

Affiliation / Country: **University of Lisbon/Portugal**

# The Spatial Distribution of PAHs and Other Pollutants in Lichens for Fingerprinting of Air-Pollution

Cristina Máguas, Sofia Augusto, Pedro Pinho, MJ Pereira, and Cristina Branquinho



# Planetary Boundaries: Exploring the safe operating space for humanity in the Anthropocene

nature | Vol 461:24 September 2009

## FEATURE

### A safe operating space for humanity

Identifying and quantifying planetary boundaries that must not be transgressed could help prevent human activities from causing unacceptable environmental change, argue **Johan Rockström** and colleagues.

Although Earth has undergone many periods of significant environmental change, the planet's environment has been unusually stable for the past 10,000 years\*. This period of stability — known to geologists as the Holocene — has seen human civilizations arise, develop and thrive. Such stability may now be under threat. Since the Industrial Revolution, a new era has arisen, the Anthropocene†, in which human actions have become the main driver of global environmental change\*. This could see human activities push the Earth system outside the stable environmental state of the Holocene, with consequences that are detrimental or even catastrophic for large parts of the world.

During the Holocene, environmental change occurred naturally and Earth's regulatory capacity maintained the conditions that enabled human development. Rapid temperature, freshwater availability and biogeochemical flux all varied within a relatively narrow range. Now, largely because of a rapidly growing reliance on fossil fuels and



**SUMMARY**  
 • New approach proposed for defining preconditions for human development  
 • Crossing certain biophysical thresholds could have disastrous consequences for humanity  
 • Three of nine interlinked planetary boundaries have already been overstepped

industrialized forms of agriculture, human activities have reached a level that could damage the systems that keep Earth in its desirable Holocene state. The result could be irreversible and, in some cases, abrupt environmental change, leading to a state less conducive to human development\*. Without pressure from humans, the Holocene is expected to continue for at least several thousands of years\*.

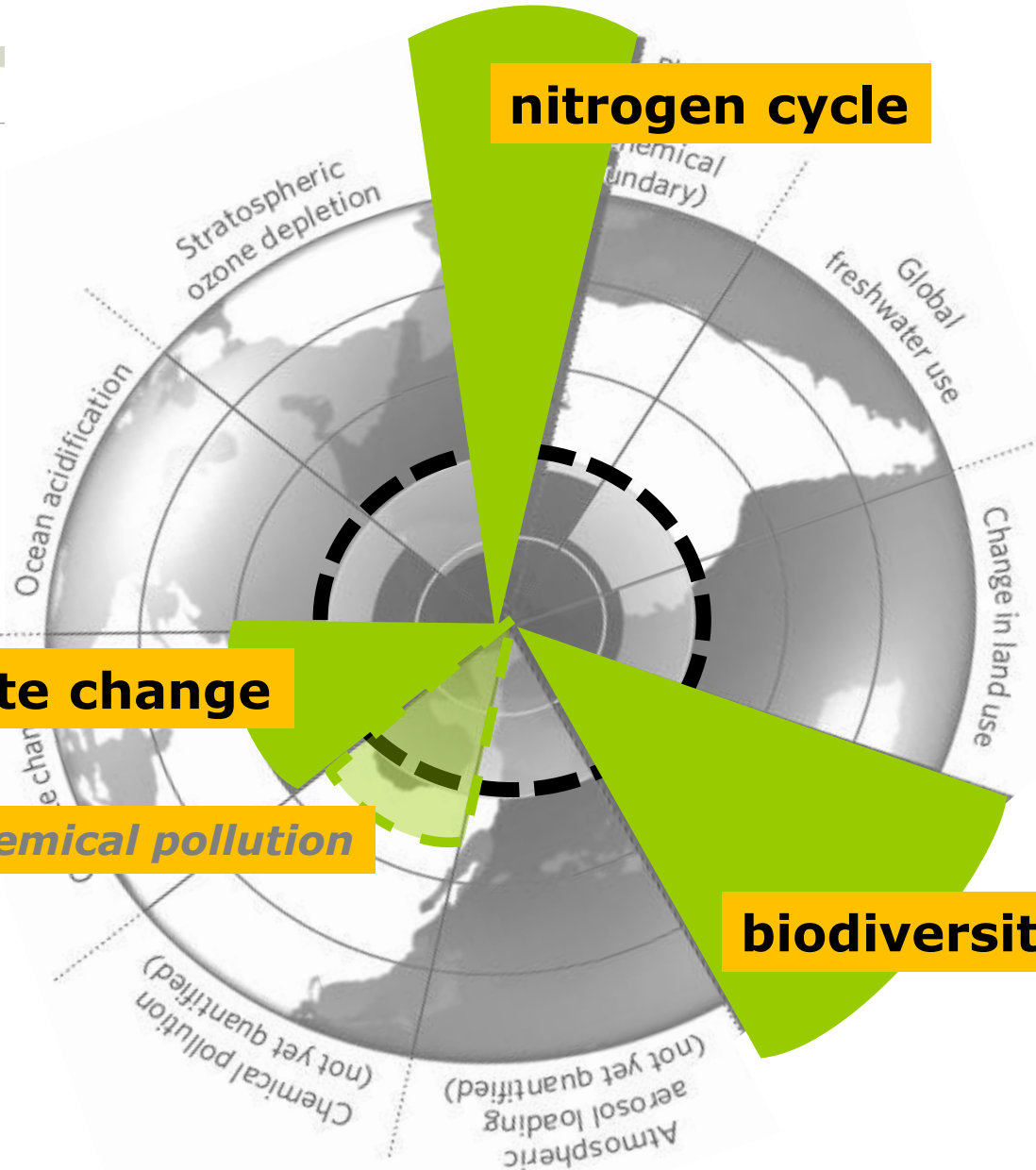
**Planetary boundaries**  
 To meet the challenge of maintaining the Holocene state, we propose a framework based on 'planetary boundaries'. These

boundaries define the safe operating space for humanity with respect to the Earth system and are associated with the planet's biophysical subsystems or processes. Although Earth's complex systems sometimes respond smoothly to changing pressures, it seems that this will prove to be the exception rather than the rule. Many subsystems of Earth react in a nonlinear, often abrupt, way, and are particularly sensitive around threshold levels of certain key variables. If these thresholds are crossed, then important subsystems, such as a meaneosystem, could shift into a new state, often with deleterious or potentially even disastrous consequences for humans\*\*.

Most of these thresholds can be defined by a critical value for one or more control variables, such as carbon dioxide concentration. Not all processes or subsystems on Earth have well-defined thresholds, although human actions that undermine the resilience of such processes or subsystems — for example, land and water degradation — can increase the risk that thresholds will also be crossed in other processes, such as the climate system.

We have tried to identify the Earth-system processes and associated thresholds which, if crossed, could generate unacceptable environmental change. We have found nine such processes for which we believe it is necessary to define planetary boundaries: climate change; rate of biodiversity loss (terrestrial and marine); interference with the nitrogen and phosphorus cycles; stratospheric ozone depletion; ocean acidification; global freshwater use; change in land use; chemical pollution; and atmospheric aerosol loading (see Fig. 1 and Table).

In general, planetary boundaries are values for control variables that are either at a 'safe' distance from thresholds — for processes with evidence of threshold behaviour — or at dangerous levels — for processes without



**Figure 1 Beyond the boundary.** The inner grey shading represents the proposed safe operating space for nine planetary systems. The red wedges represent an estimate of the current position for each variable. The boundaries in three systems (rate of biodiversity loss, climate change and human interference with the nitrogen cycle) have already been exceeded.

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climate change

chemical pollution

biodiversity loss

To develop a framework for the use of lichens as ecological-indicator of environmental changes in Mediterranean type ecosystems.



**Mediterranean: *biodiversity hotspot***



***Biomonitoring consists of using living organisms to quantify gradients of pollution.***

(Manning & Feder, 1980; Martin & Coughtrey, 1982; Puckett, 1988; Sloof, 1993)



## Advantages of biomonitors

**High spatial resolution (possible to obtain information at many sampling sites – low cost).**

**Accumulate pollutants over their lifetime, reflecting a chronic exposure.**

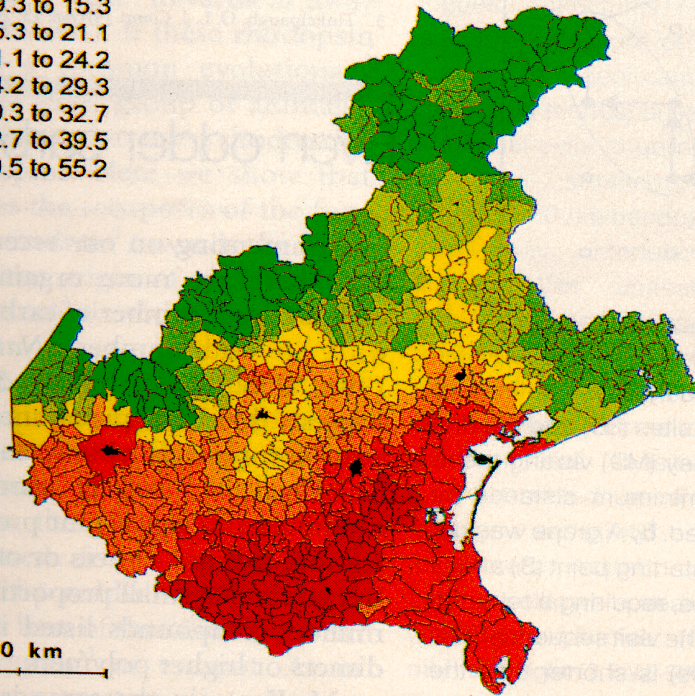
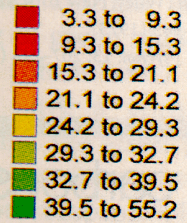
**Biological response, which is not possible using conventional monitoring methods.**

## **Why are Lichens excellent ecological-indicators of atmospheric conditions ?**

- **symbiosis fungus and a photobiont: a green algae and/or a cyanobacteria;**
- **water content equilibrate constantly with the surrounding atmosphere;**
- **no roots or cuticle: they absorb both nutrients and pollutants directly from the atmosphere;**
- **damage to any of the partners results in losses to the entire individual;**
- **ubiquitous on land ecosystems and dominant as epiphytes on Mediterranean ones;**
- **can be collected and identified throughout the year;**
- **lichens are long-living organisms and integrate the effects of multiple environmental factors;**

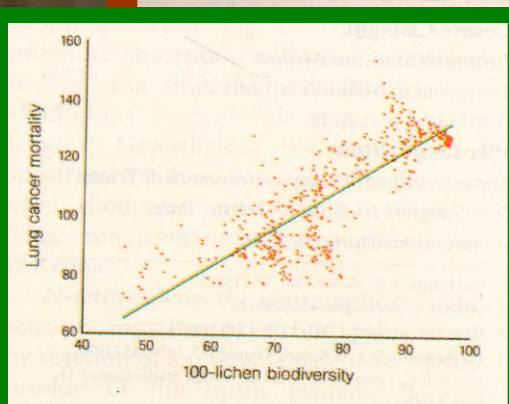
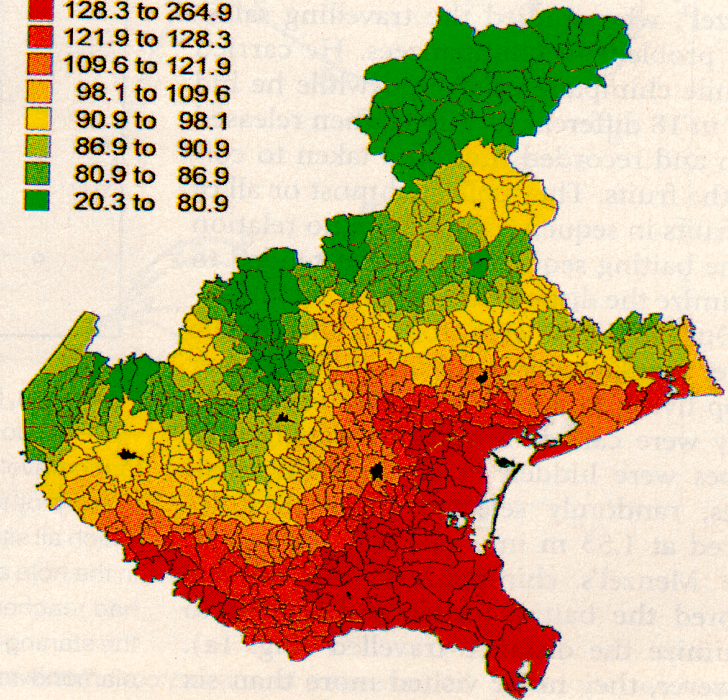
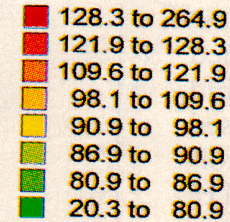
# Lichen biodiversity and public health

Lichen biodiversity index

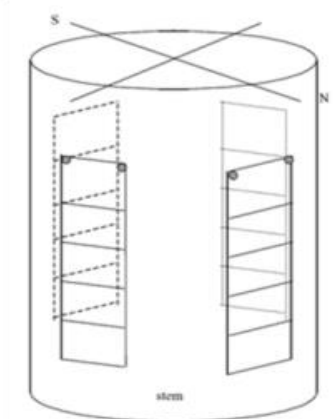


b

Lung cancer mortality



Cislaghi and Nimis, 1997  
Nature Vol. 387:463-464



$$\sum_a^d \frac{\sum_1^n freq}{n}$$

where freq is the frequency of each species (1-n), in each of the four main aspects of the trunk (a,d) and n is the number of sampled trees

**The field collection**

*Asta, J., et al, 2002. Mapping lichen diversity as an indicator of environmental quality, in: Nimis, P., Scheidegger, C., Wolseley, P. (Eds.), Monitoring with Lichens- Monitoring Lichens. Kluwer Academic Publisher, The Netherlands, pp. 273-279.*



# The laboratory



**IRMS**

**HPLC**



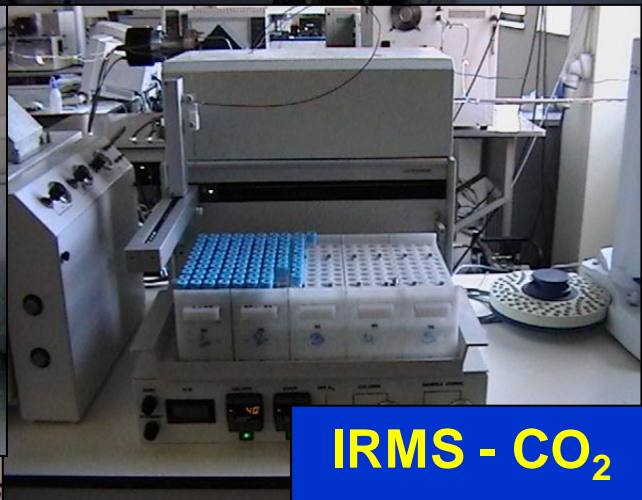
**Elemental analysis**



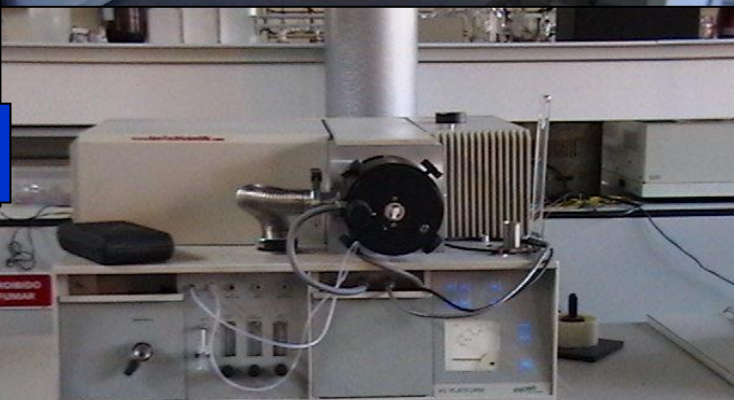
**GC-MS**



**HPLC**



**IRMS - CO<sub>2</sub>**



**LC-MS**

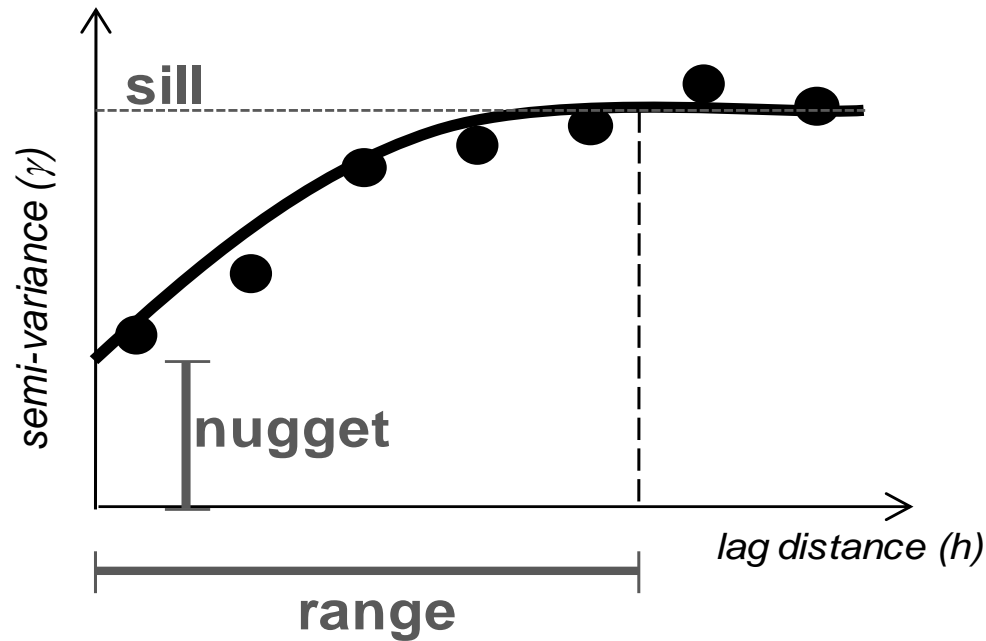


**Spectrophotometry UV VIS**



**Crio-Destillation**

**A spatial explicit analysis is needed for relating lichens to environmental factors**



**geostatistical analysis & interpolation by ordinary kriging**

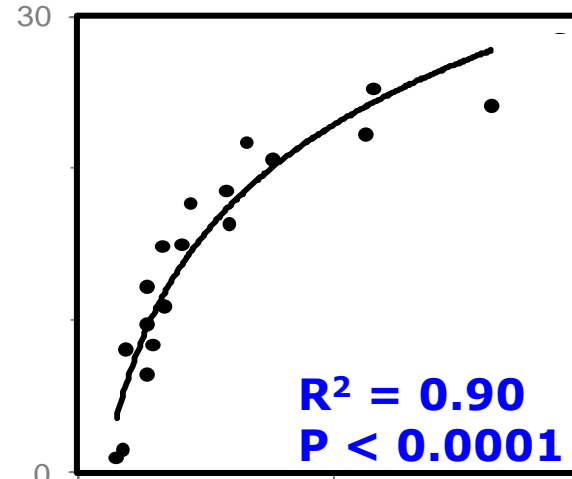
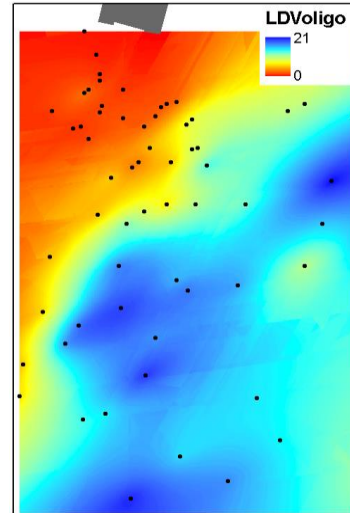
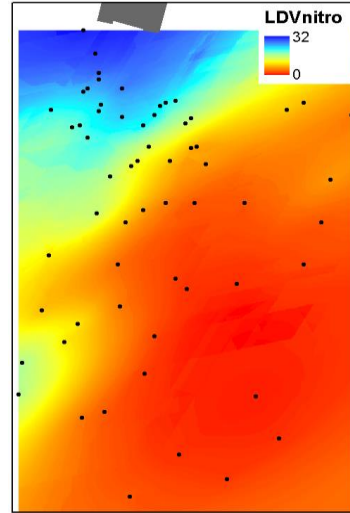
# Nitrogen Pollution

What is the impact of nitrogen pollution in biodiversity in Mediterranean areas?

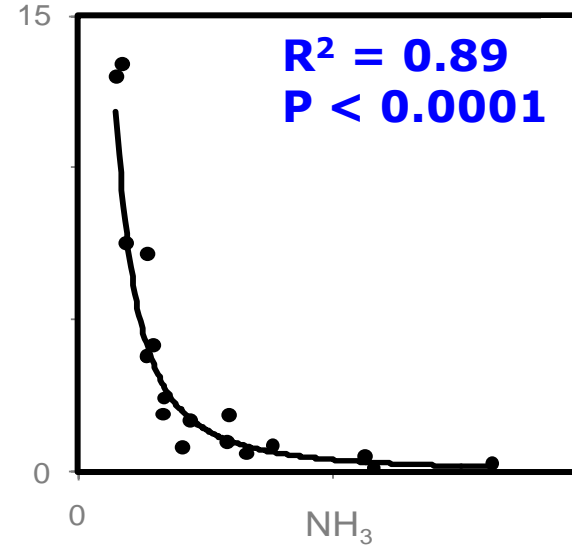
A perspective of the most sensitive components of the ecosystem: lichen communities.

# Single atmospheric NH<sub>3</sub> source

LDV



nitrophytic



oligotrophic

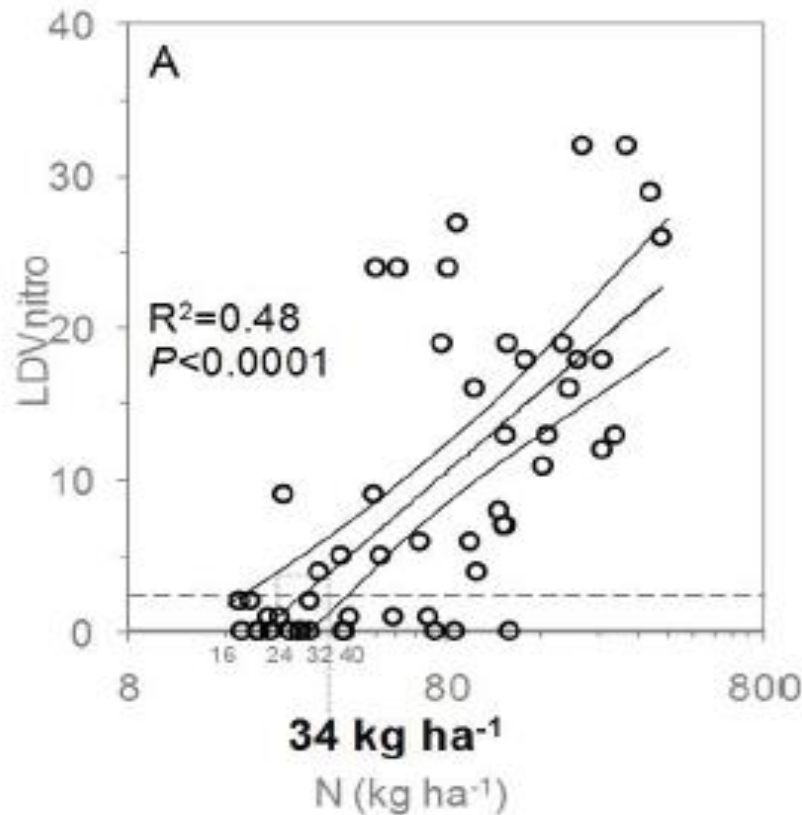
NH<sub>3</sub> ( $\mu\text{g m}^{-3}$ )



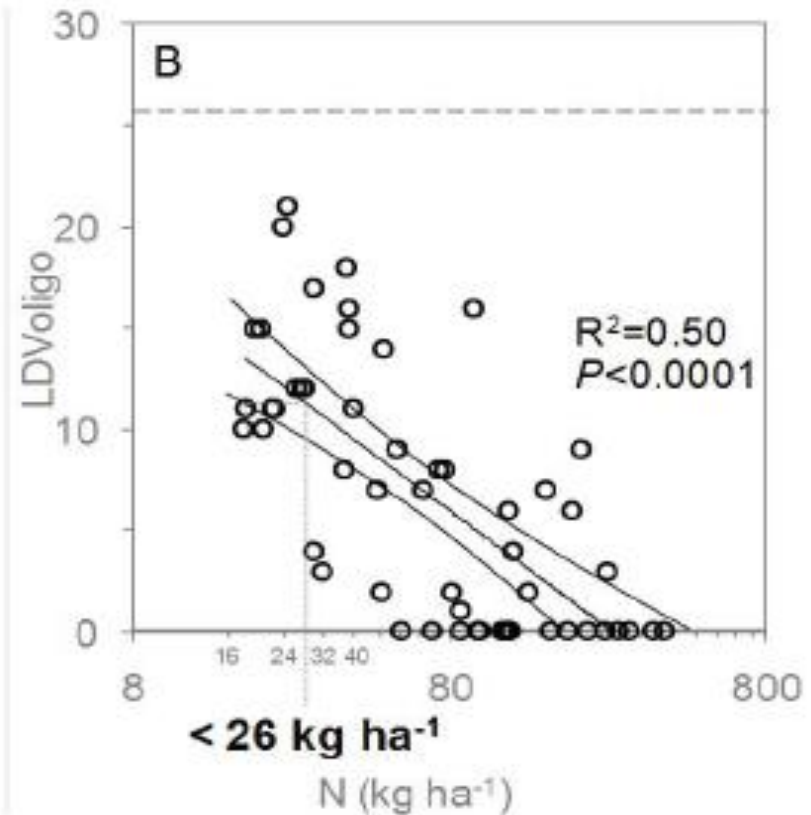
- barn
- ▲ NH<sub>3</sub> sampling sites
- Lichen sampling sites

# Critical loads for N deposition

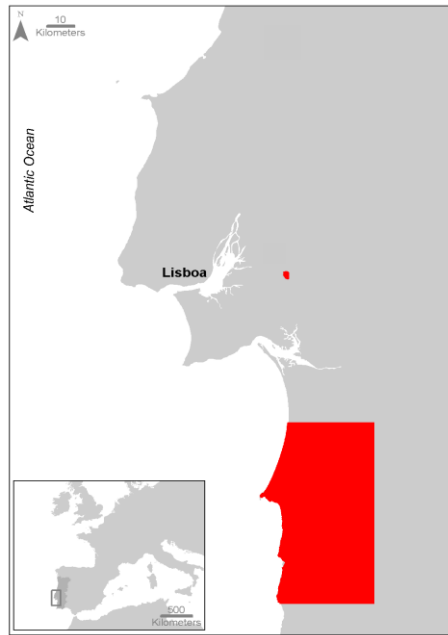
nitrophytic



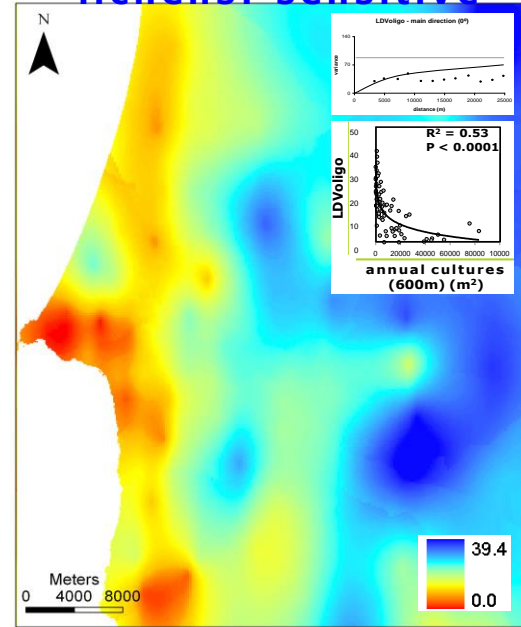
oligotrophic



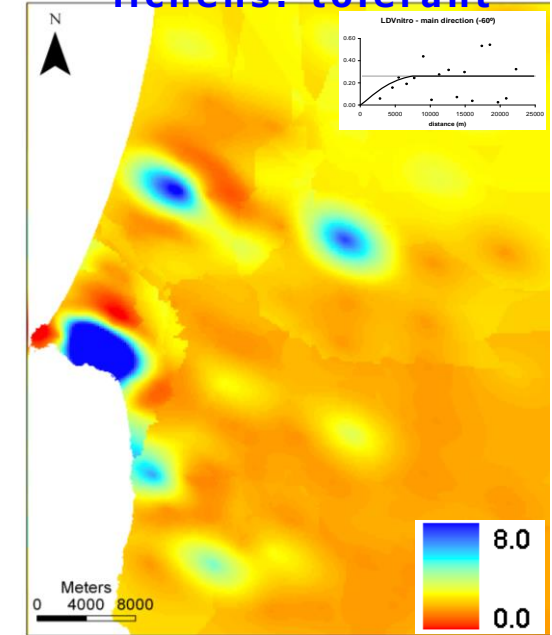
# nitrogen pollution: from regional to local scale



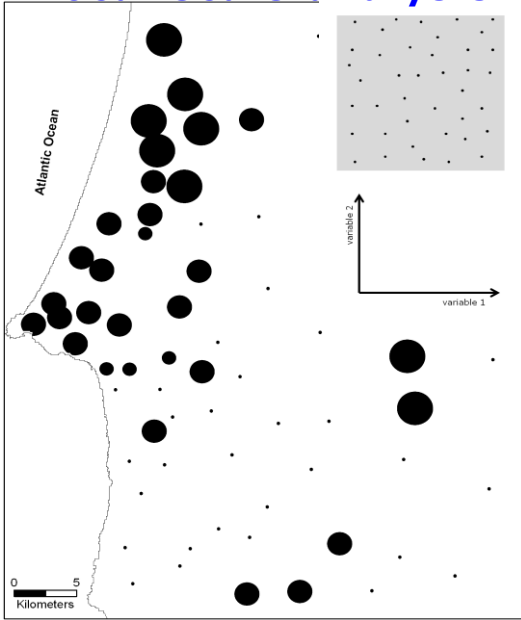
lichens: sensitive



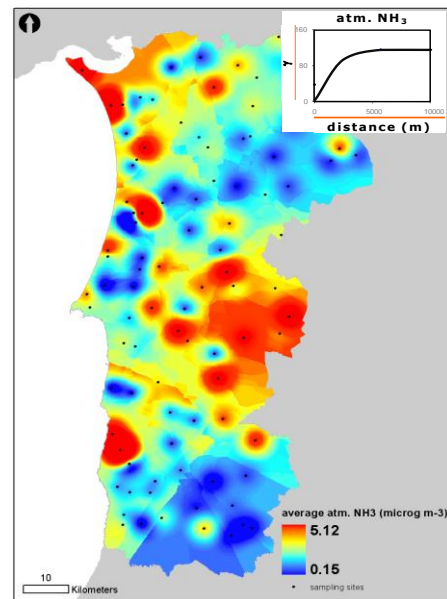
lichens: tolerant



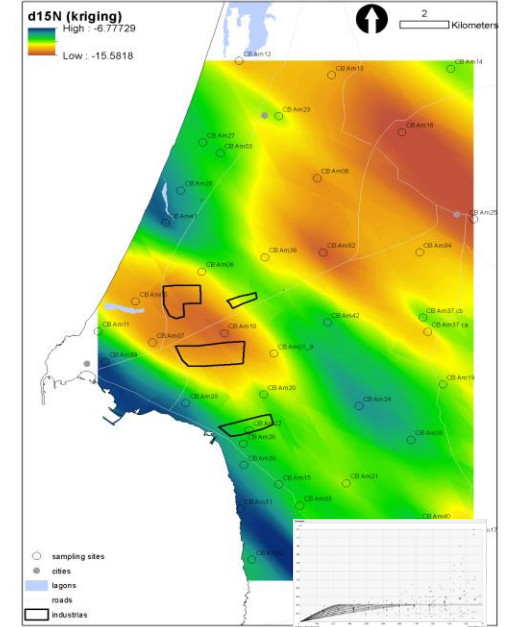
local scale analysis



atmospheric NH3

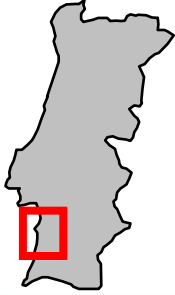


δ<sup>15</sup>N- source fingerprint

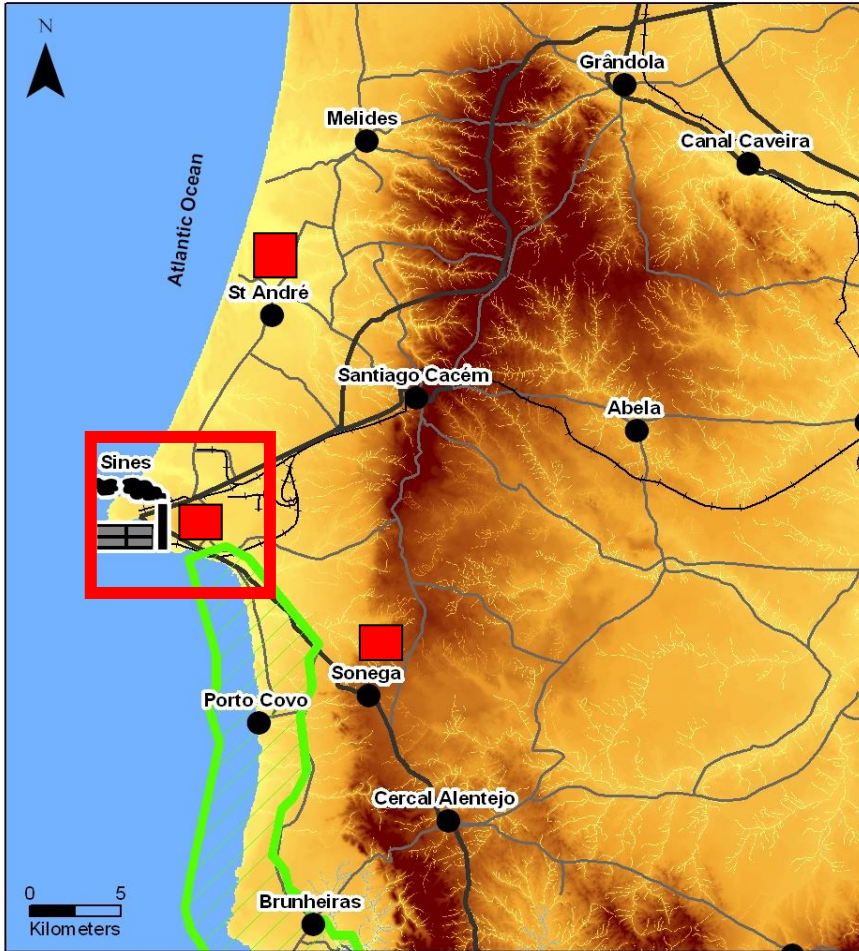


# Heavy metals, dust and industrial particles

Can we disentangle the impact of a complex mixture of pollutants from different origins within a complex landscape?

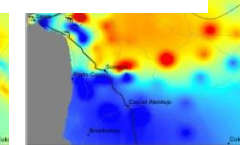
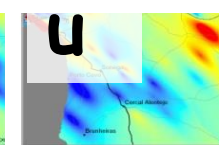
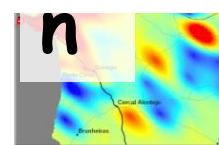
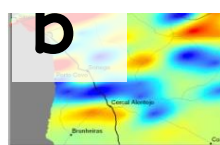
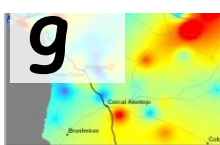
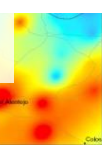
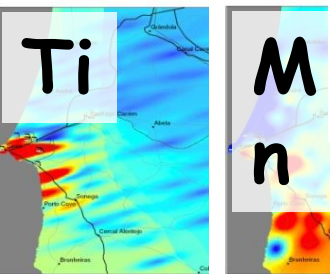
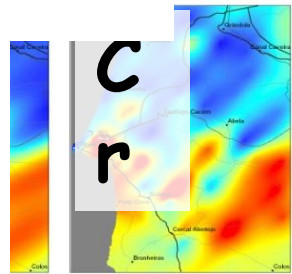
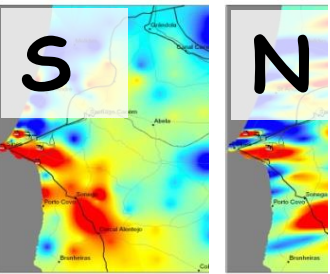
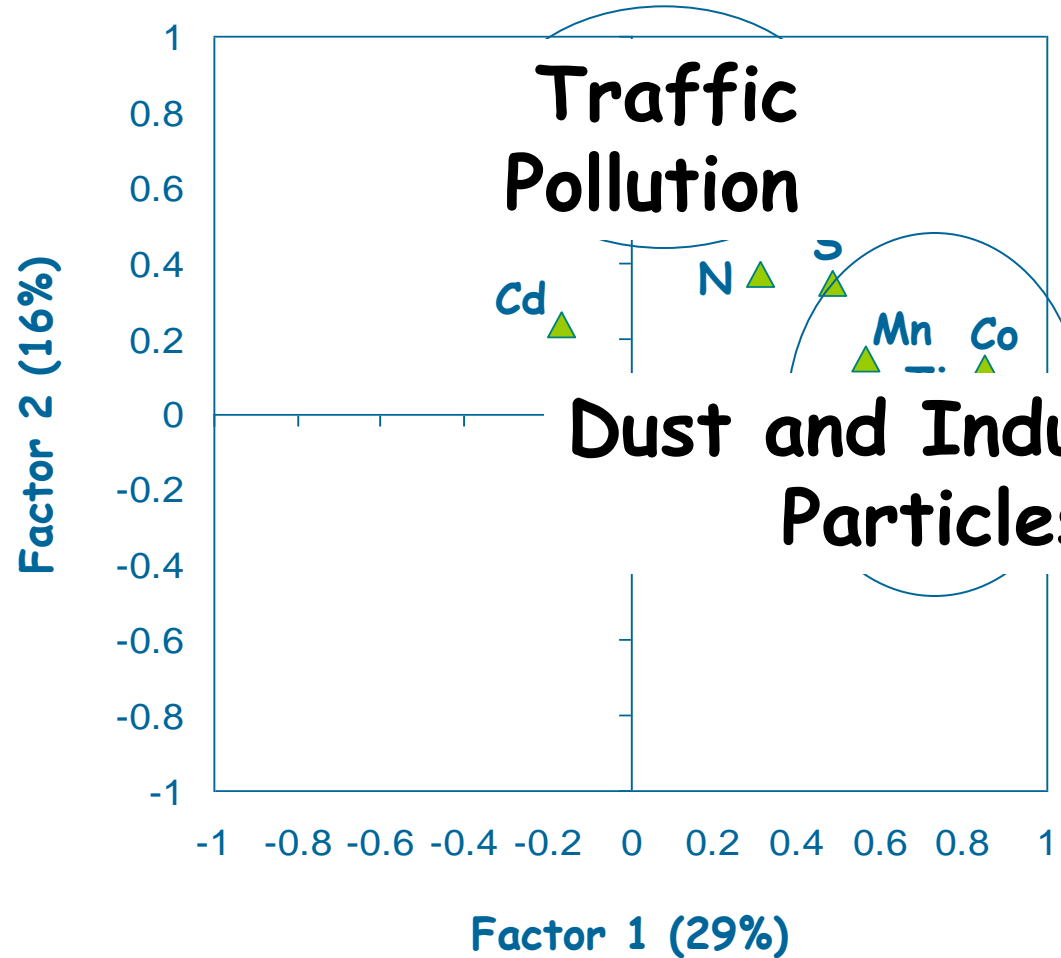
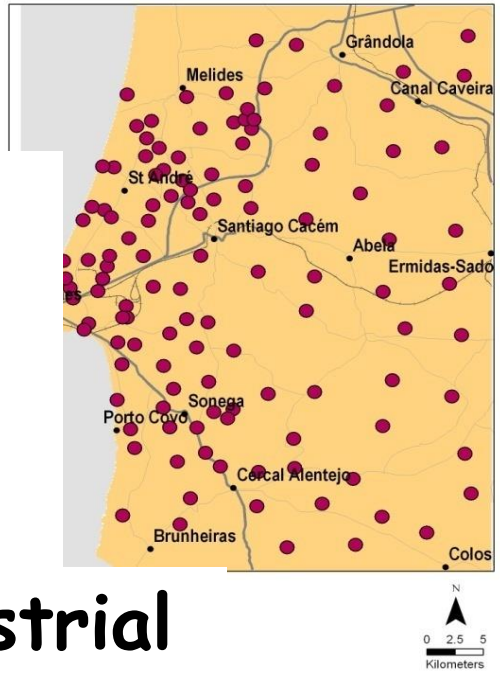


# MULTIPLE Land-Uses and pollution sources





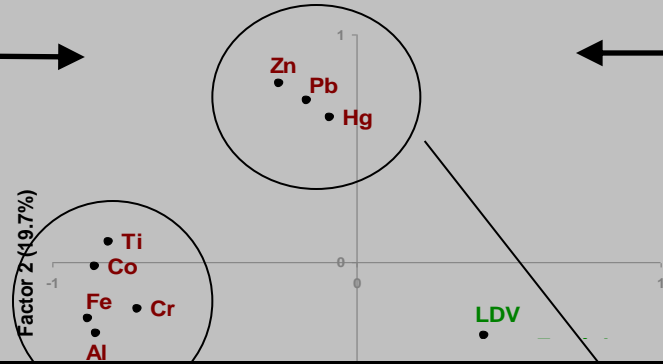
# Lichen Pollutants



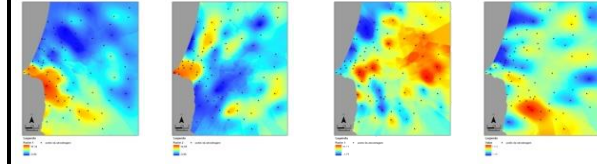
Data from the model of lichen diversity in the region



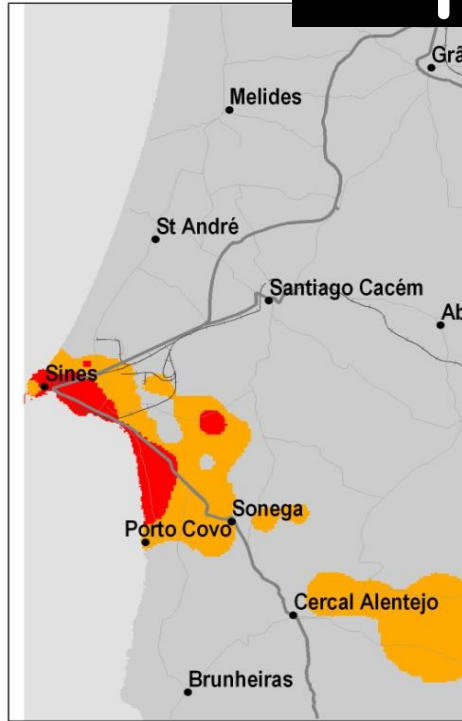
Factor 1 e 2 da ACP



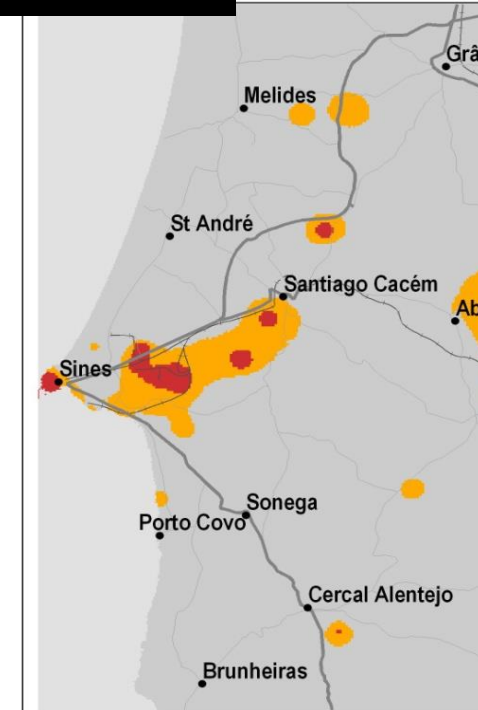
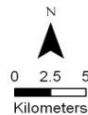
Data from the model of all pollutants in the region



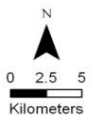
# Map of the "Chronic Pollution"



- Legenda**
- Principais Cidades e Vilas
  - Estradas Secundárias
  - Caminho de Ferro
  - Estradas Principais
- Factor 1 (biodiversidade & poluentes)**
- muito degradado
  - degradado
  - não degradado



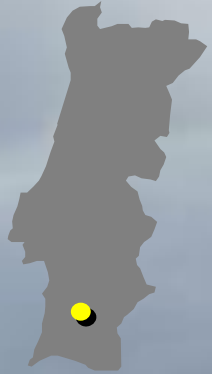
- Legenda**
- Principais Cidades e Vilas
  - Estradas Secundárias
  - Caminho de Ferro
  - Estradas Principais
- Factor 2 (biodiversidade & poluentes)**
- não degradado
  - degradado
  - muito degradado



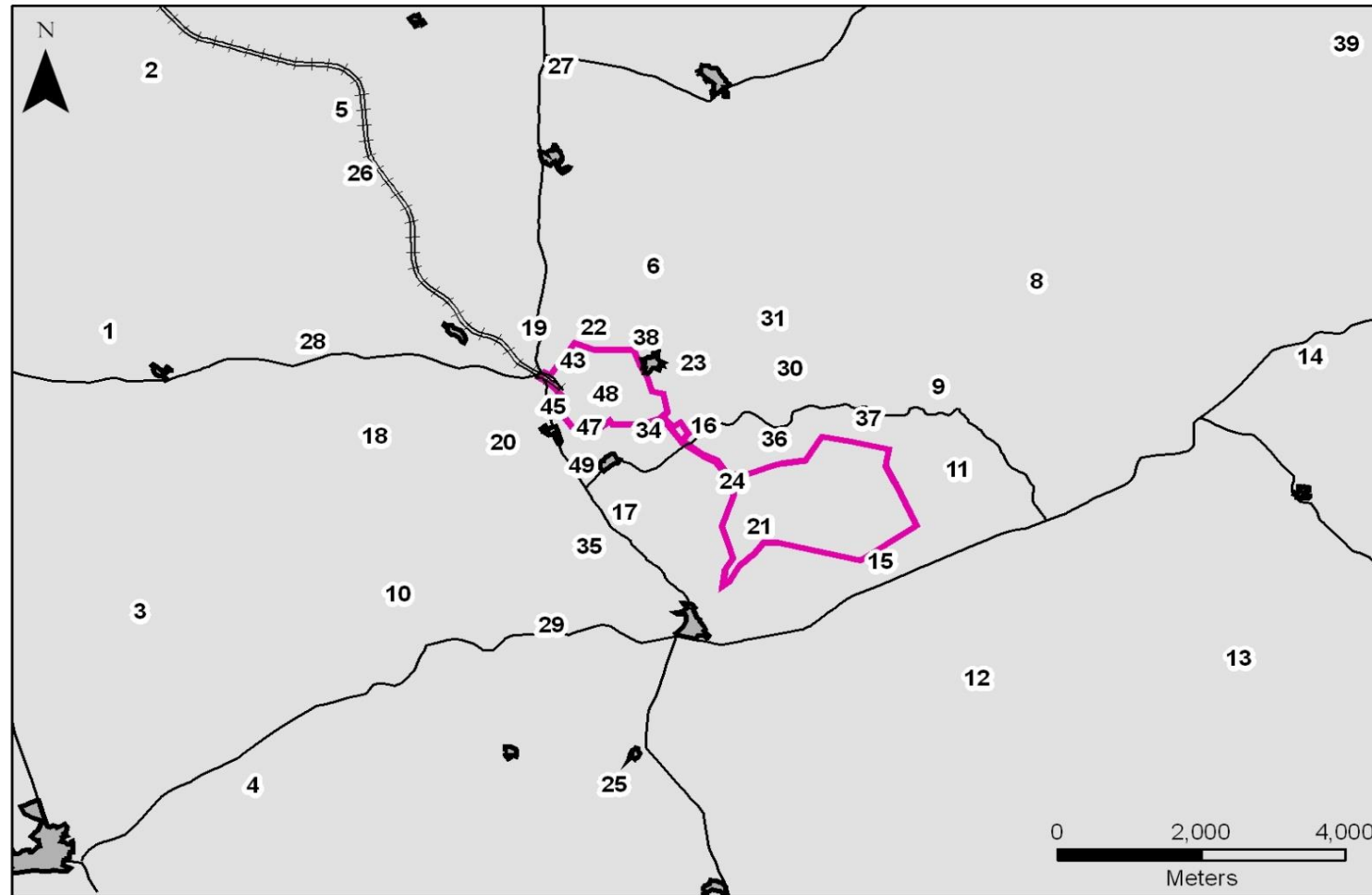
# The impact of a Cu-mine on lichen diversity and its potential use as biomonitor of air quality



# Study-site Underground Cu-mine



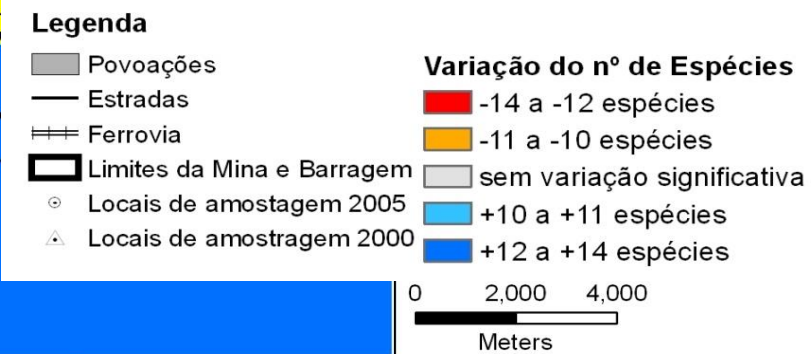
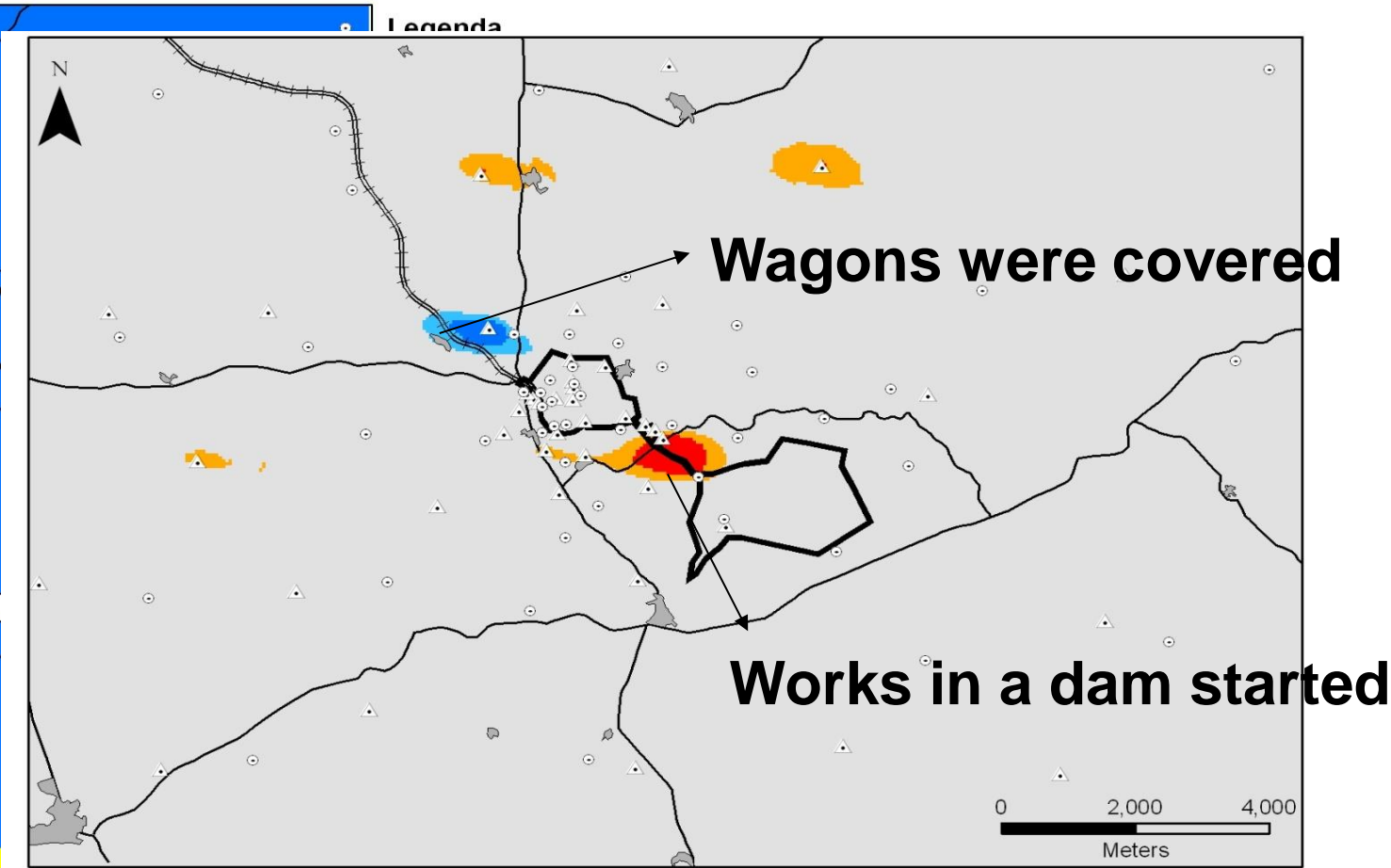
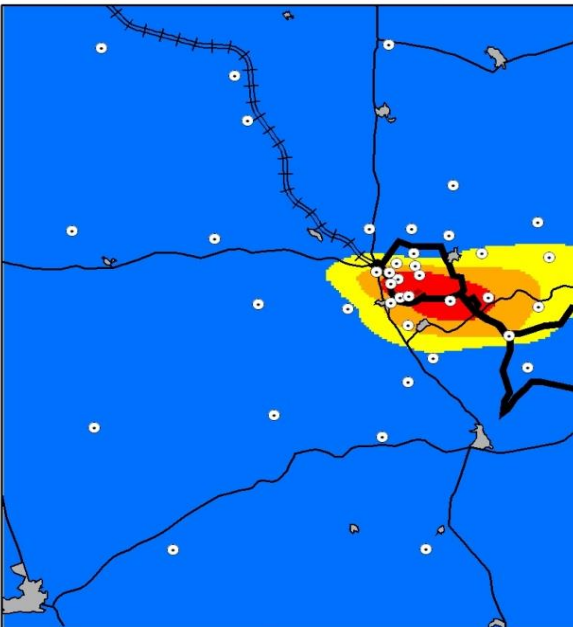
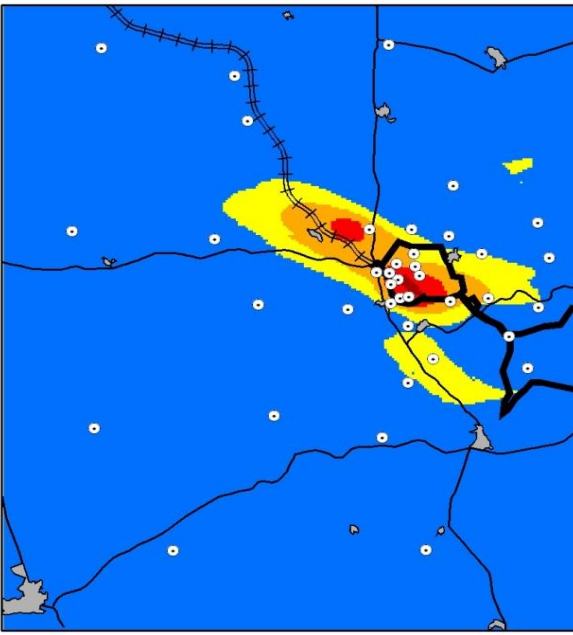
Castro Verde  
Neves Corvo



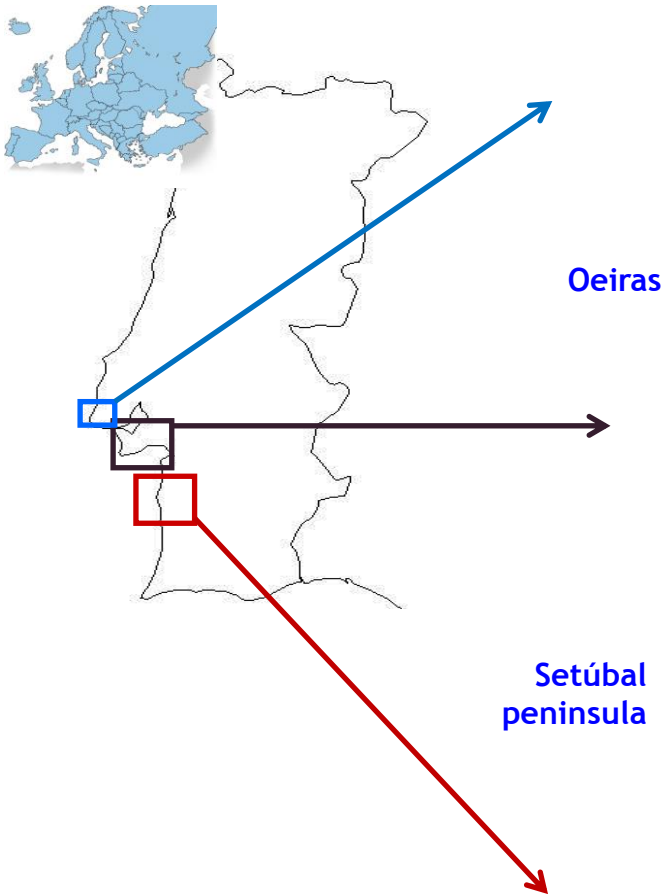
## Legenda

- Povoações
- Estradas
- Ferrovia
- Limites da Mina e Barragem
- Locais de amostagem

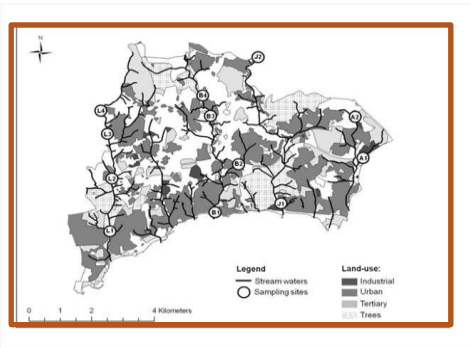
# Comparing spatial models along time – evaluate environmental quality



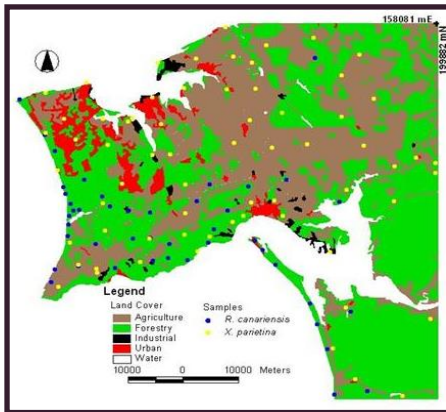
# **The studies concerning persistent organic pollutants (PCDD/Fs and PAHs)**



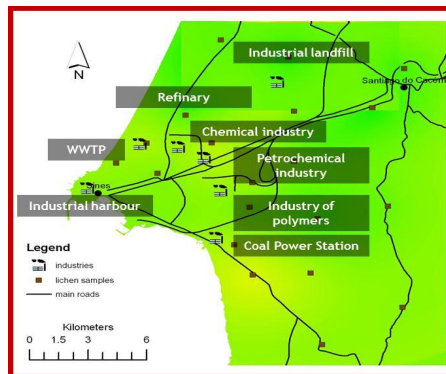
Oeiras



Setúbal peninsula



Sines region



17 toxic PCDD/Fs  
(GC-MS)

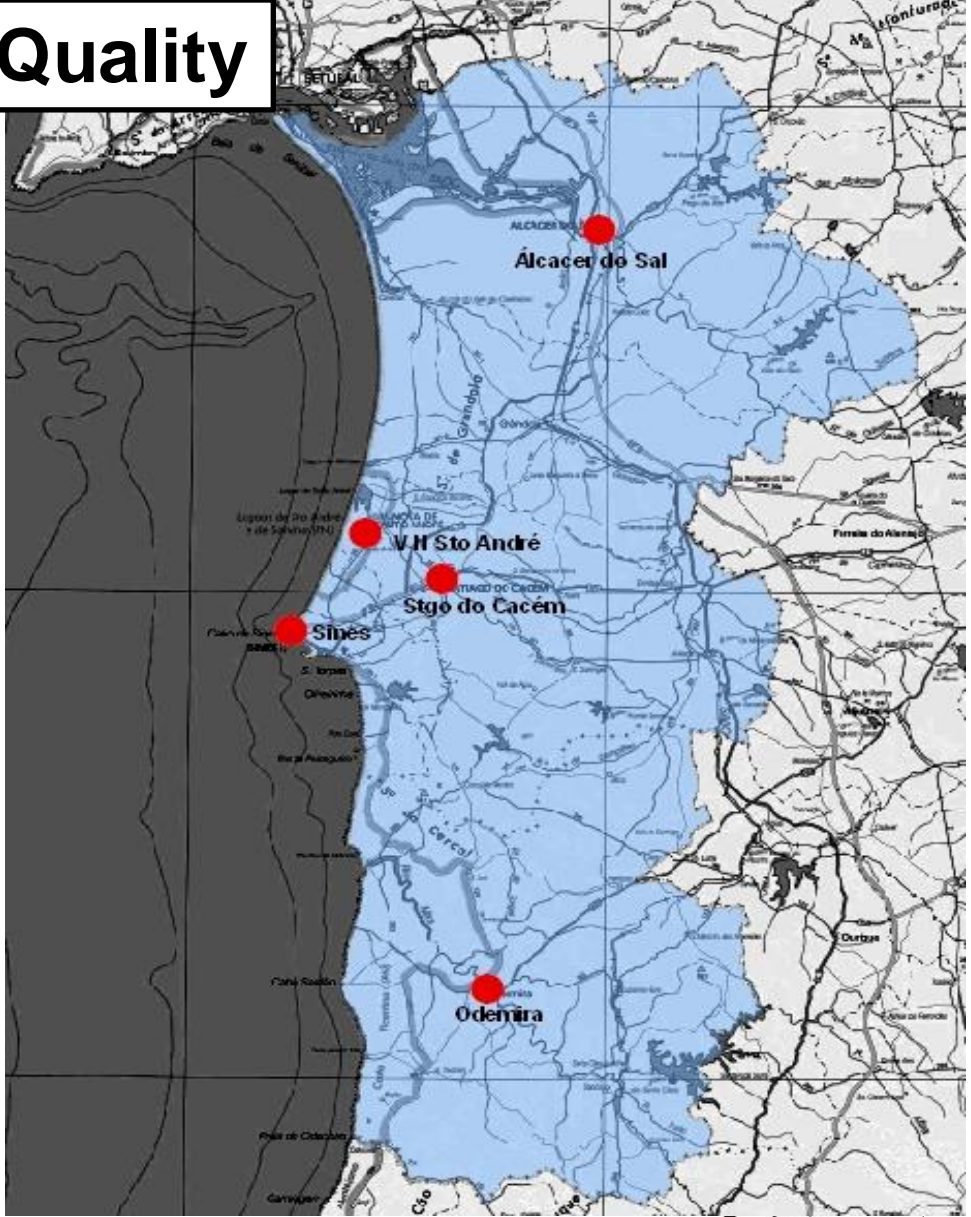
16 EPA-PAHs  
(HPLC)

# Urban Air Quality



# GISA

Gestão Integrada Saúde e Ambiente



Dez 2007 a Dez 2011

5 municípios  
Saúde: ARSLVT  
Ambiente: CCDR-A  
FCUL; IST; ISCTE  
Ricardo Jorge  
12 empresas

Organização:



Câmara Municipal de Sines

Parceiros:



Apoio:



Regi



# GISA General Objectives

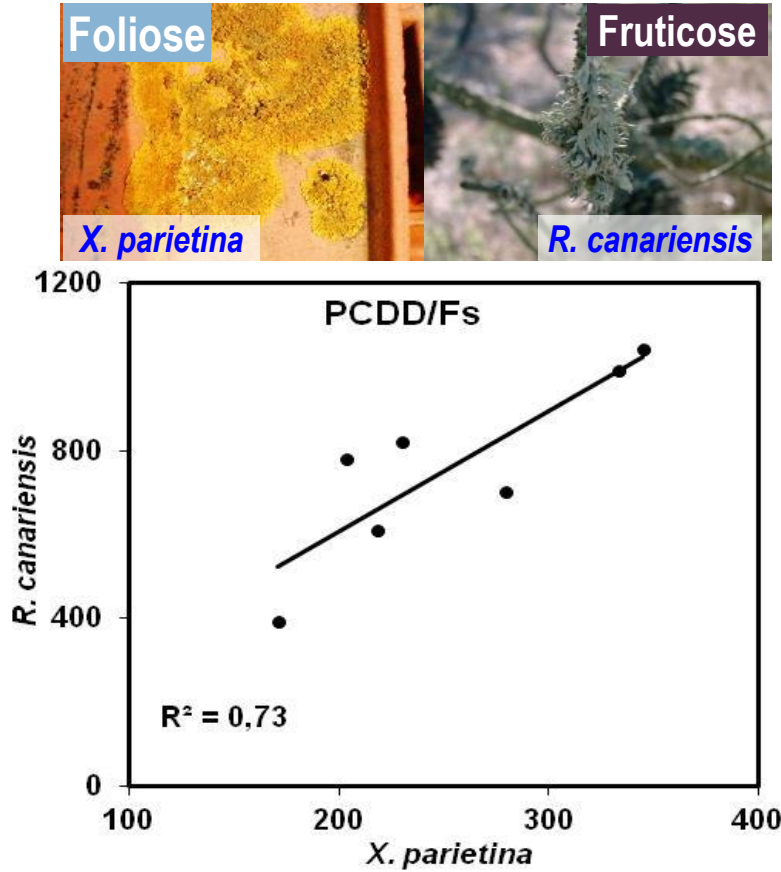
**Develop an integrated technology based on biomonitors to assess environmental pollution and to estimate human exposure to persistent organic pollutants (PCDD/Fs and PAHs)**

# Which factors affect POP accumulation by lichens?

## Substrate

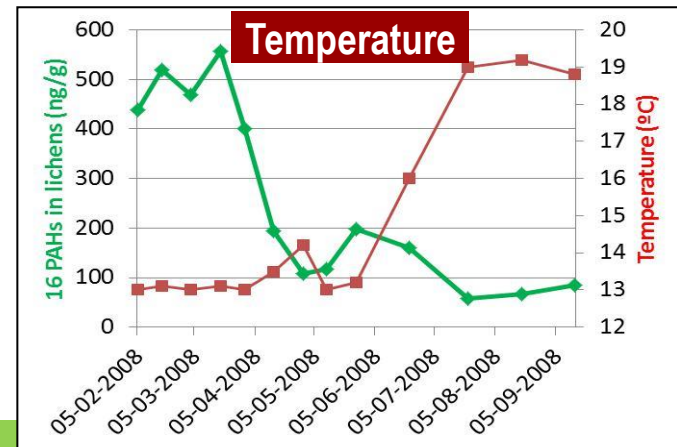
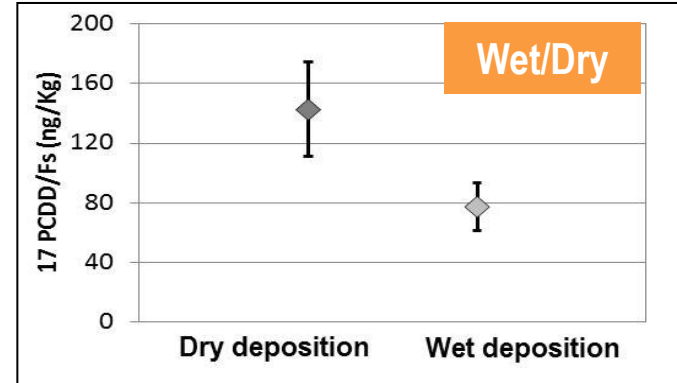


## Growth form



## Climatic factors

### PCDD/F concentrations



➤ No difference was found POPs in lichens collected from different substrates

➤ It's possible to translate PCDD/F concentrations of one lichen species to the equivalent ones of other lichen species enabling to use both in the same study

➤ Dry deposition was associated with higher concentrations of POPs in particles.

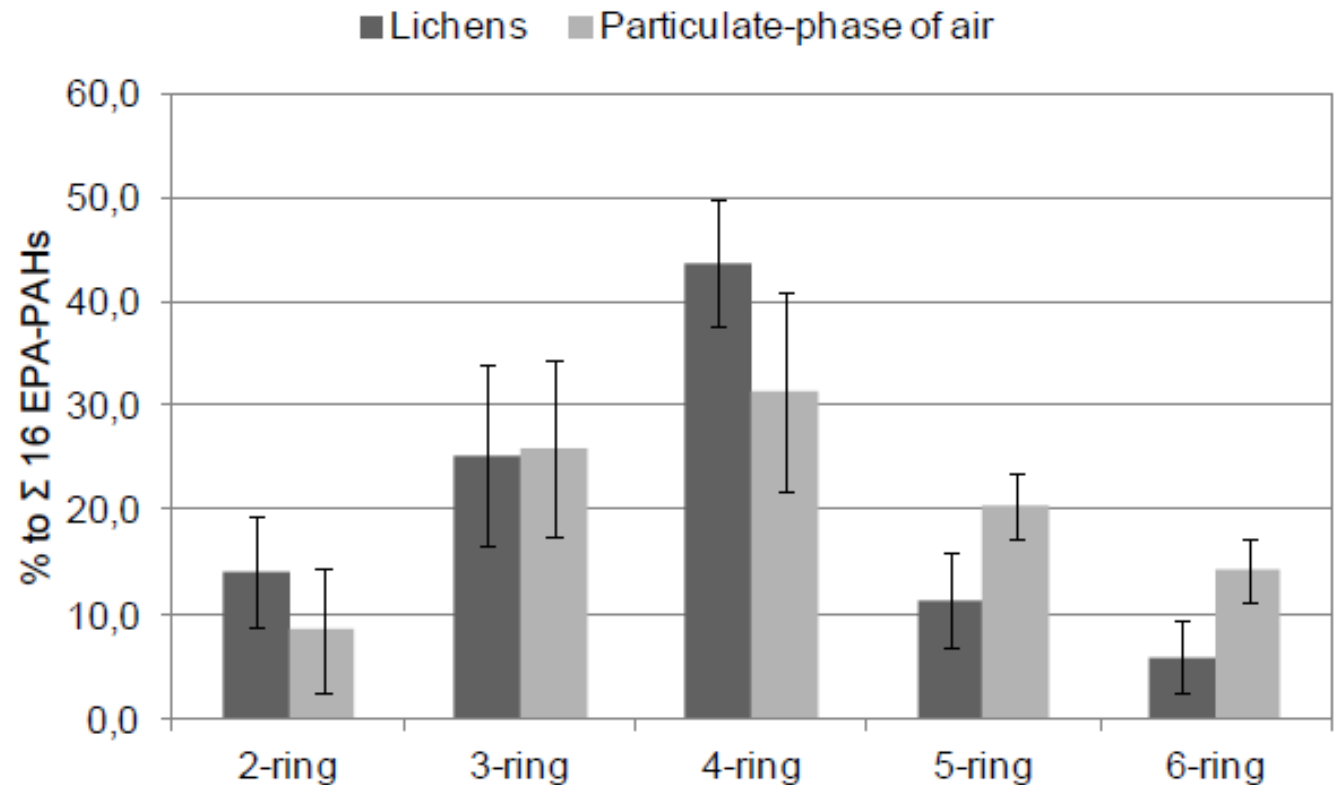
➤ Temperature decreases the concentration of more volatile POPs both in lichens and air.

# Lichens and reference methods (soil and air)



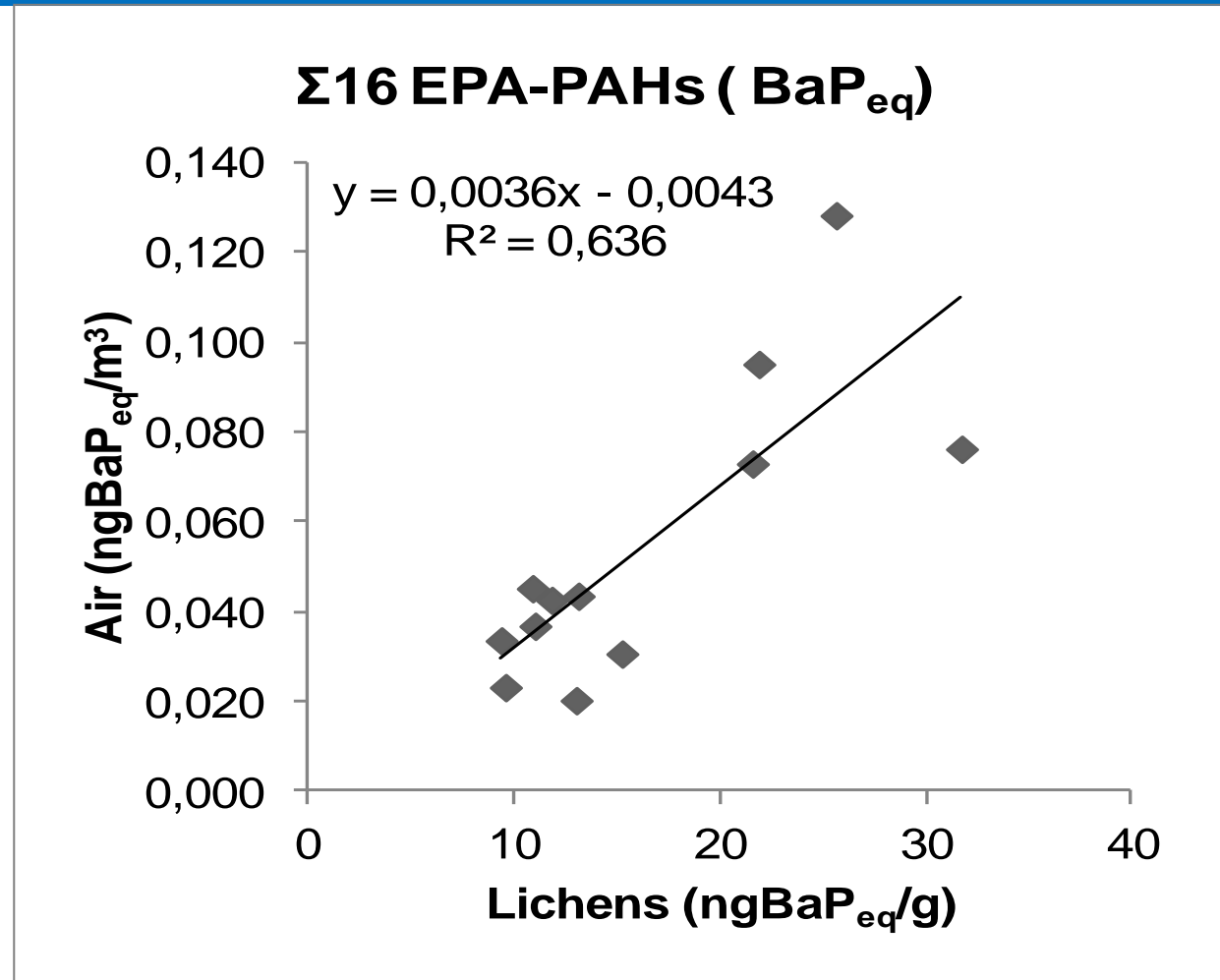
Augusto et al., Submitted. A step towards the use of biomonitors as estimators of atmospheric PAHs for regulatory purposes.

PAH ring profile



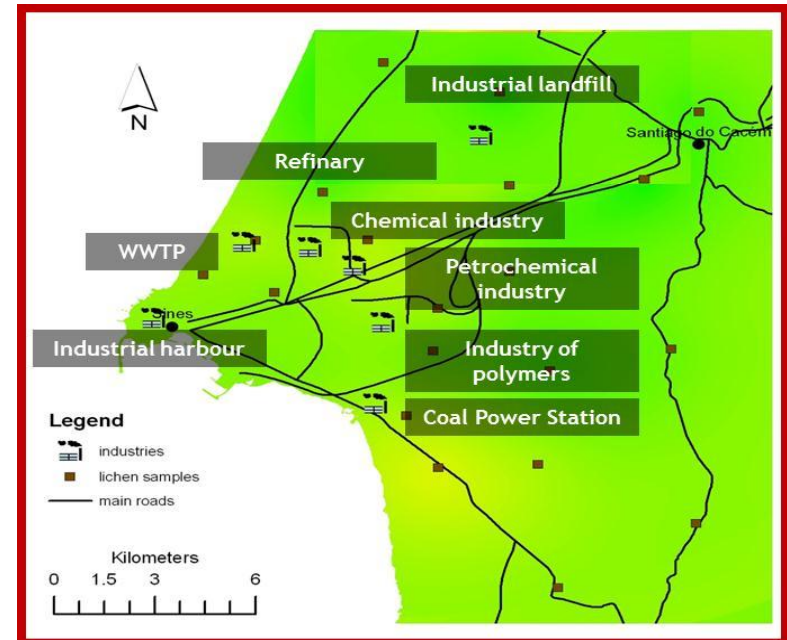
- Lichens and air show similar PAH profiles, with highest contribution of 4-ring PAHs.
- Particulate-phase of air: higher contribution of HMW-PAHs (5- and 6-ring PAHs).
- Lichens integrate both the particulate- and gas-phase of air.

# Lichens and reference methods (soil and air)



➤ It's possible to translate PAH concentrations in lichens into the equivalent ones for air.

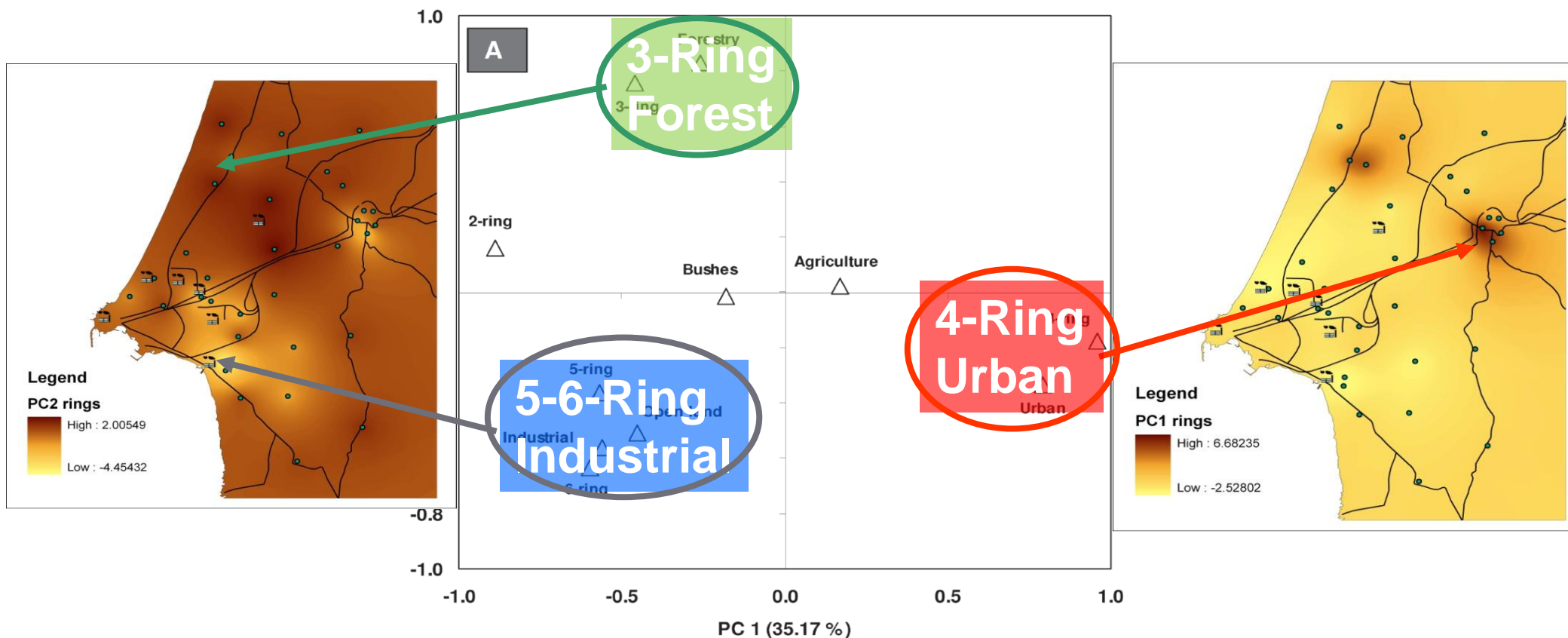
# Using lichens to track pollution sources in the industrial region of Sines; Fingerprinting pollution sources using biomonitoring tools



Highly industrialized region of Sines, located on the SW coast of continental Portugal.

Relative cover of each land-use class in circular buffers (1 Km radius) centered at each sampling site.

# Using lichens to track pollution sources in the industrial region of Sines

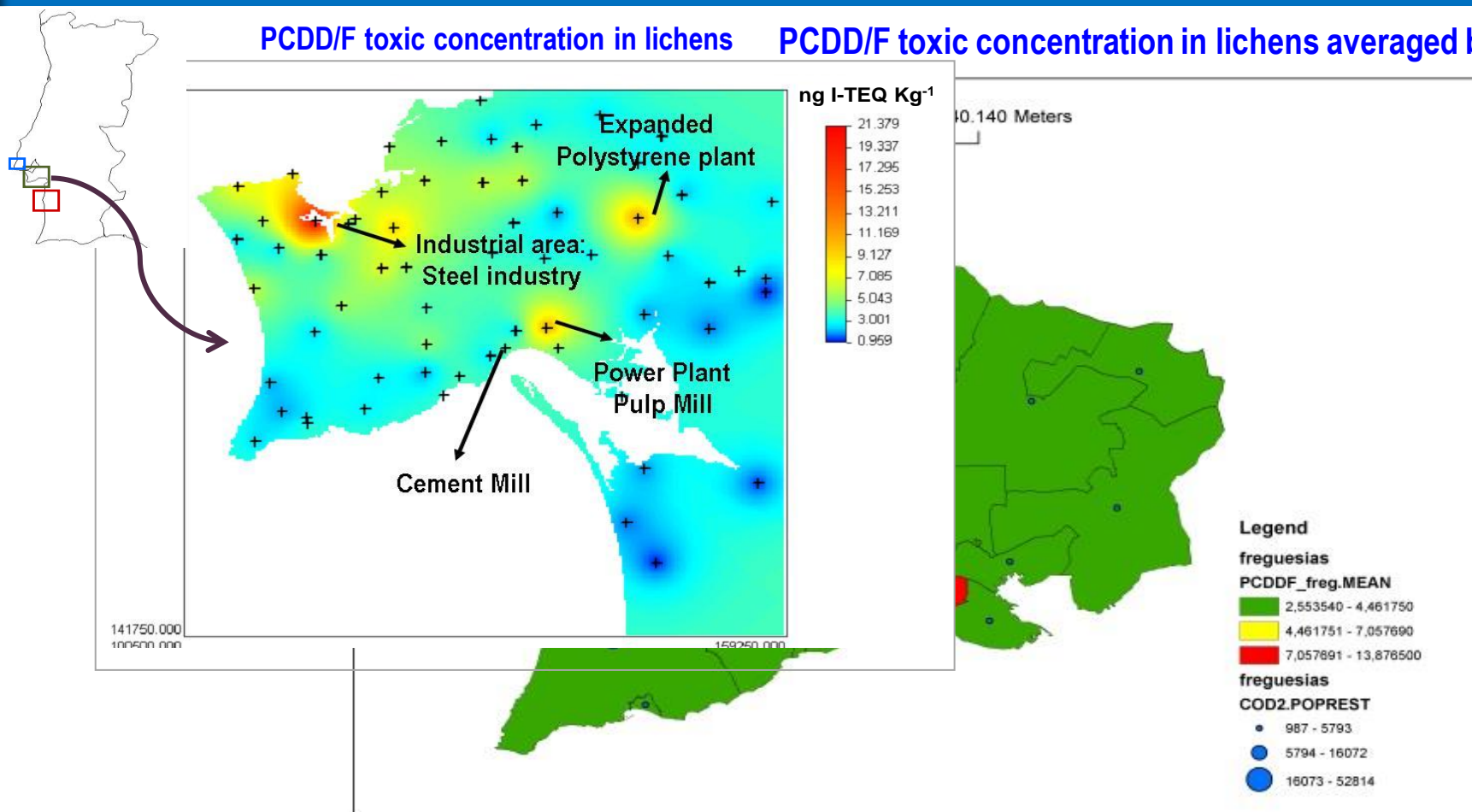


➤ Lichens allow fingerprinting different pollution sources in multisource areas.

# How can we integrate biomonitor information into human health risk studies?

PCDD/F toxic concentration in lichens

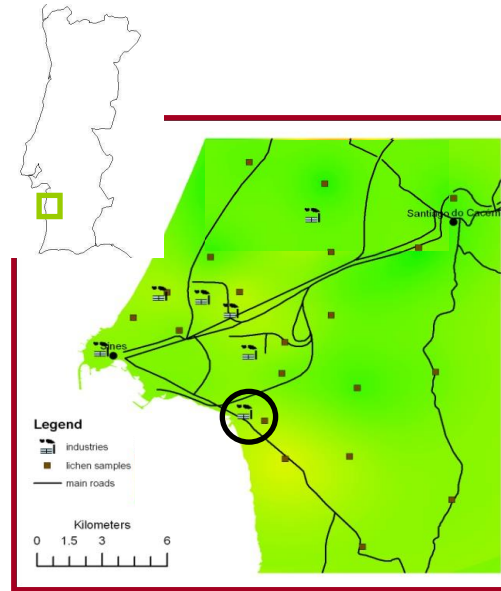
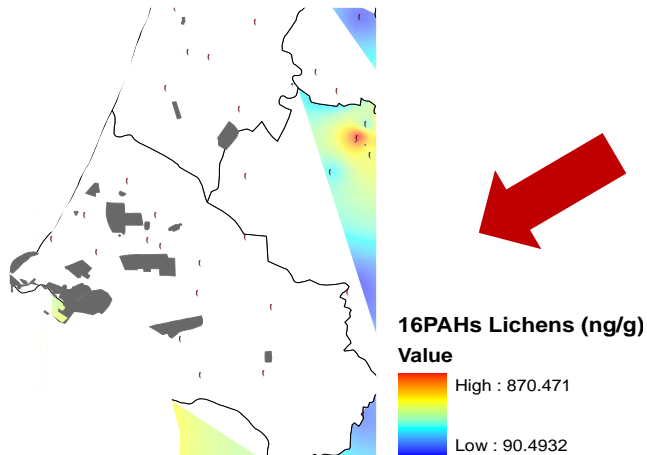
PCDD/F toxic concentration in lichens averaged by parish



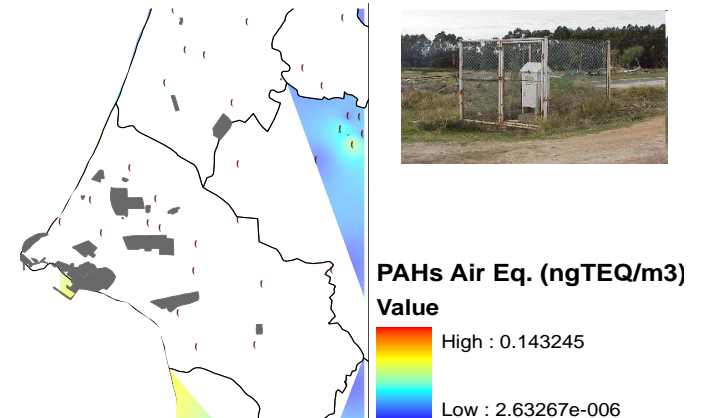
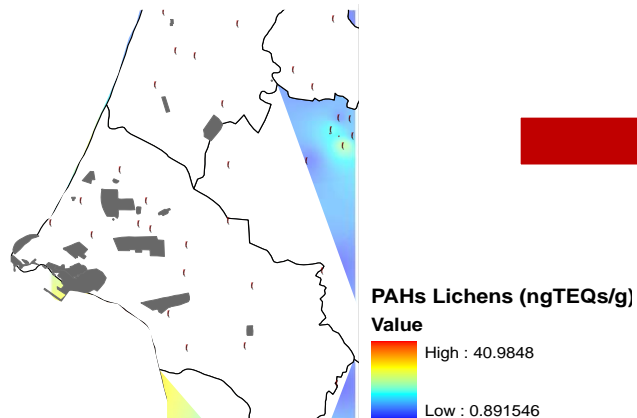
- Biomonitoring allows obtaining high spatial resolution maps for POP deposition, enabling to identify which populations are exposed to environmental pollutants and which ones can be considered as control.

# How to integrate lichens into health studies?

Using PAH concentrations in lichens to create high spatial resolution maps



Using the equivalent PAH concentrations for air to estimate the levels inhaled by humans





- In this work it was shown how **environmental biomonitors can be used to complement conventional monitoring methods.**
- A **spatial explicit analysis allowed us to disentangle the effects of multiple factors** and map them with the confidence with high spatial resolution.
- Lichens functional groups can be used as **early-warning and universal ecological indicators** for factors associated to global changes: excess nitrogen atmospheric deposition and climate changes
- Lichens and aquatic mosses have shown to be **useful biomonitors, accumulating POPs** over detection limits and allowing to track different pollution sources.
- The high spatial resolution maps obtained using biomonitors allow getting a **real picture of dispersion and deposition of atmospheric POPs**, enabling to identify control and exposed populations for further human health studies.
- Translating POP concentrations in lichens into the equivalent ones for air, allows integrating biomonitors into human exposure and **human health risk assessments.**



# Future

- To continue the development of a framework that will provide a better knowledge of pollutants origin and source- *Fingerprint analysis*
- To contribute to the development of new technologies based on our knowledge on ecological indicators, in particularly lichens- *Efficient new sensors*
- To interact and exchange experiences and knowhow- *Networking*



**Thank you for your attention**

➤ Serra da Arrábida, Portugal  
(38° 28' 40" N, 8° 59' 34" W)