European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

INTERNATIONAL WG1-WG4 MEETING on

New Sensing Technologies and Modelling for Air-Pollution Monitoring

Institute for Environment and Development - IDAD

Aveiro, Portugal, 14 - 15 October 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016 - Year 3: 2014-15 (*Ongoing Action*)

Spatial Distribution and Origin of Pollutants in Lichens for Fingerprinting of Air-Pollution

U LISBOA | UNIVERSIDADE DE LISBOA

cba Centro de Biologia Ambiental

Cristina Máguas

Function in the Action: (WG Member)

CBA/ Center for Ecolog, Evolution and Environmental Changes (Ce3C), ULisboa/ Portugal

EUROPEAN SCIENCE FOUNDATION ESF provides the COST Office through a European Commission contract

Presentation Outline

- Main goals
- Tools and methodologies
- Case studies: innovation and confirmation of earlier results
- Conclusions
- Future directions

COST goals:

To develop new sensing methodologies for air and environment quality and control at integrated temporal and spatial scales

Objectives and Main Research Areas

Main Goals:

To develop new sensing methodologies for air and environment quality and control at integrated temporal and spatial scales

Main methodologies:

1. **Ecological indicators (biodiversity; establishment of critical thresholds; pollution sources)**
2. **Physical and chemical analysis (calibration methods; innovative applications and methods)**
3. **Geostatistical modelling**

Current Activities

1. COST Actions

COST Action TD1209. European Information System for Alien Species (Coordinator Helen Roy, UK) (2013-2016)
COST Action ES 1104 Arid Lands Restoration and Combat of desertification: Setting up a dryland and desert restoration Hub (Coordinator Benz Kotzen, UK).

2. I&D projects (FP7, National funds)

Nitrogen deposition, critical loads and biodiversity/ecosystem services/public health

3. Contracts with private companies

Monitorization of ecological Impacts related with land-use changes, POP, mining activities

Lichens as ecological-indicators of atmospheric conditions

• symbiosis fungus and a photobiont: a green algae and/or a cyanobacteria;

• poikilohydric: 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;

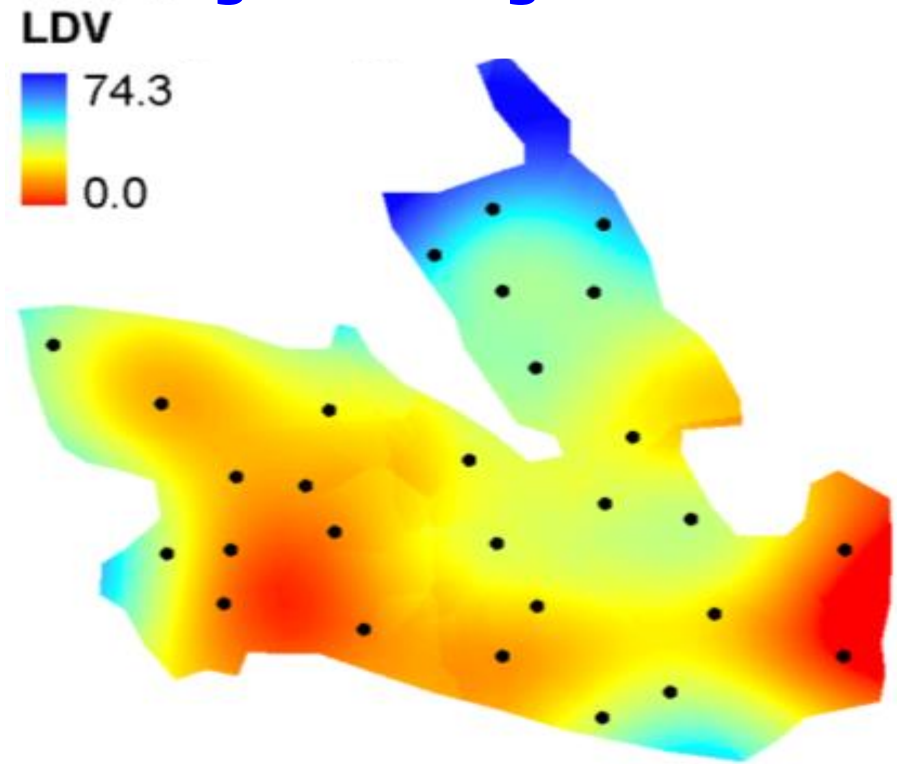
• can be collected and identified throughout the year;

• are long-living organisms and integrate the effects of multiple environmental factors;

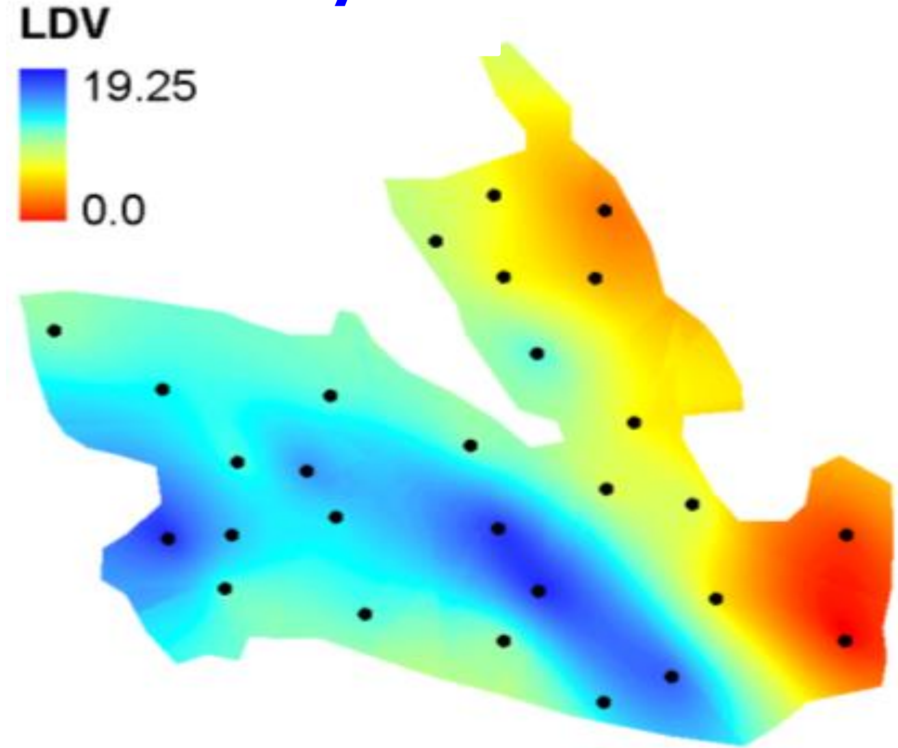
• lichens are powerful indicators for processes dependent on the atmosphere

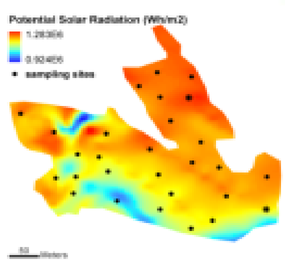
Interpolation within a forest patch

green-algae lichen



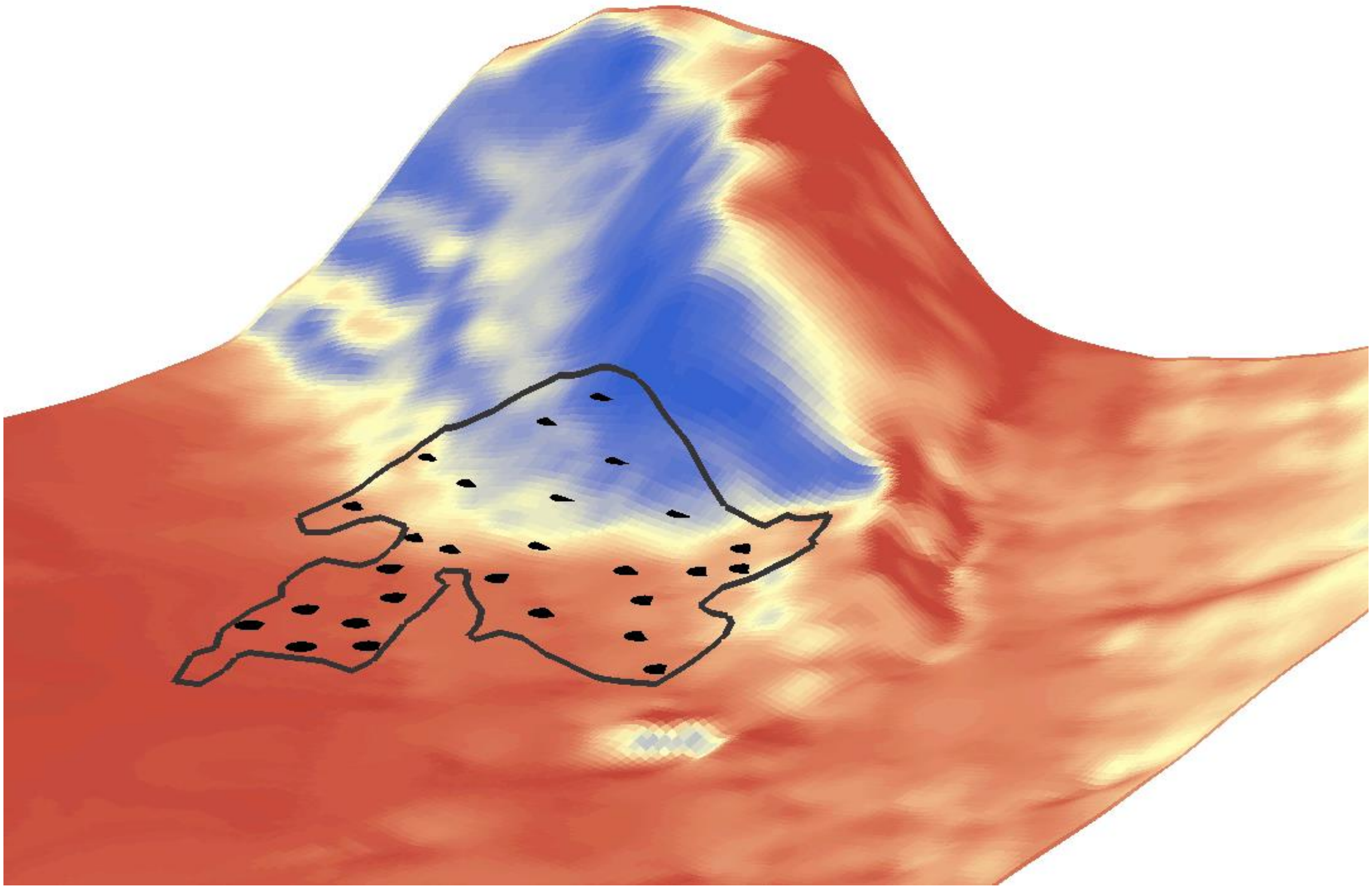
cyanolichens

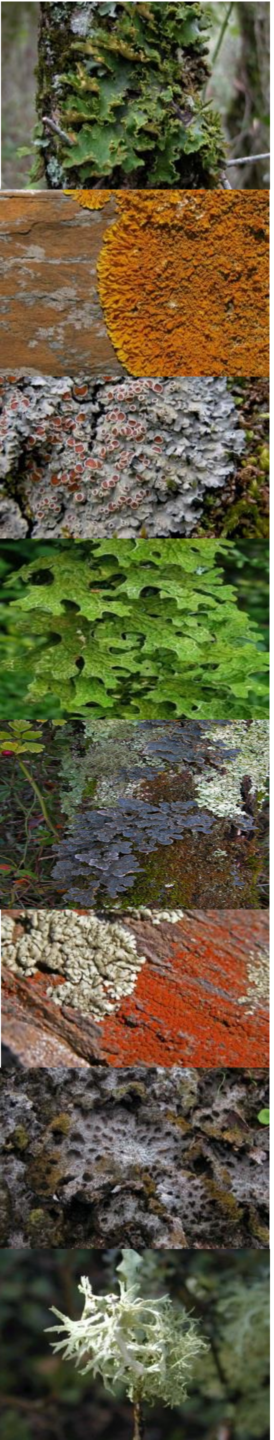




Pinho, Branquinho, Soares, Pereira, Maguas, submitted to Global Change Biology

Potential energy

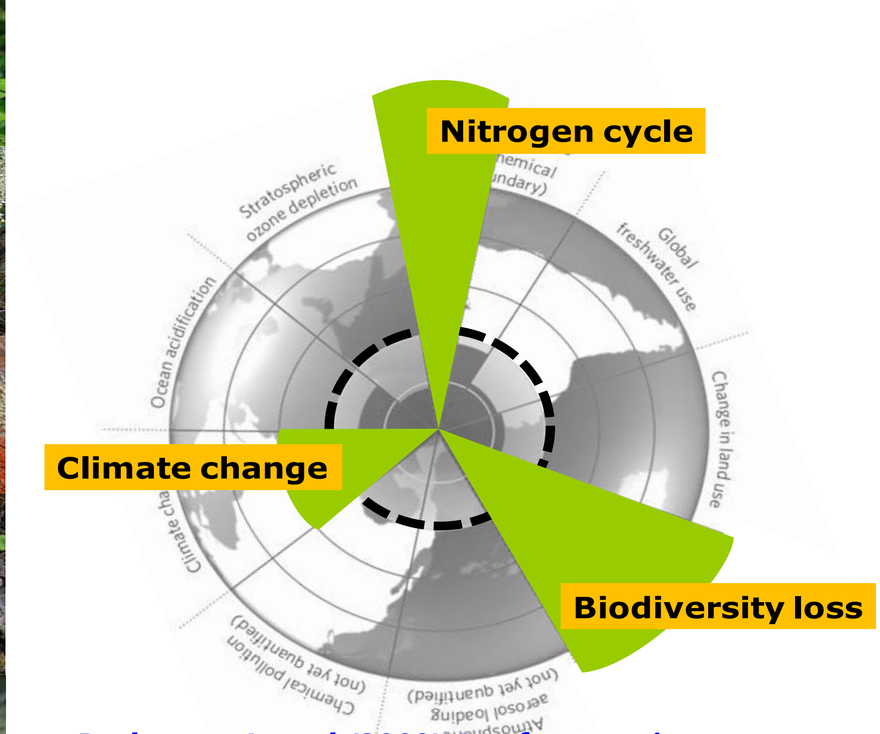




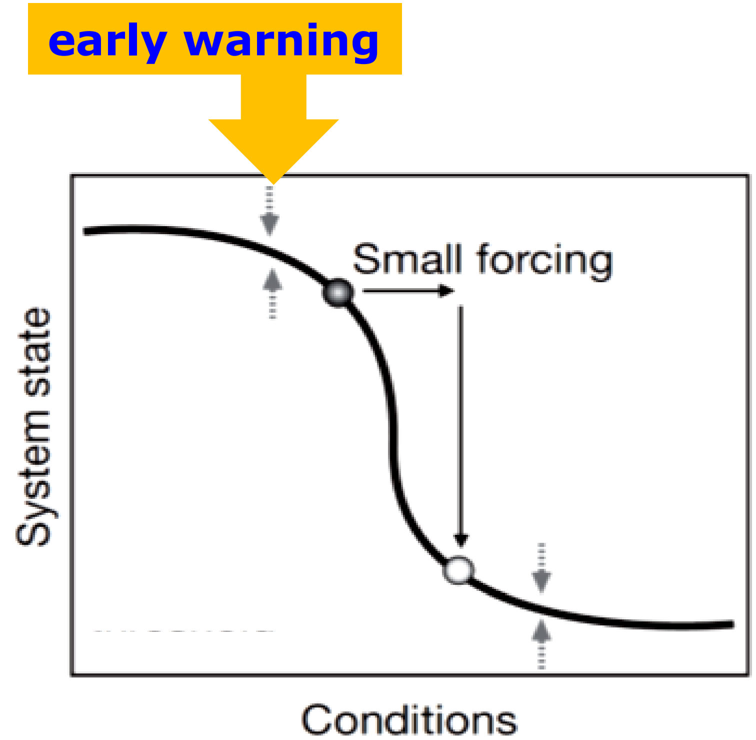
Global change drivers

Lichens respond to microclimate changes and may not be the best to respond to global changes....

However if we use gradientes, we may model such changes



Rockstrom J, et al (2009) A safe operating space for humanity. Nature 461:472-475.



Scheffer M, et al. 2009. Early-warning signals for critical transitions. Nature 461:53-59

Biomonitoring persistent organic pollutants with Lichens: *Some results*

Sofia Augusto, Cristina Máguas & Cristina Branquinho

cba Centro de Biologia Ambiental

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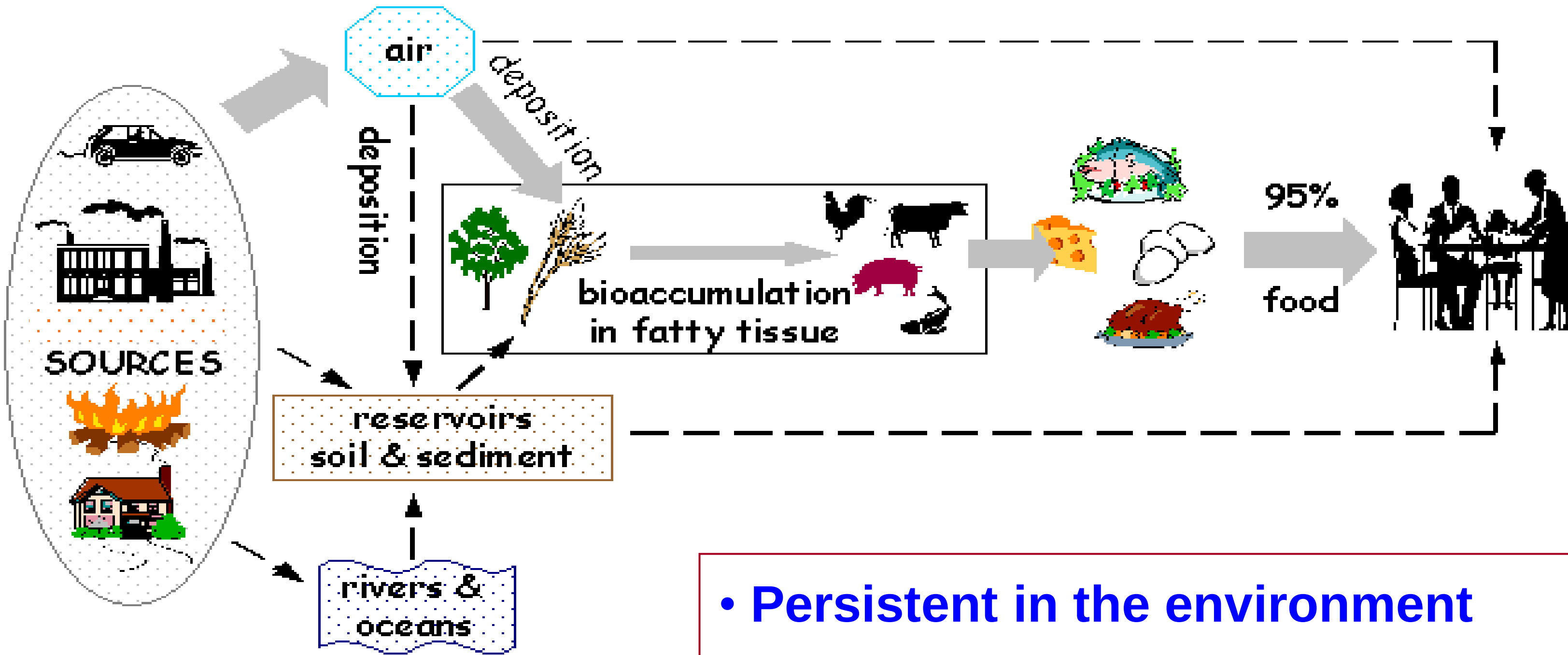
FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

Persistent Organic Pollutants (POPs)



- Persistent in the environment
- Lipophilic compounds
- Bioaccumulate in the food chain

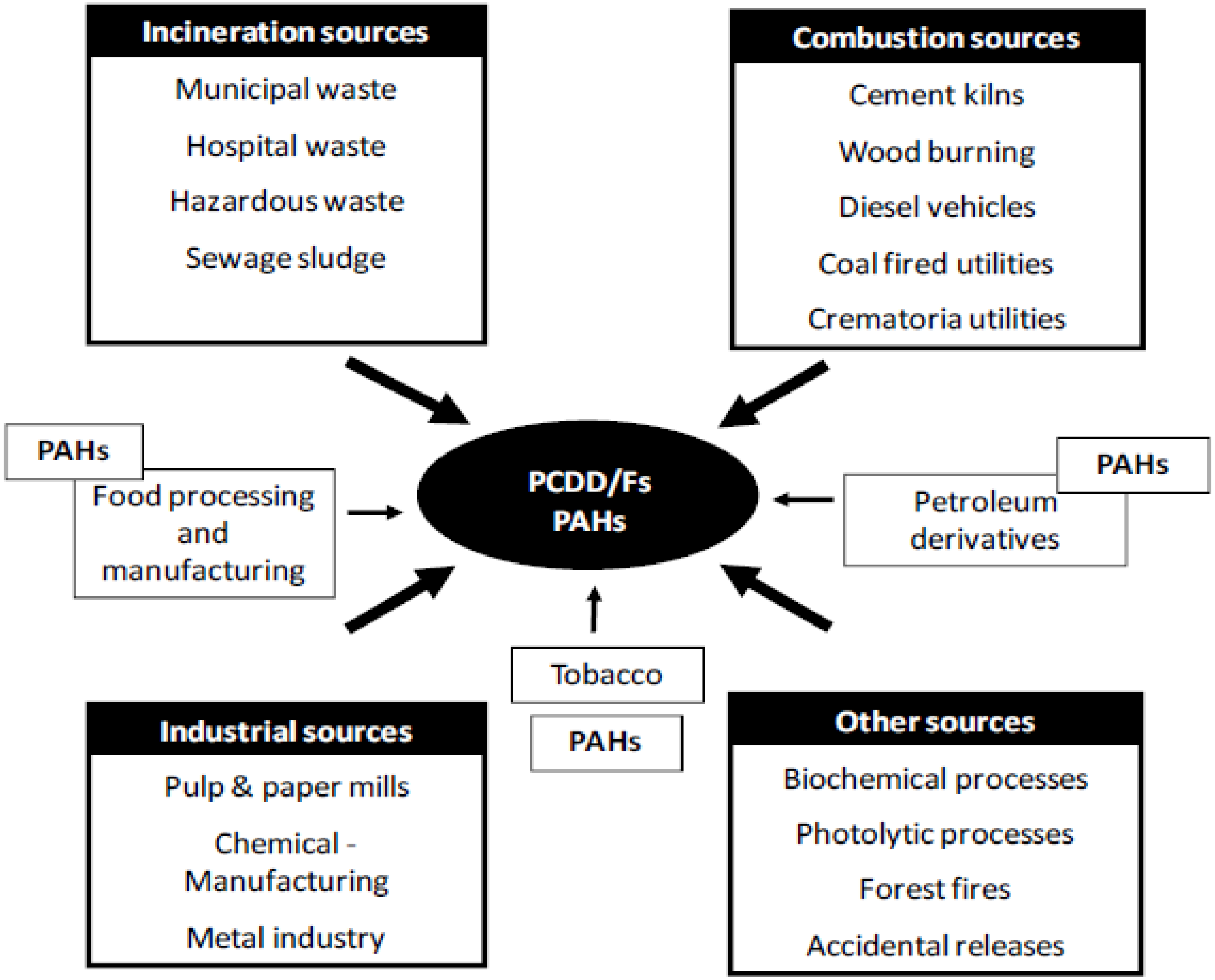
CHRONIC TOXICITY

Endocrine disruptors

Carcinogenic, mutagenic and teratogenic

(Jones and Voogt, 1999)

Sources of PCDD/Fs and PAHs



(adapted from Kulkarni et al., 2008)

Designing the biomonitoring program

STEP 1 – Objective

STEP 2 – Study area

STEP 3 – Collect background information

1) Sources and emissions
2) Land-use pattern
3) Meteorological information
4) Topographical information
5) Previous air/soil/water quality information
6) Demography and population growth
7) Health and epidemiological studies

STEP 4 – Designing the sampling grid

Are lichens existent in the study area?

Yes → Same species existent in all sites?

- Yes → STEP 5
- No → Calibration between species is needed

No → Transplants are needed

Transplants are needed

1) Test exposure period
2) Perform vitality measurements
3) Calculate enrichments in relation to initial control samples

Calibration between species is needed

1) Collect both species at the same sampling sites and at the same time.
2) Cover different land-uses with different intensities of pollution.
3) Repeat the sampling during each spatial sampling campaign.

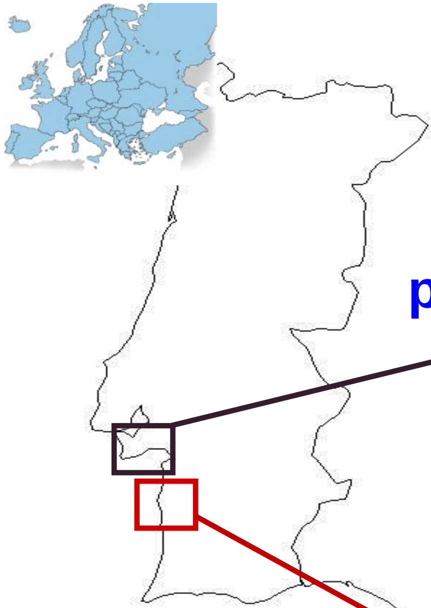
STEP 5 – Spatial sampling

1) Sample under constant weather.
2) Collect from 5 to 10 phorophytes at each sampling site at a height more than 1.5m from the soil.
3) Place samples inside dark glass bottles and keep refrigerated until analysis.

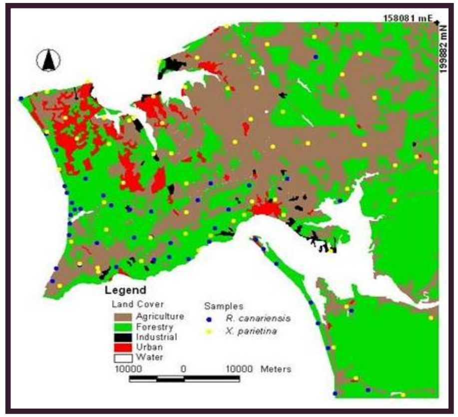
STEP 6 – Chemical analysis

STEP 7 – Data analysis

Case studies

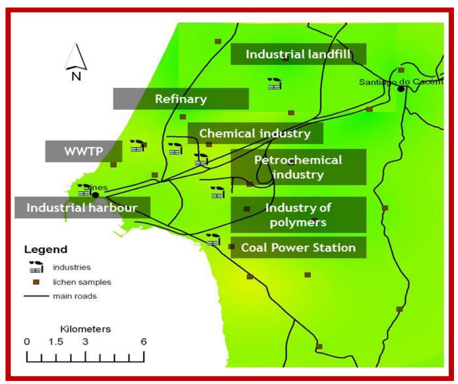


Setúbal peninsula



PCDD/Fs

Industrial region of Sines – Southwest Alentejo



PAHs

Environmental monitoring of PAHs and PCDD/Fs

Air analyses

Air

Pollution sources

Soil and sediments

Streams, rivers, oceans

Filter → Particulate-phase

Sponge → Gas-phase

Short-term indicator

Lack of detection

Air monitoring stations are not enough to cover large territories.

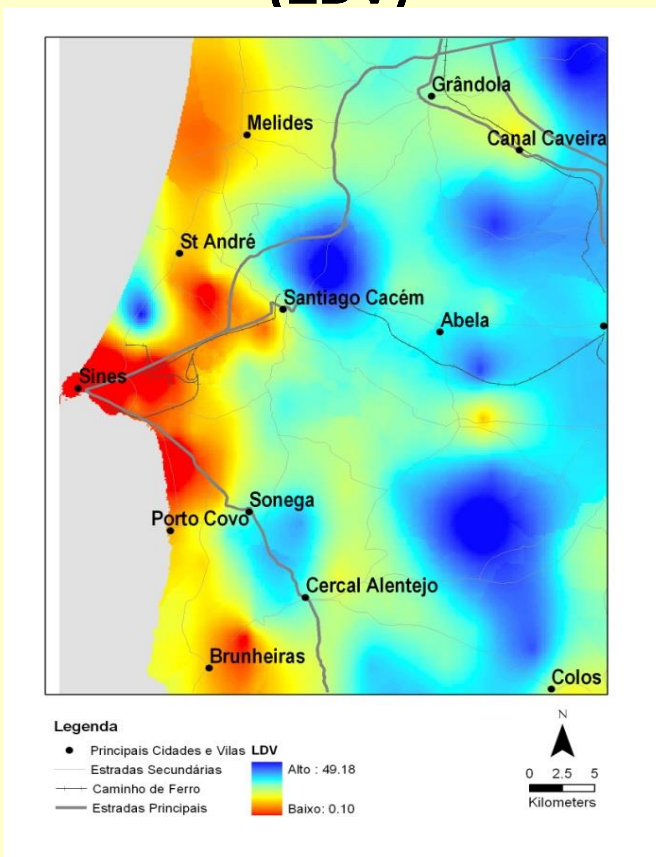
Industrial region of Sines



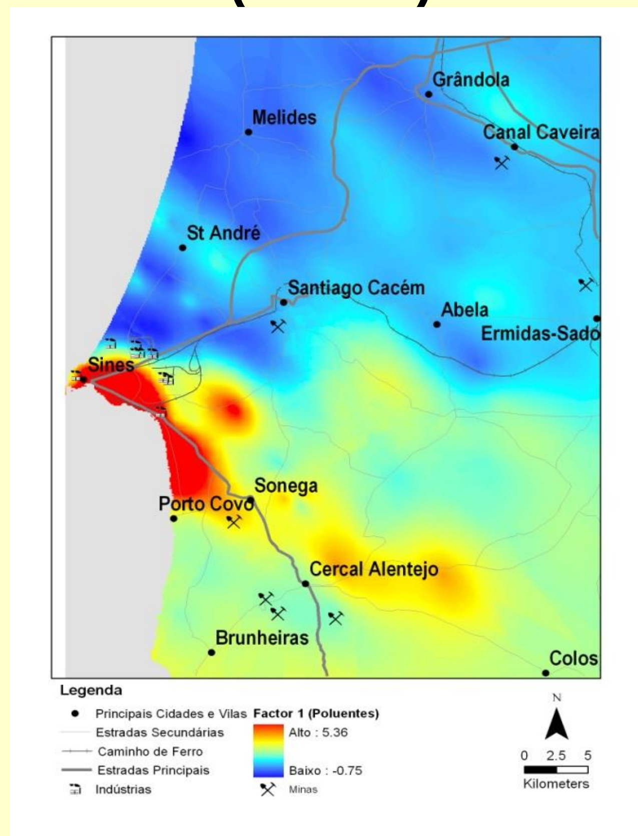



Monitoring records using lichens

Biodiversity (LDV)



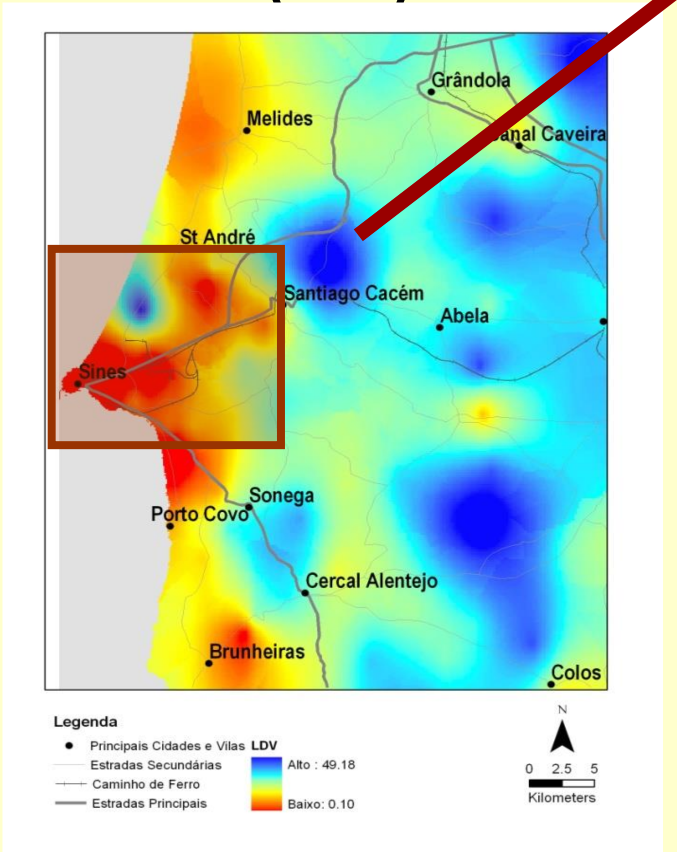
Pollutant accumulation (metals)



Monitoring records using lichens

PAHs?

Biodiversity (LDV)



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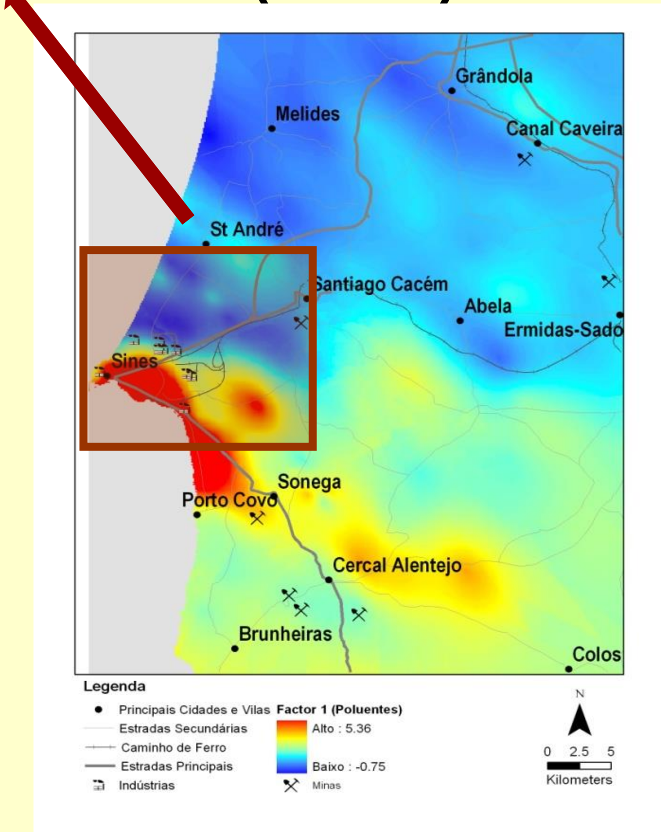


Main topics

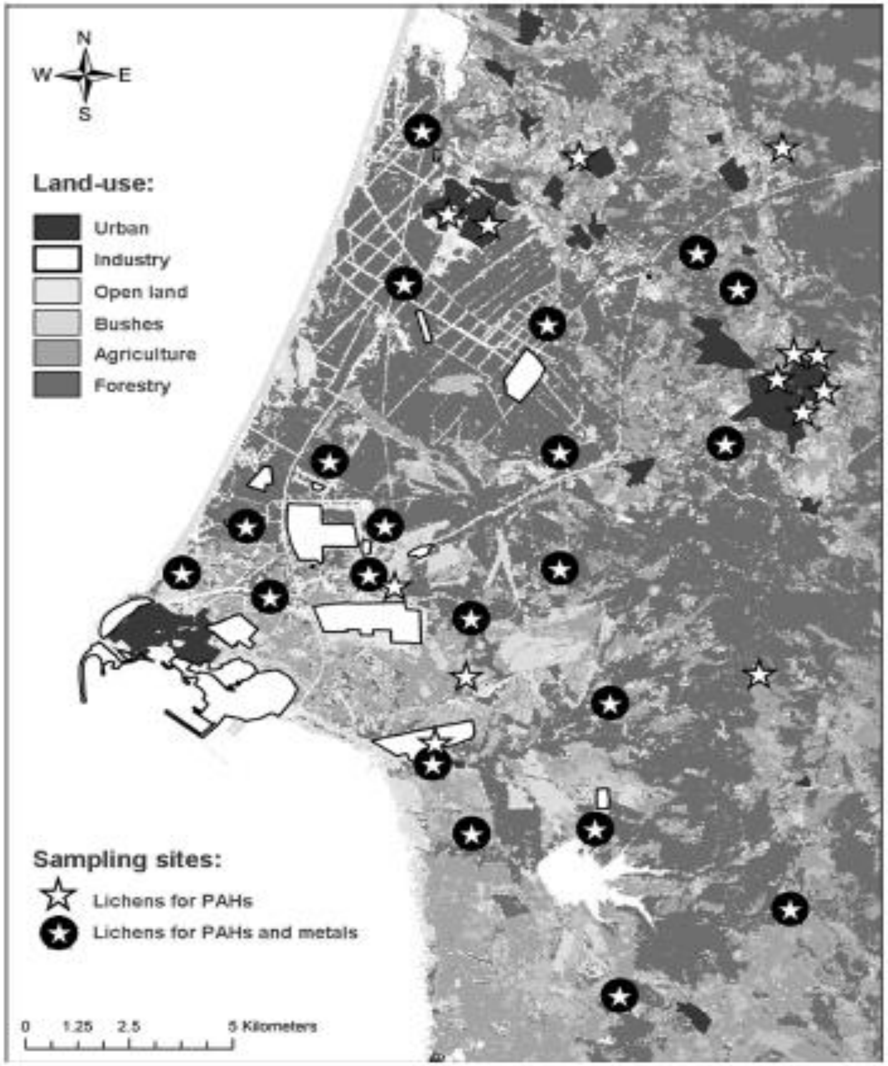
I - Using lichens to track PAH pollution sources

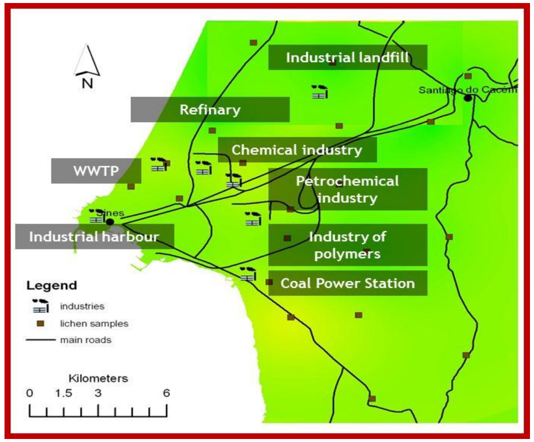
II - Using lichens as models for human exposure to PAHs

Main topics

I - Using lichens to track PAH pollution sources

Lichen sampling

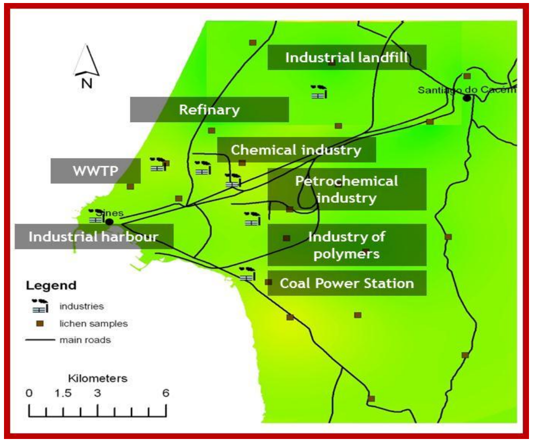




- **Collection of the foliose lichen *Parmotrema hypoleucinum* in 34 sampling sites from *Quercus suber*.**
- **Samples were placed in ambar glass bottles and stored at 4ºC in the dark until chemical analysis.**
- **Sampling was perfomed during 3 days under constant climatic conditions (no precipitation events) (Jan 2008).**

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

Characterization of land-use



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

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

Using lichens to track pollution sources

TABLE 1. PAH Concentrations (ng PAH/g Lichen) Measured in Lichens Collected from Sites with Different Dominating Land-Use Classes within a Buffer of 1 km Centered at Each Sampling Site[a]

		industrial	urban	ind + urb	forest	agriculture
2-ring PAHs	average	20.9	20.1	64.0	16.4	25.1
	SD	14.5	3.8	70.2	5.6	8.0
	min	18.3	13.6	14.9	10.6	13.5
	max	58.8	25.9	175.3	25.6	33.3
3-ring PAHs	average	56.3	74.4	112.5	38.5	55.8
	SD	22.1	40.0	59.5	10.9	20.8
	min	32.3	37.5	65.2	27.7	38.9
	max	91.3	137.1	217.9	54.8	88.4
4-ring PAHs	average	75.1	180.4	226.2	58.8	91.9
	SD	35.0	133.2	77.1	20.0	21.6
	min	32.4	60.6	127.9	27.7	68.5
	max	149.0	426.2	325.9	85.3	124.4
5-ring PAHs	average	11.5	11.2	33.6	7.7	13.5
	SD	10.0	3.0	30.7	4.9	6.0
	min	2.8	6.8	11.0	4.3	5.4
	max	35.7	16.4	86.6	17.4	21.7
6-ring PAHs	average	6.9	3.7	18.3	2.1	4.6
	SD	7.6	1.3	24.9	0.8	3.8
	min	0.9	1.6	3.1	1.1	0.0
	max	24.0	4.8	66.2	3.4	8.9
16 EPA-PAHs	average	178.9	289.7	454.5	123.3	191.0
	SD	80.0	174.5	233.9	30.2	50.7
	min	93.6	126.8	232.9	90.5	128.4
	max	332.0	599.2	871.8	157.1	264.9

[a] Industrial sites (0.93 to 18.98% covered by industrial areas, *N* = 9), urban sites (0.11 to 43.87% covered by urban areas, *N* = 8), industrial and urban mixed sites (21.40 to 64.64% covered by industrial and urban areas, *N* = 6), forest sites (50.45 to 71.91% covered by wooded areas, *N* = 6), and agricultural sites (27.78 to 47.48% covered by agricultural areas, *N* = 5).

- **Mixed areas – urban and industrial – show the highest PAH concentrations (16 EPA-PAHs)**

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Using lichens to track pollution sources

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	max	91.3	137.1	217.9	54.8	88.4
4-ring PAHs	average	75.1	180.4	226.2	58.8	91.9
	SD	35.0	133.2	77.1	20.0	21.6
	min	32.4	60.6	127.9	27.7	68.5
	max	149.0	426.2	325.9	85.3	124.4
5-ring PAHs	average	11.5	11.2	33.6	7.7	13.5
	SD	10.0	3.0	30.7	4.9	6.0
	min	2.8	6.8	11.0	4.3	5.4
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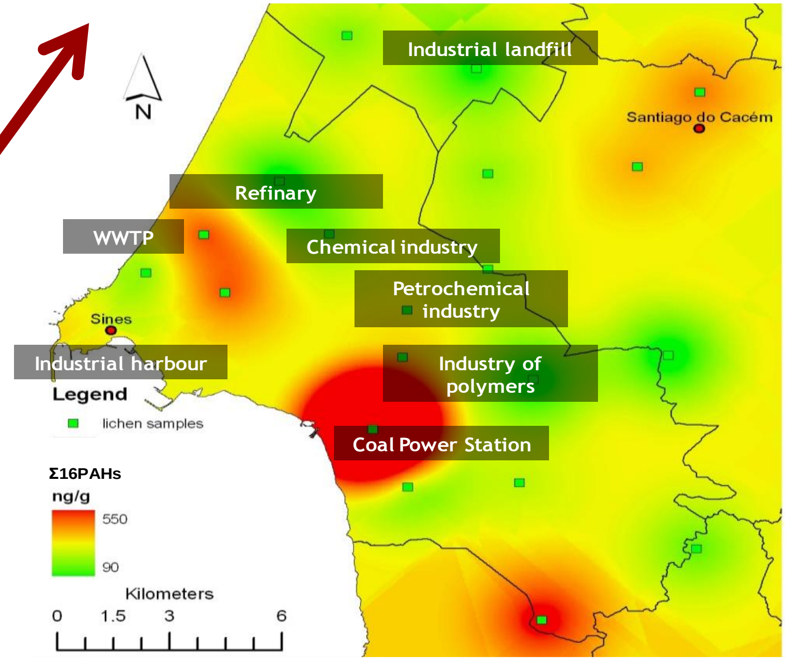
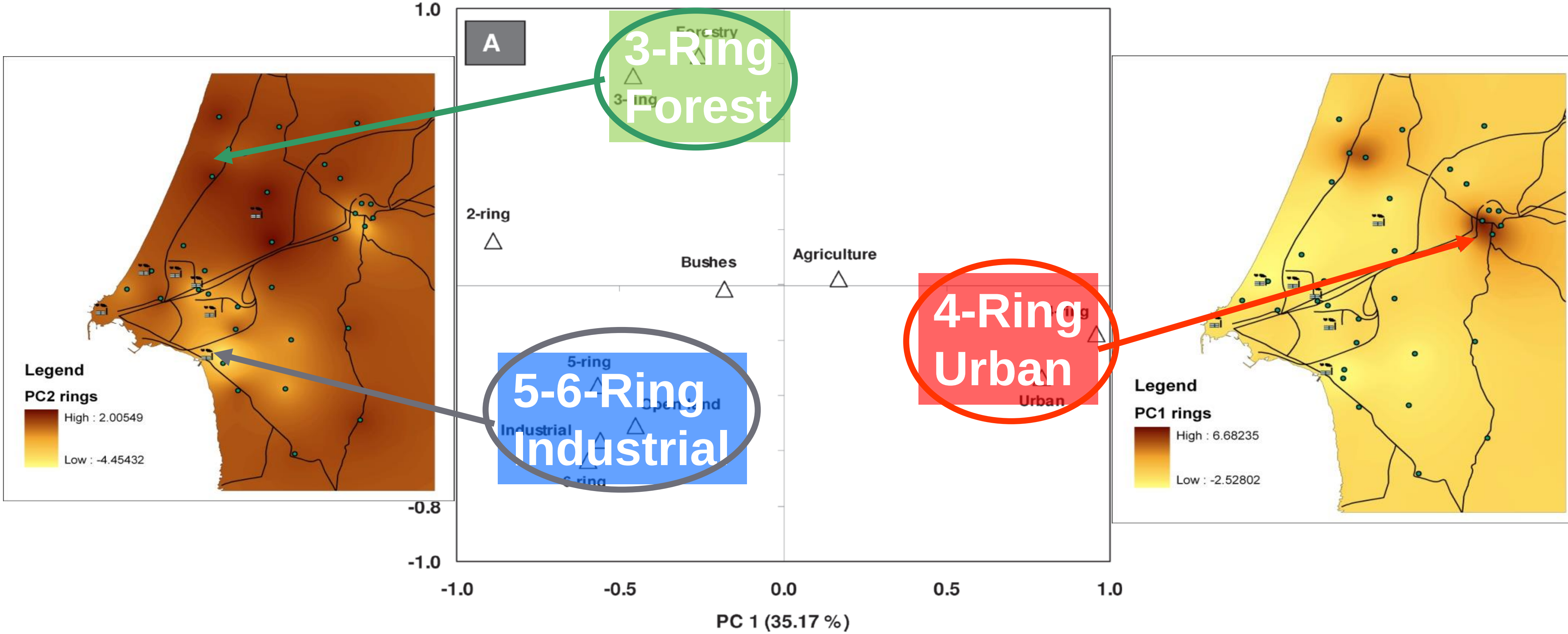
- **Mixed areas – urban and industrial – show the highest PAH concentrations (16 EPA-PAHs)**



Map of the interpolattion of the concentration of the 16PAHs, using lichens as biomonitors (n=34)

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

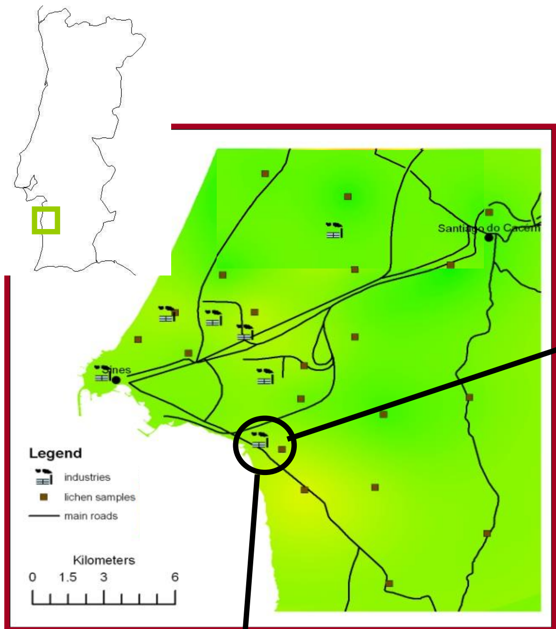
Using lichens to track pollution sources

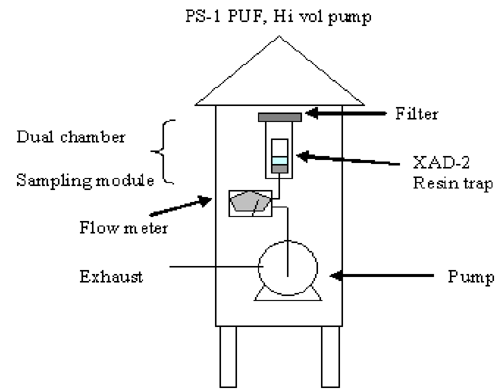


➢ **Lichens allow fingerprinting different pollution sources in multisource areas.**

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

PAHs in lichens *versus* air - calibration





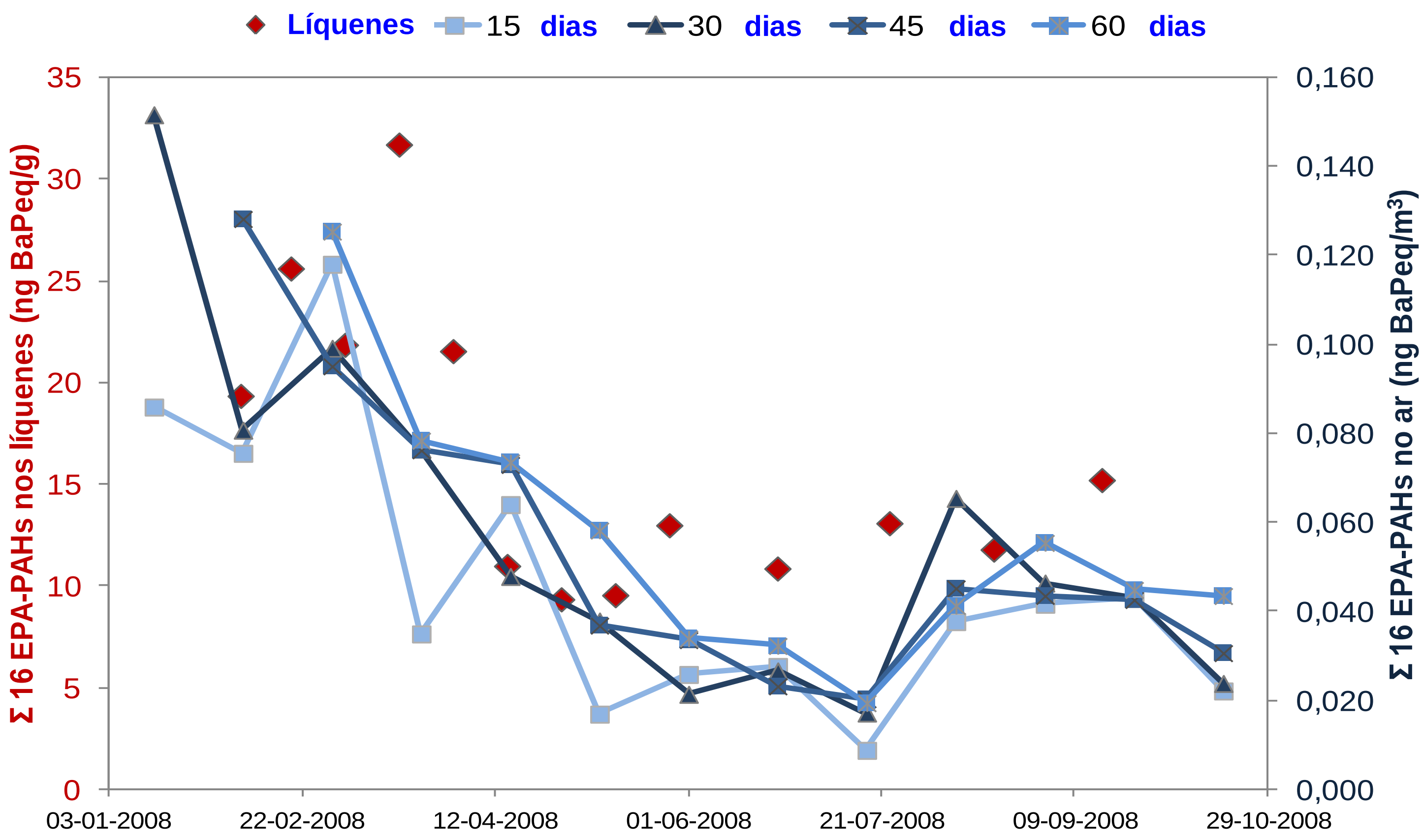
Air quality monitoring station:
Collection of particulate-phase of air (TSP) using filters in an active sampler, over an eight month period (Jan-Sep 2008); each filter was exposed for 48 hours.


P. hypoleucinum

Lichen sampling:
Every 15 days native lichens (*Parmotrema hypoleucinum*) were collected from the available phorophytes.

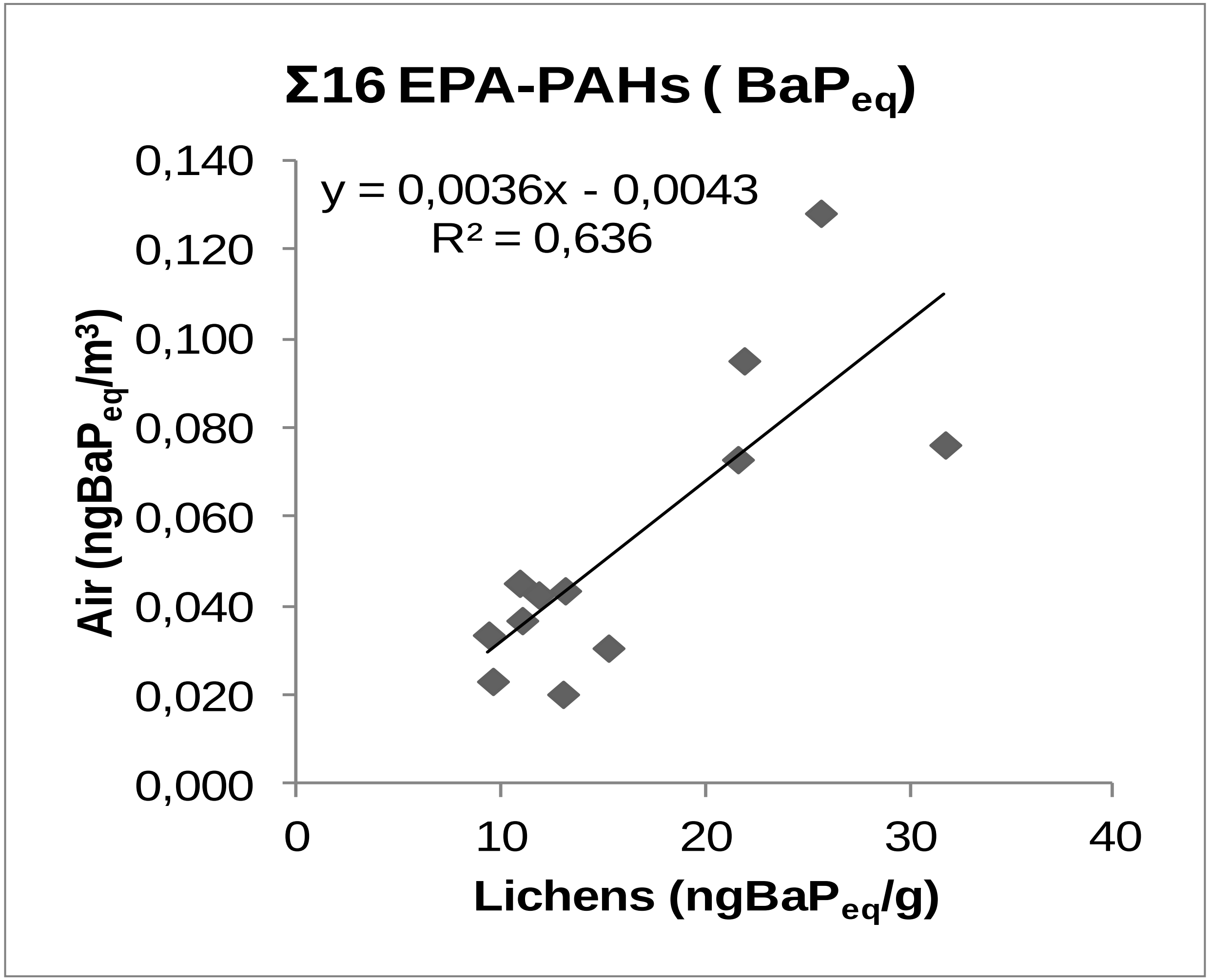
All samples were extracted and analyzed for the 16 EPA-PAHs; filters from each 15-day period (corresponding to the lichen samples exposure) were polled together.

PAHs in lichens *versus* air - calibration



Relation over time between PAH concentrations in lichens and PAHs in air from the 15, 30, 45 and 60 days prior to lichen collection.

PAHs in lichens *versus* air - calibration



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

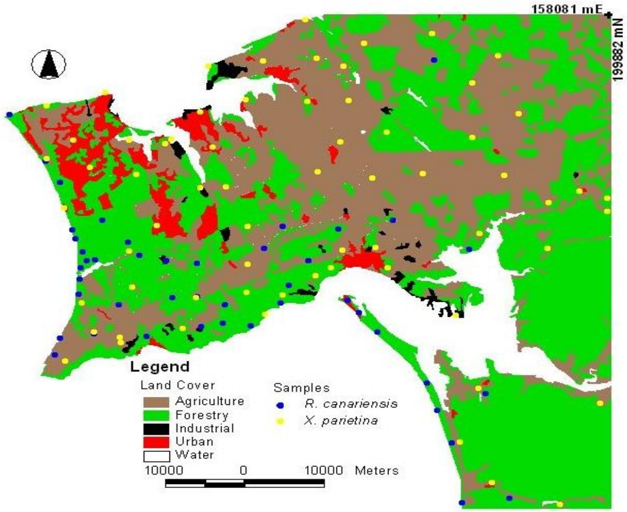
Augusto et al., Submitted. A step towards the use of biomonitors as estimators of atmospheric PAHs for regulatory purposes.

Main topics

I - Using lichens to track PAH pollution sources

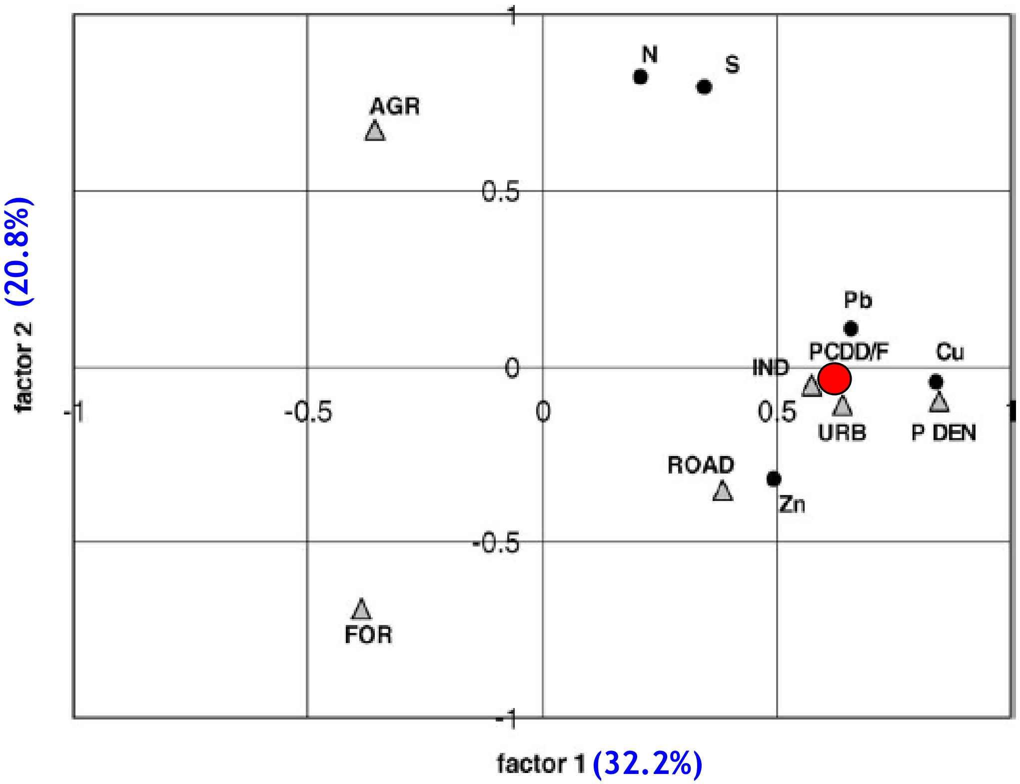
II - Using lichens as models for human exposure to PAHs

PCDD/Fs in Setúbal peninsula



Lichen *Xanthoria parietina* was collected in 66 sampling sites from house roof tiles.

The 17 toxic PCDD/Fs were analysed through GC-MS.



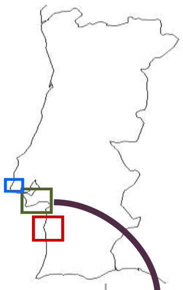
Principal component analysis between PCDD/Fs in lichens and the relative cover of each land-use class in buffers of 2Km centered in each sampling site.

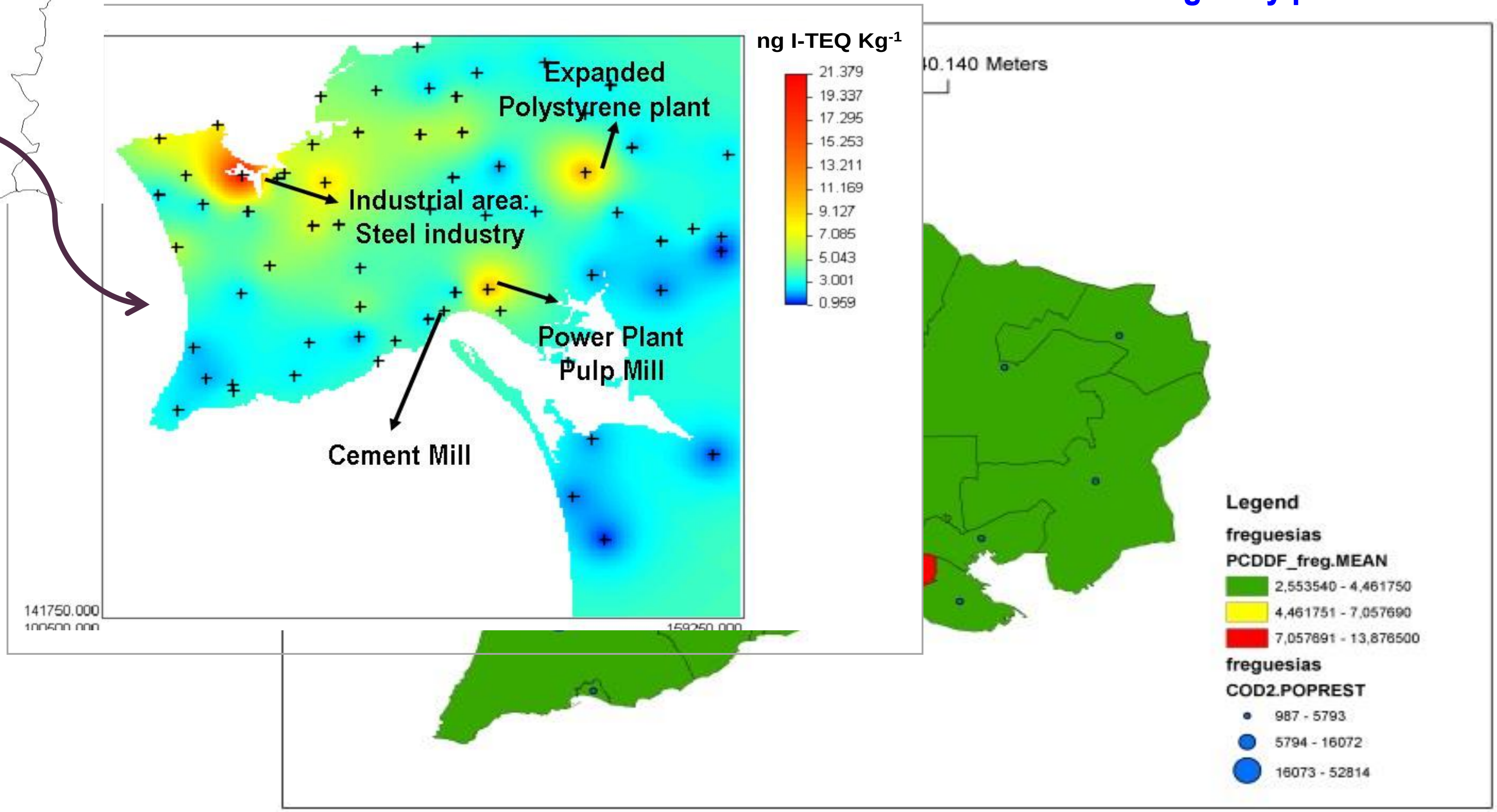
(Augusto et al, 2004. Atmospheric dioxin and furan deposition in relation to land-use and other pollutants: a survey with lichens. *Journal of Atmospheric Chemistry* 49:53-65)

PCDD/Fs in Setúbal peninsula

PCDD/F toxic concentration in lichens

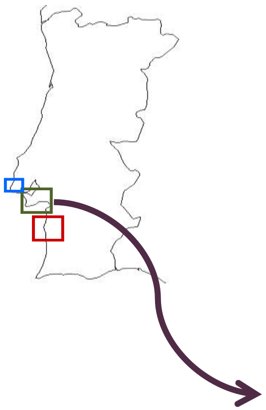
PCDD/F toxic concentration in lichens averaged by parish



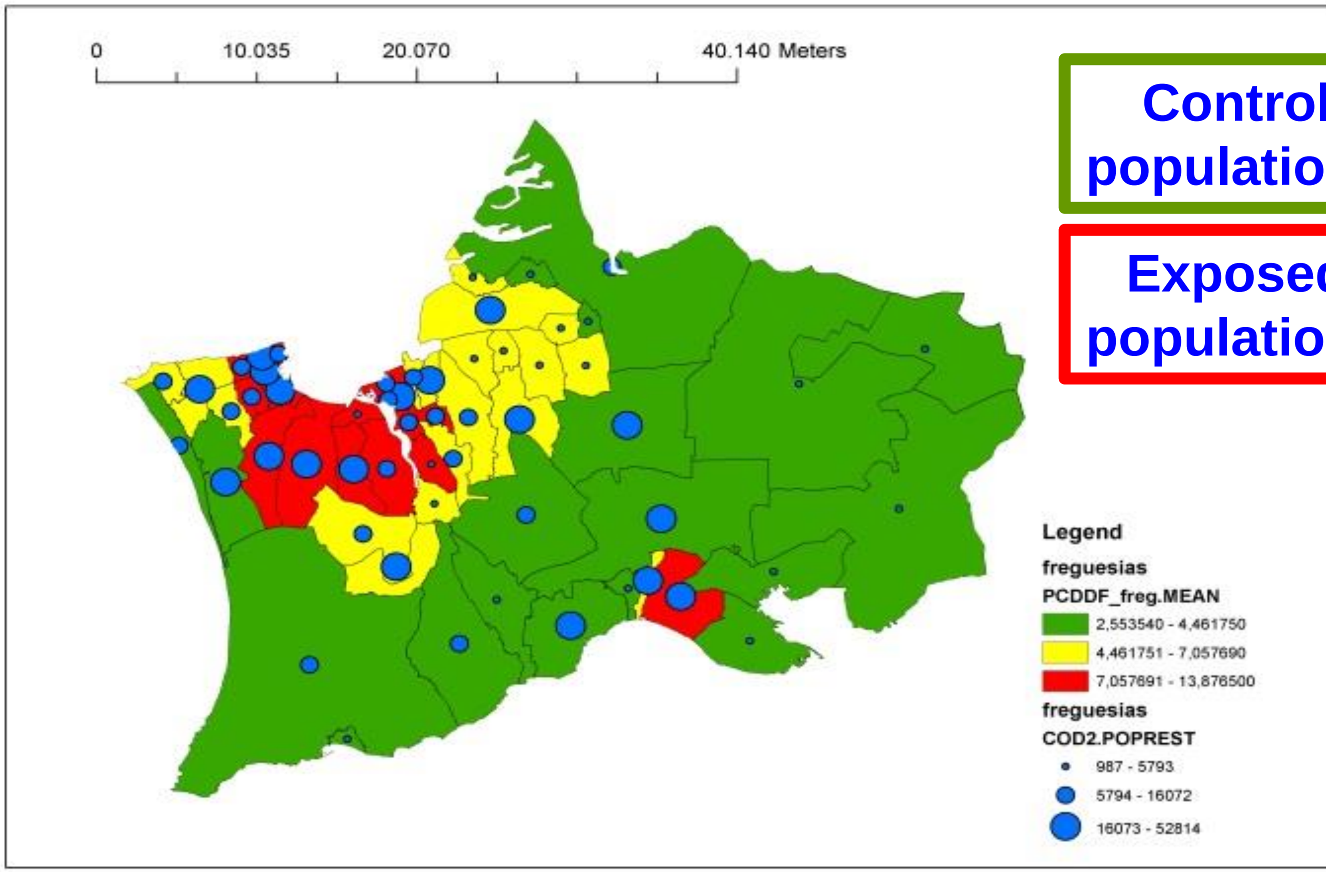


Augusto et al., 2007. The contribution of environmental biomonitoring with lichens to assess human exposure to dioxins. International Journal of Hygiene and Environmental Health 210:433-438

PCDD/Fs in Setúbal peninsula



PCDD/F toxic concentration in lichens averaged by parish



Control populations

Exposed populations

Epidemiological studies

Augusto et al., 2007. The contribution of environmental biomonitoring with lichens to assess human exposure to dioxins. International Journal of Hygiene and Environmental Health 210:433-438

Guidelines to measure the impact of reactive nitrogen on ecosystems: the use of lichens as biomonitors under global change

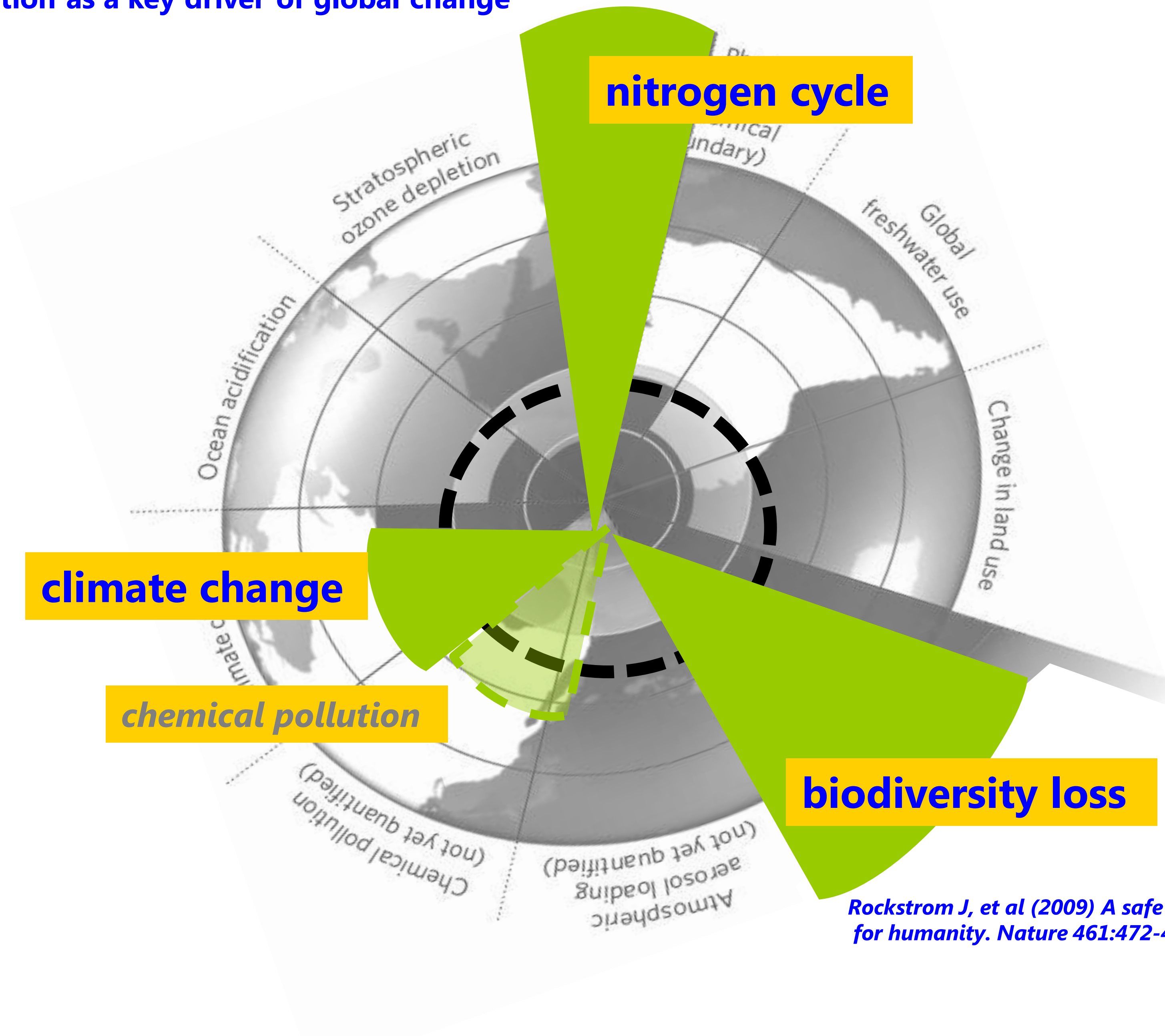
Pedro Pinho | Cristina Máguas | Cristina Branquinho

Sofia Augusto | Silvana Munzi | Paula Matos

AIMS:

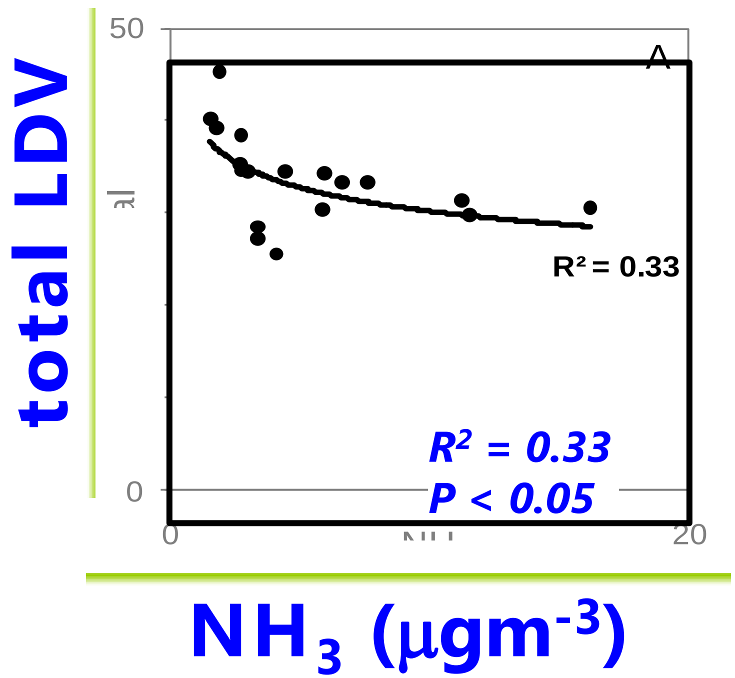
to provide a common framework to assess the effect of nitrogen on ecosystems based on the use of lichens as ecological indicators

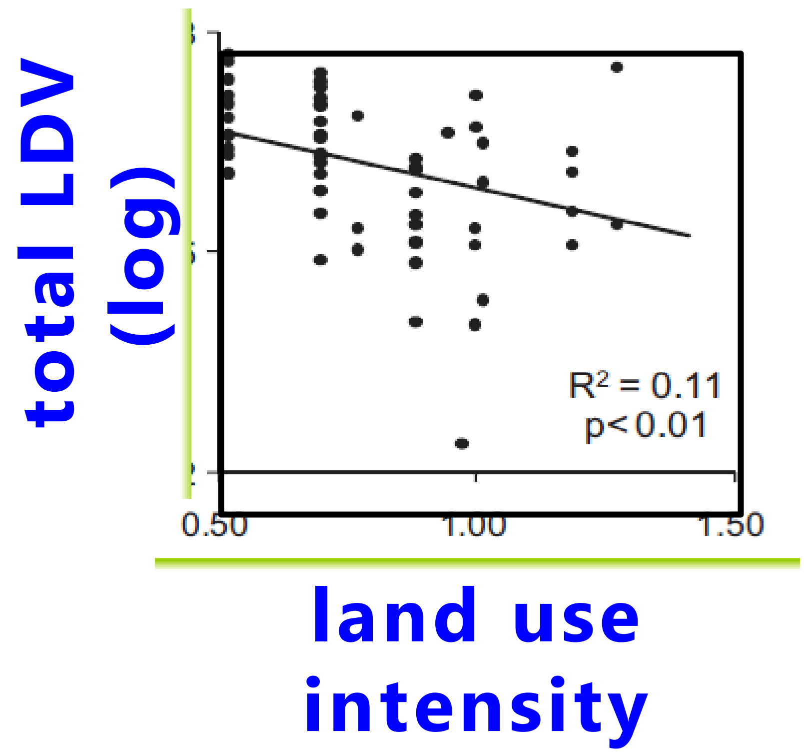
Organic pollutants
Nitrogen pollution as a key driver of global change



Rockstrom J, et al (2009) A safe operating space for humanity. Nature 461:472-475

what lichen-variables should we use to monitor N-effect?





Pinho P, Branquinho C, Cruz C, Tang S, Dias T, Rosa, AP, Máguas C, Martins-Loução MA, Sutton M. (2009). Assessment of critical levels of atmospherically ammonia for lichen diversity in cork-oak woodland, Portugal. Chapter: Critical Loads. In "Atmospheric Ammonia - Detecting emission changes and environmental impacts - Results of an Expert Workshop, Mark Sutton, Stefan Reis and Samantha Baker (eds), Springer, 464p. (http://dx.doi.org/10.1007/978-1-4020-9121-6_10)
Pinho P, Bergamini A, Carvalho P, Branquinho C, Stofer S, Scheidegger C, Maguas C (2012) Lichen functional groups as ecological indicators of the effects of land-use in Mediterranean ecosystems. Ecological Indicators 15: 36-42. (http://dx.doi.org/10.1016/j.ecolind.2011.09.022)

lichens *response* functional groups to eutrophication

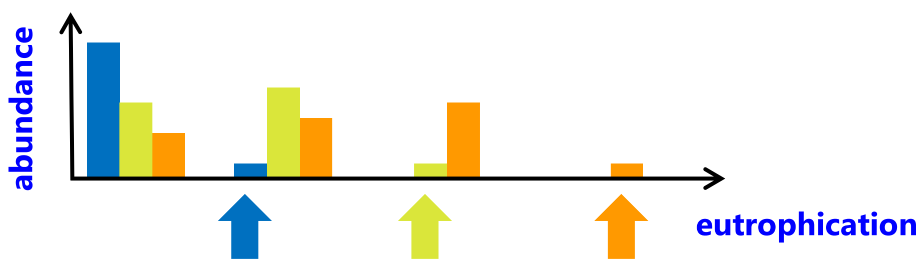
less tolerant → **more tolerant**


oligotrophic


mesotrophic

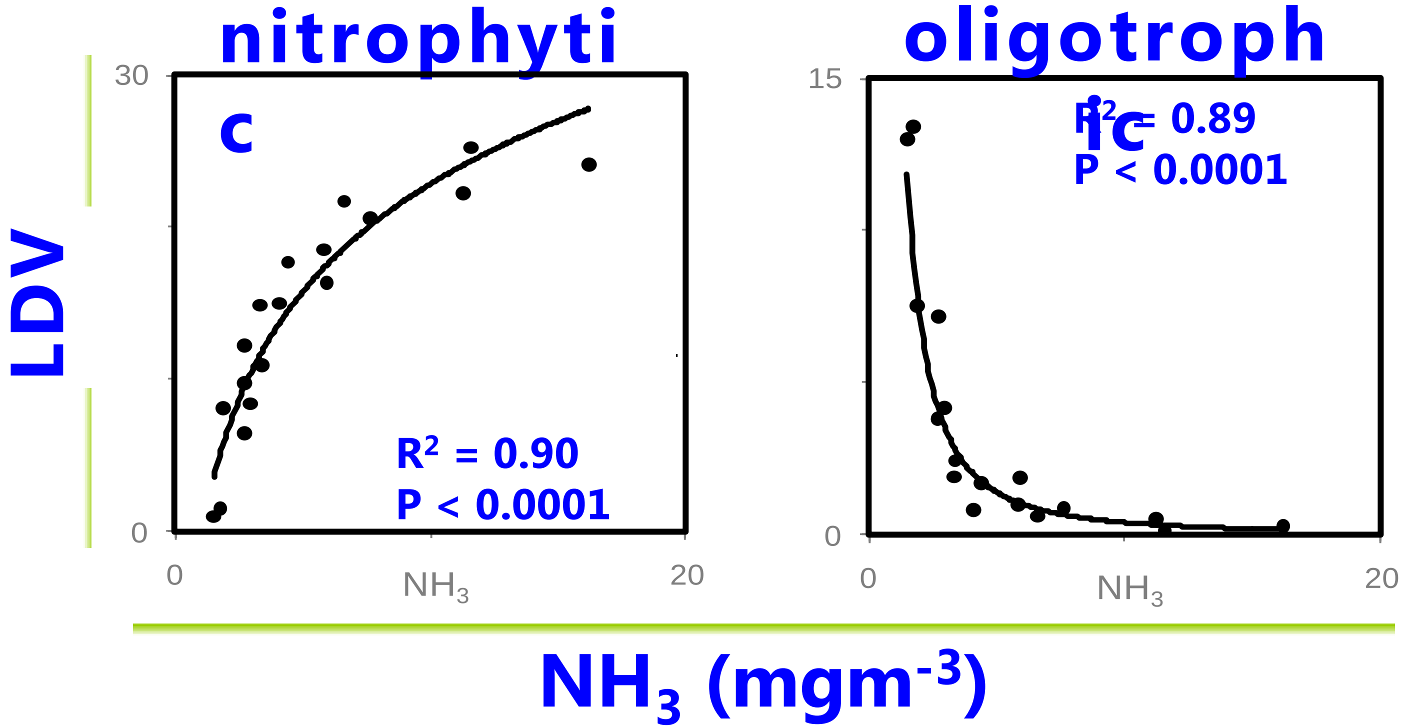

nitrophytic

based on a priory expert-knowledge classification



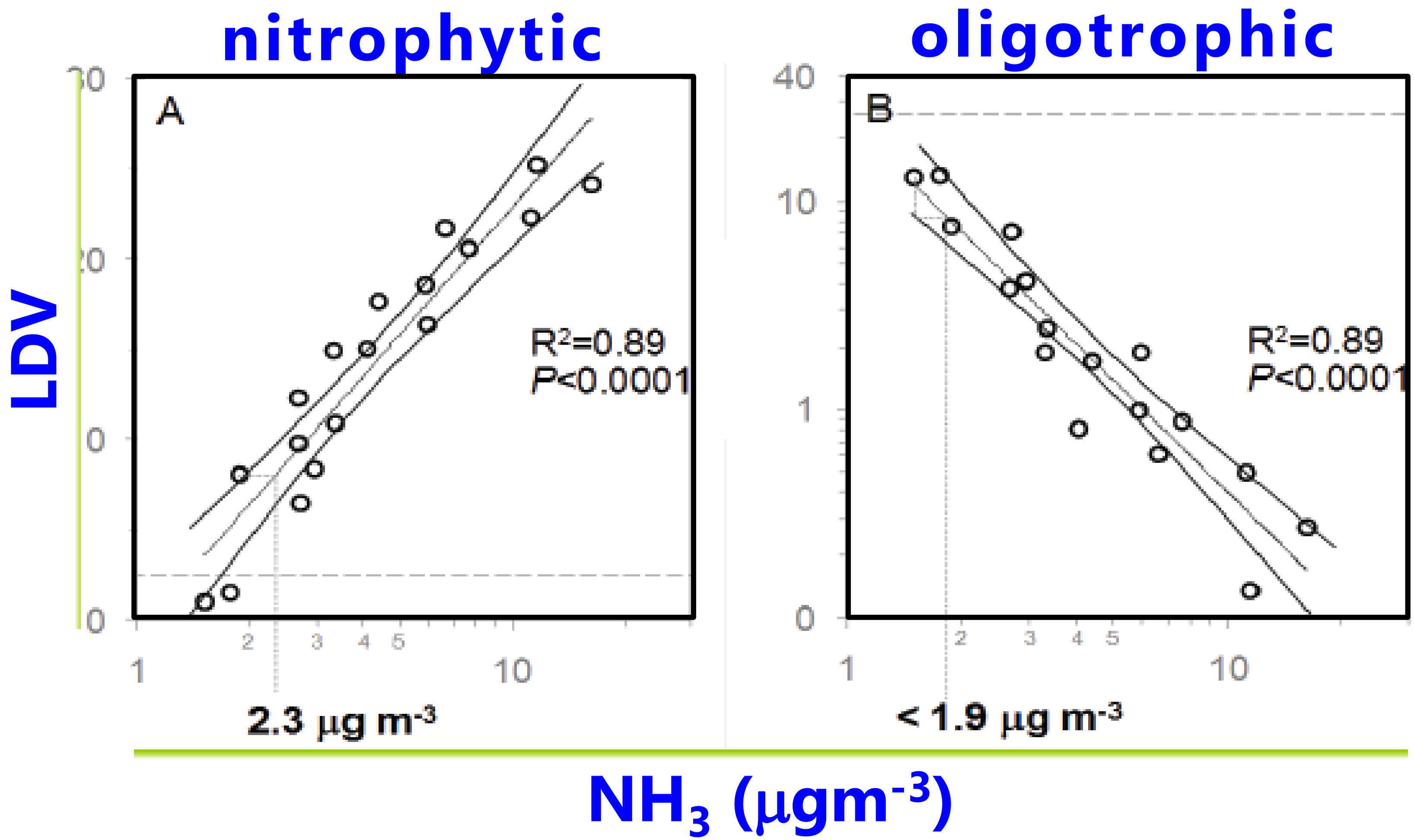
Nimis, P., Martellos, S., 2008. ITALIC e the Information System on Italian Lichens v. 4.0. University of Trieste, Dept. of Biology. IN4.0/1.

effects on functional groups (eutrophication tolerance)



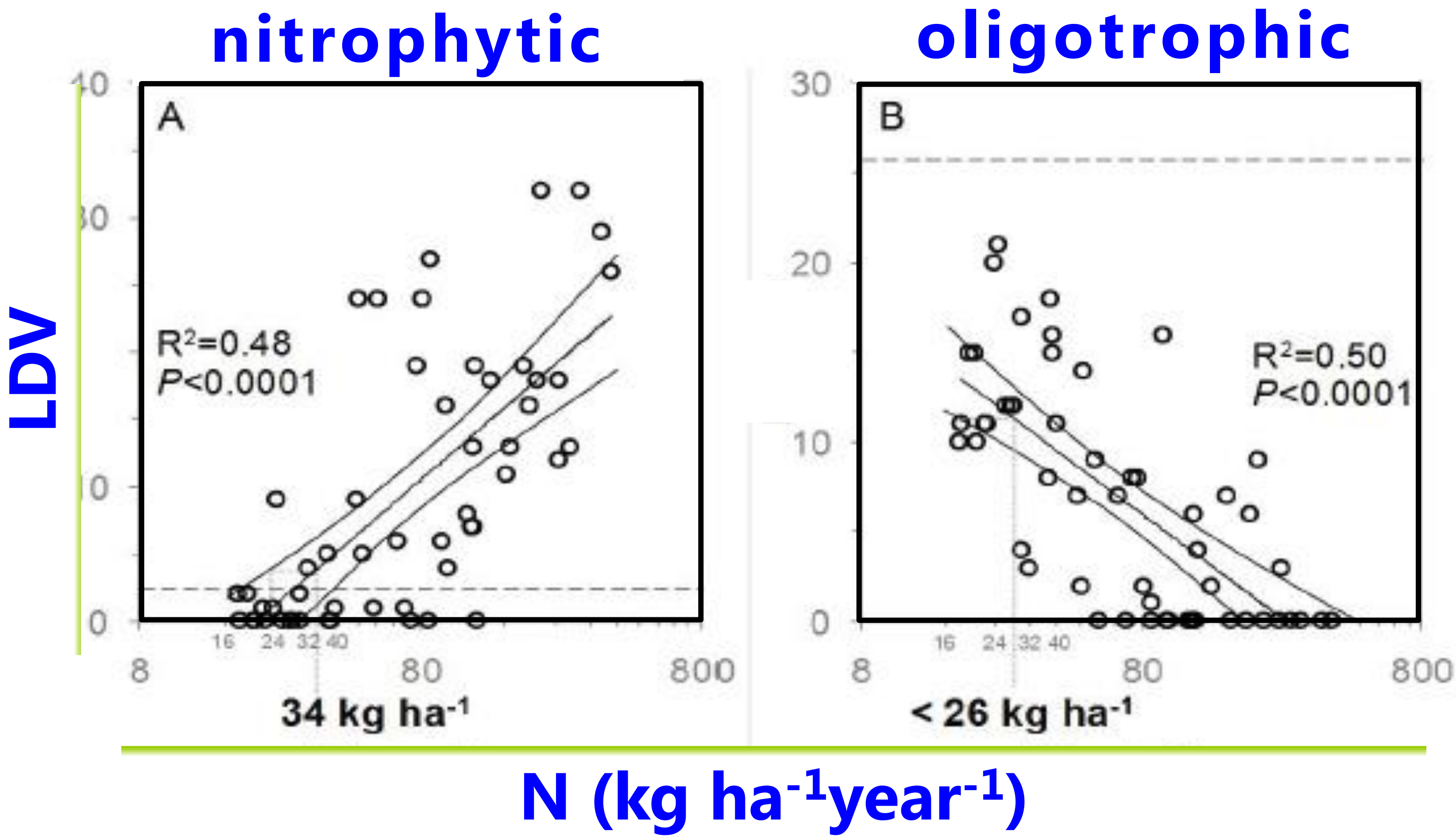
Pinho P, Dias T, Cruz C, Sim YT, Sutton MA, Martins-Loução MA, Máguas C, Branquinho C (2011) Using lichen functional-diversity to assess the effects of atmospheric ammonia in Mediterranean woodlands. Journal of Applied Ecology 48: 1107-1116. (http://dx.doi.org/10.1111/j.1365-2664.2011.02033.x)

critical levels of NH_3



Pinho P, Theobald MR, Dias T, Tang YS, Cruz C, Martins-Loução MA, Máguas C, Sutton M, Branquinho C (2012) Critical loads of nitrogen deposition and critical levels of atmospheric ammonia for semi-natural Mediterranean evergreen woodlands. Biogeosciences 9: 1205-1215.

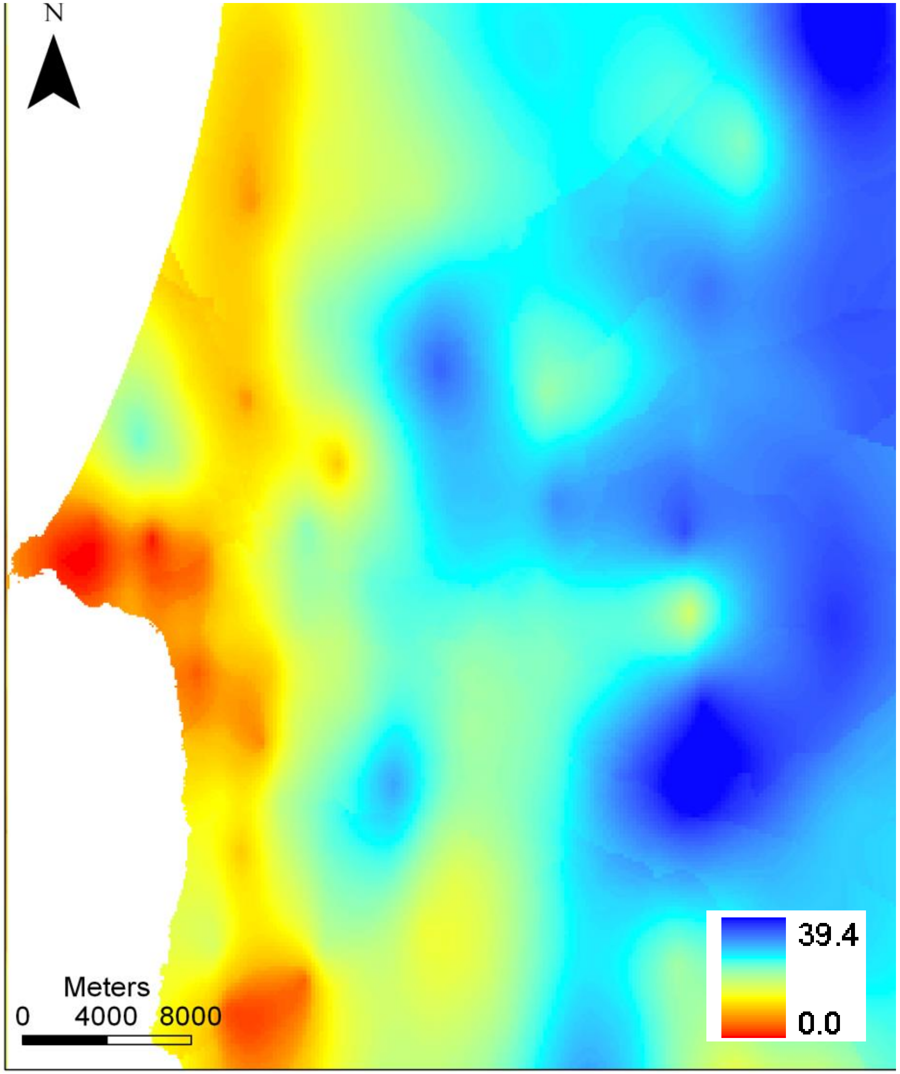
critical loads for n-deposition



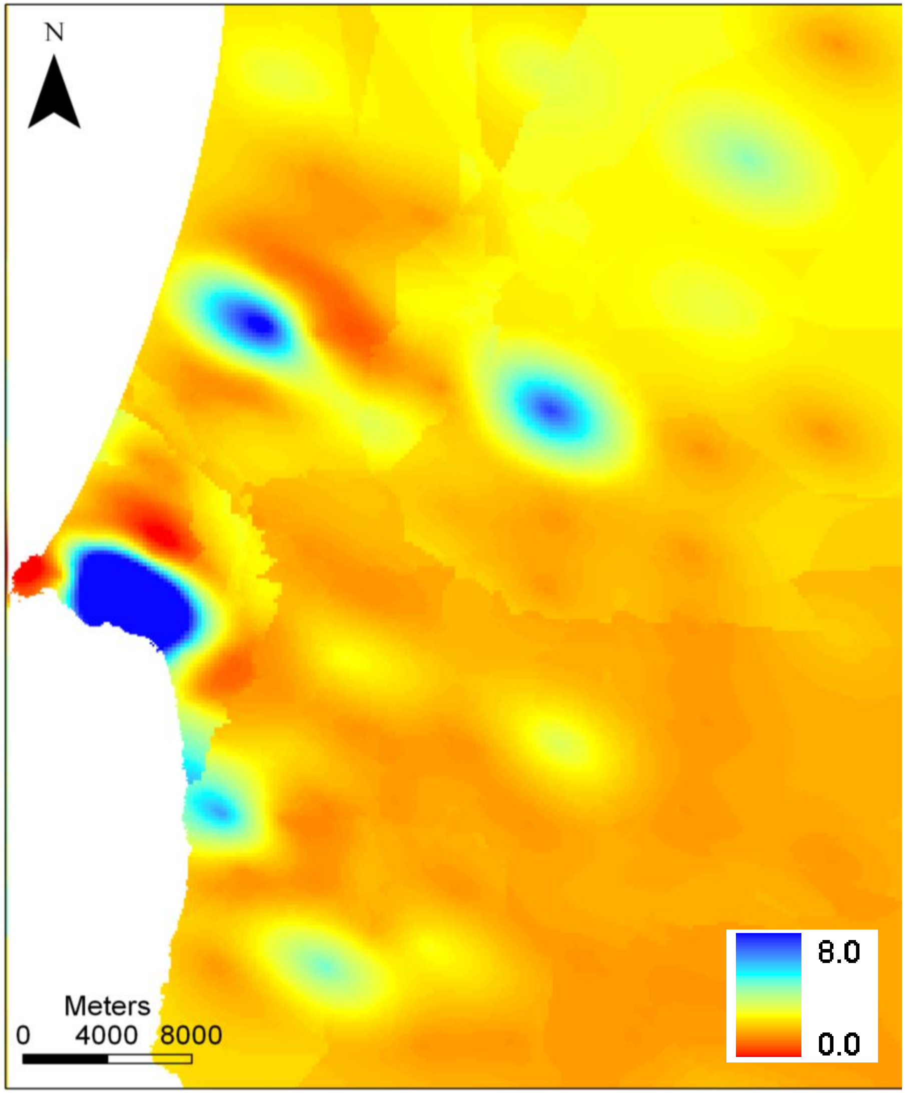
Pinho P, Theobald MR, Dias T, Tang YS, Cruz C, Martins-Loução MA, Máguas C, Sutton M, Branquinho c (2012) Critical loads of nitrogen deposition and critical levels of atmospheric ammonia for semi-natural Mediterranean evergreen woodlands. Biogeosciences 9: 1205-1215.

can factors at different spatial scales be influencing lichen-variables?

oligotrophic

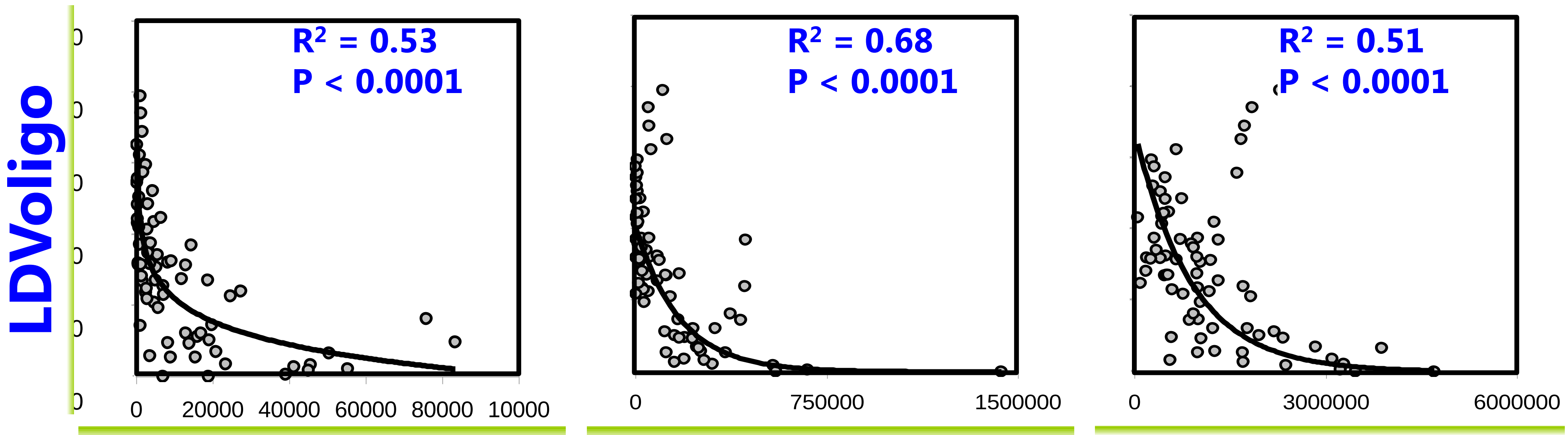


nitrophytic



Pinho P, Augusto S, Martins-Loução MA, João-Pereira M, Soares A, Máguas C, Branquinho C (2008) Causes for change in nitrophytic and oligotrophic lichen species in Mediterranean climate: impact of land-cover and atmospheric pollutants. Environmental Pollution 154: 380-389. (http://dx.doi.org/10.1016/j.envpol.2007.11.028).

distance of influence of land-cover on LDVoligo, related to the type of particles



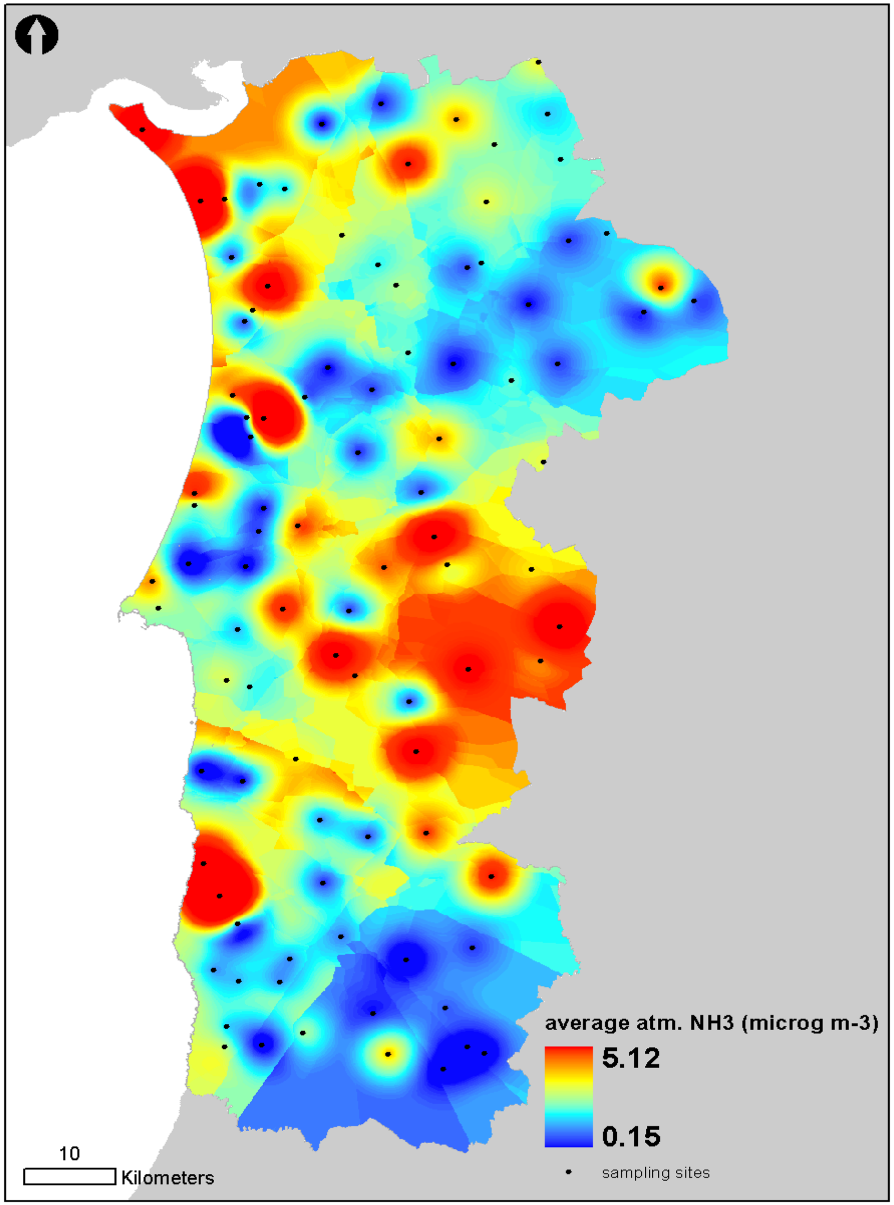
annual cultures (600m) (m^2)

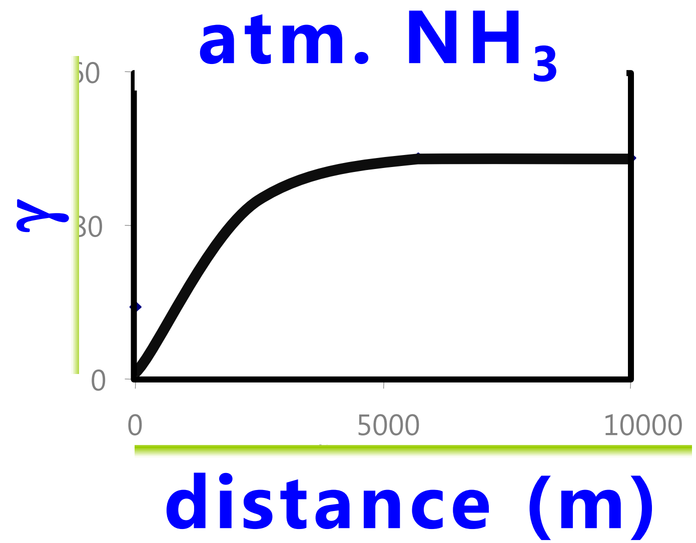
artificial areas (1000m) (m^2)

barren lands (1800m) (m^2)

Pinho P, Augusto S, Martins-Loução MA, João-Pereira M, Soares A, Máguas C, Branquinho C (2008) Causes for change in nitrophytic and oligotrophic lichen species in Mediterranean climate: impact of land-cover and atmospheric pollutants. Environmental Pollution 154: 380-389. (http://dx.doi.org/10.1016/j.envpol.2007.11.028).

atmospheric ammonia varies at a local scale



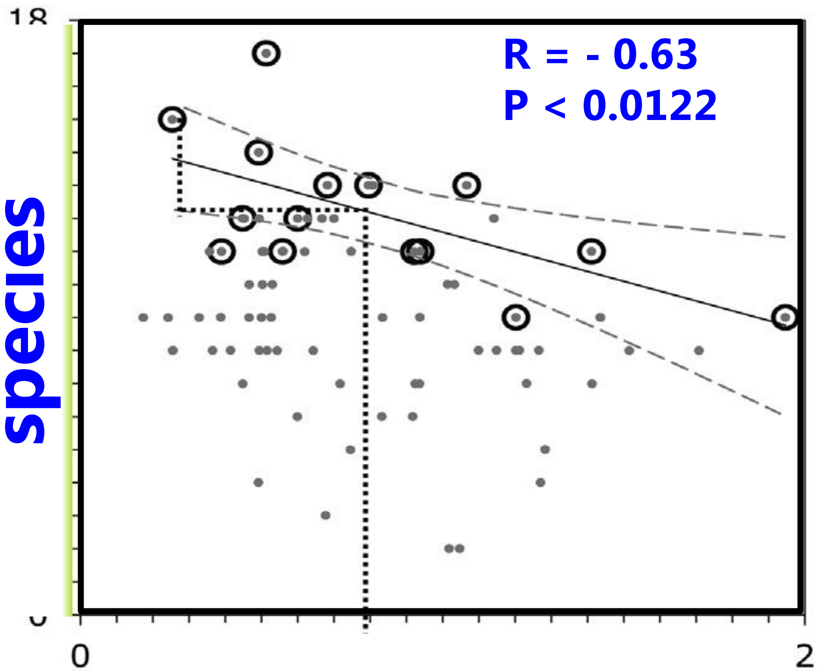


nugget / total varia		ıctures
0.0	6000 m	1

calculating critical levels in regions with the presence of multiple disturbances

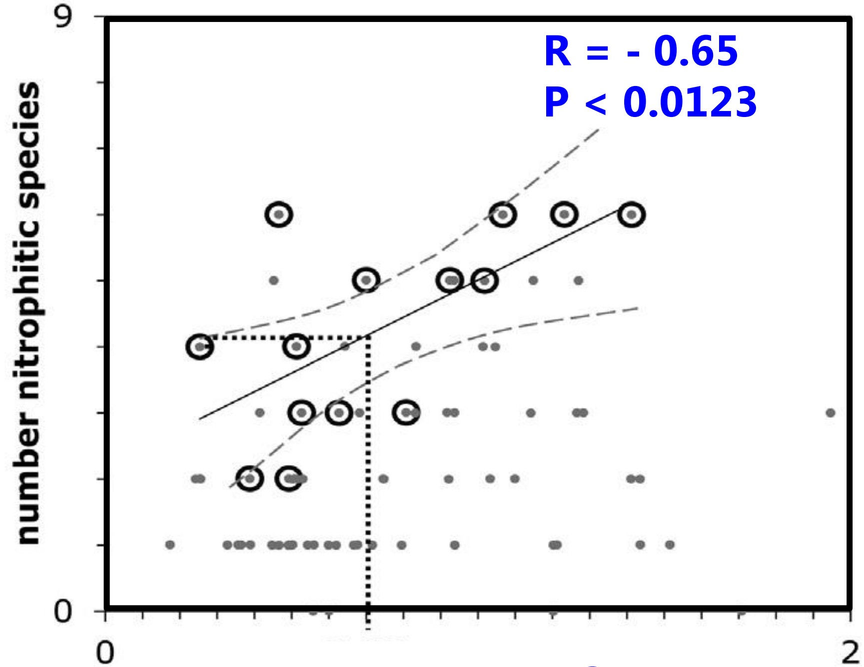
oligotrophic

number of species



0.77 mgm^{-3}

nitrophytic



0.69 mgm^{-3}

NH_3 (mgm^{-3})

STABLE ISOTOPES – Short Introduction

^{2}H ^{13}C ^{18}O ^{15}N ^{34}S stable isotopes

Element	Isotope	Abundance (%)
Carbon	^{12}C	98.89
	^{13}C	1.11
Nitrogen	^{15}N	99,63
	^{14}N	0,37
Hydrogen	^{1}H	99,98
	^{2}H	0,02
Oxygen	^{18}O	99.759
	^{16}O	0.204

$$\delta^{13}C\ [‰] = \left(\frac{\left({}^{13}C / {}^{12}C \right)_{SAMPLE}}{\left({}^{13}C / {}^{12}C \right)_{STANDART}} - 1 \right) * 1000$$

For Carbon PDB = 1.12372%

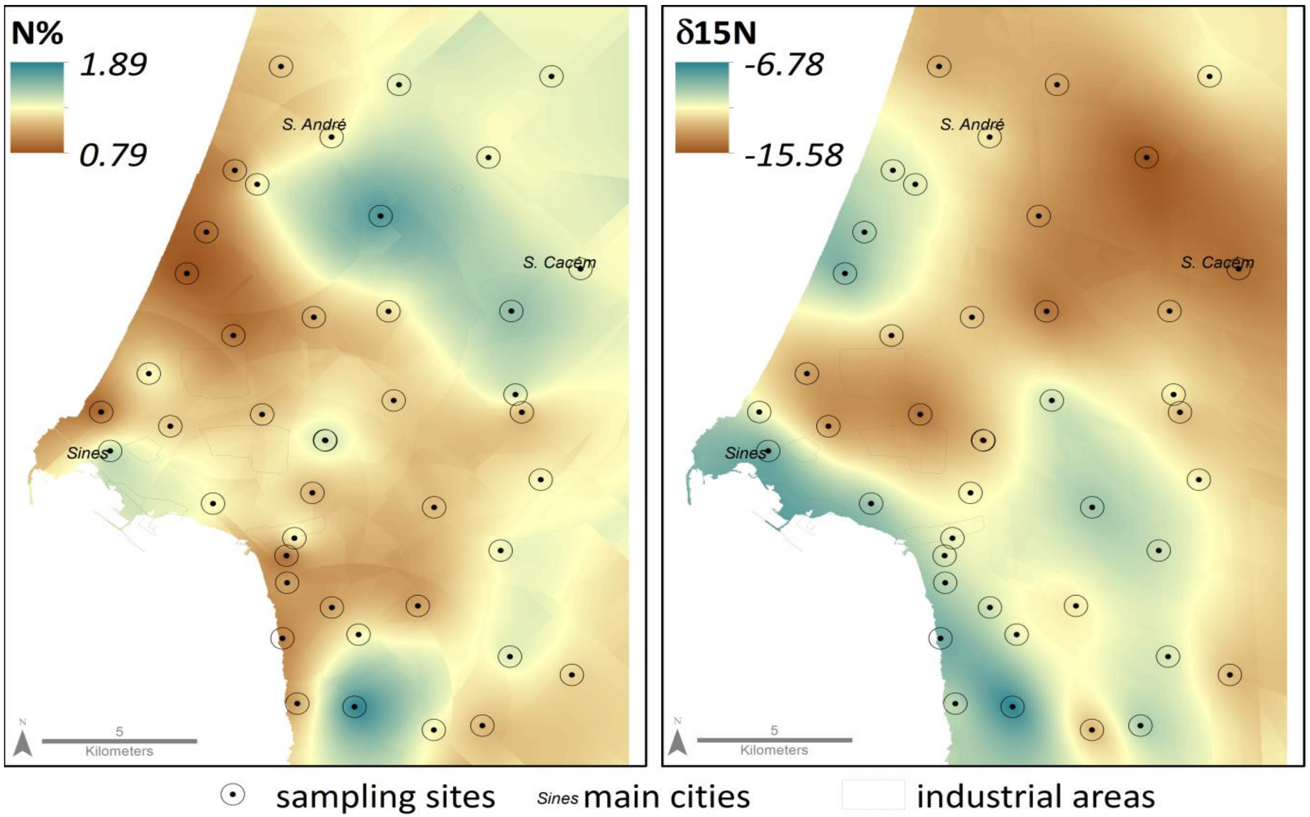
For Oxygen VSMOW = 0.20052%

After Hayes, 1983

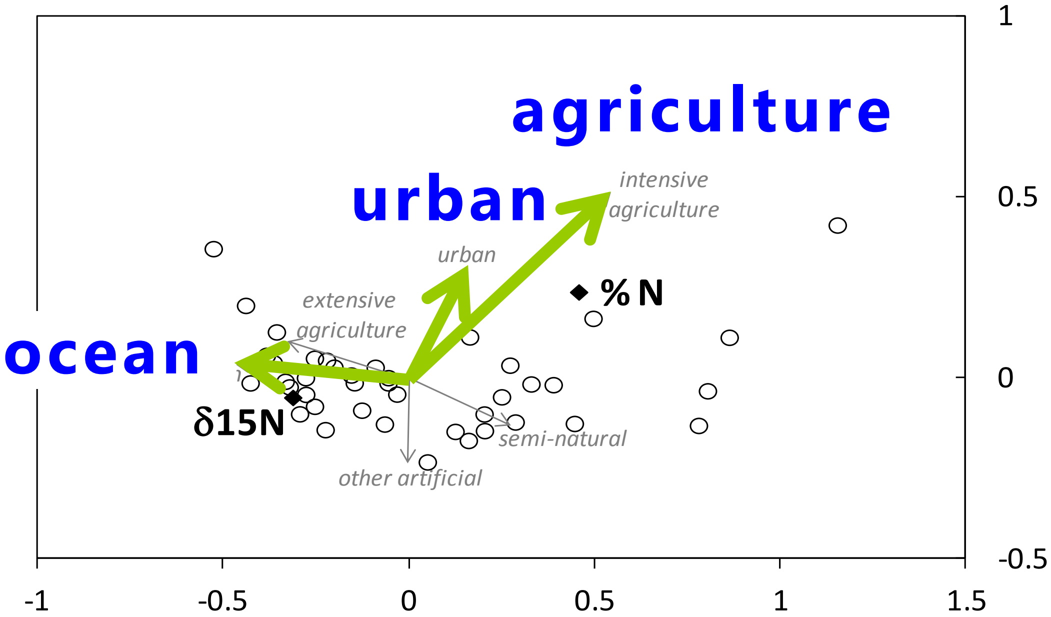
Isotopes *integrate*, *indicate*, *record* and *trace* fundamental ecological processes through the isotopic fractionation (e.g. enzymes, metabolism, altitude, temperature, land-use, geographic origin)

Mapping nitrogen concentration and nitrogen isotopic composition of lichens

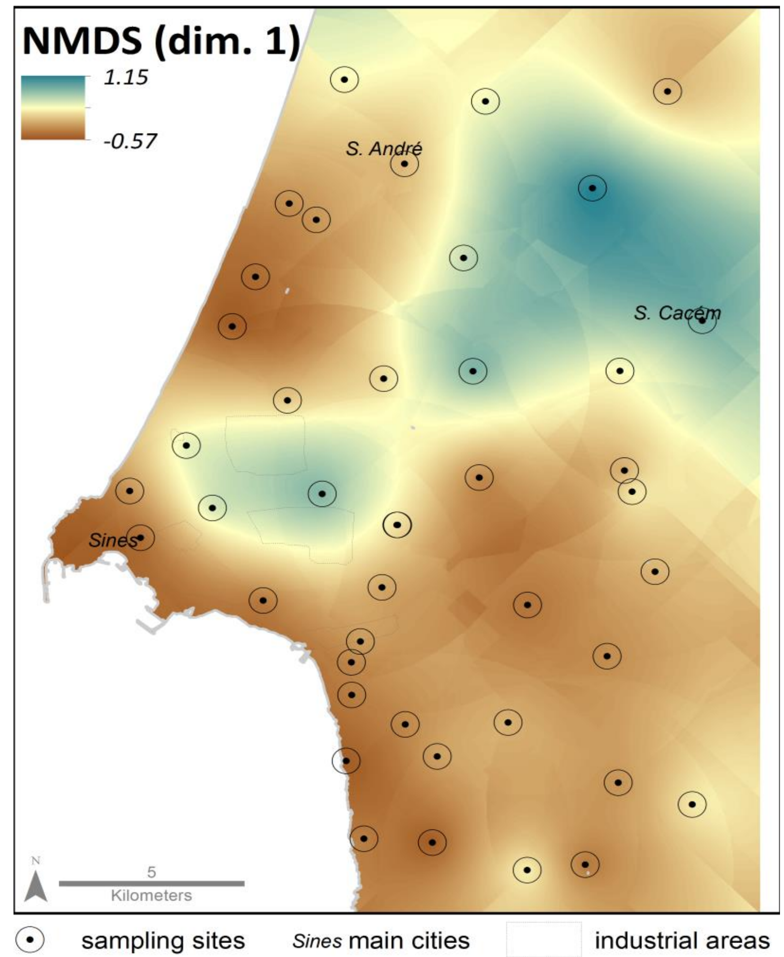
%N (N concentration) **$\delta^{15}N$ (N origin)**



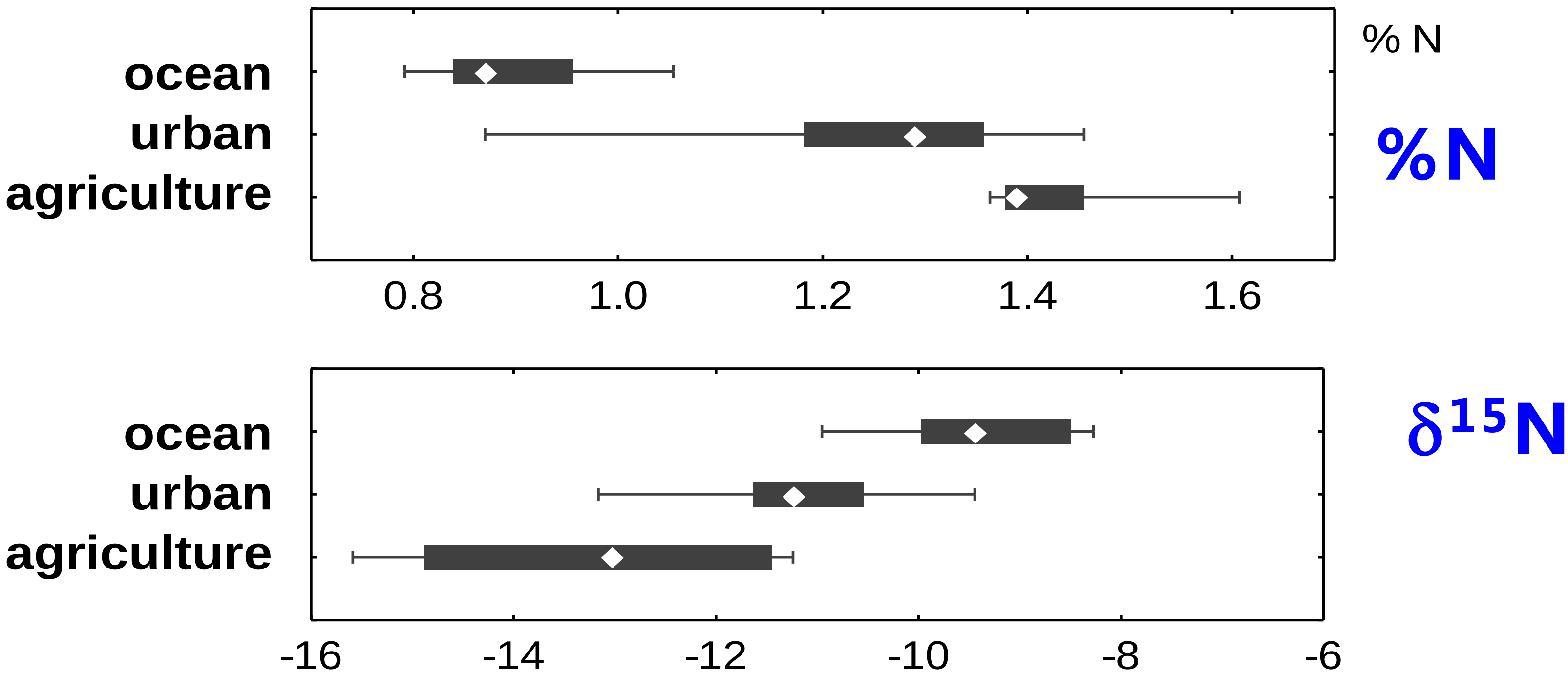
Mapping the common distribution of nitrogen concentration and nitrogen isotopic composition



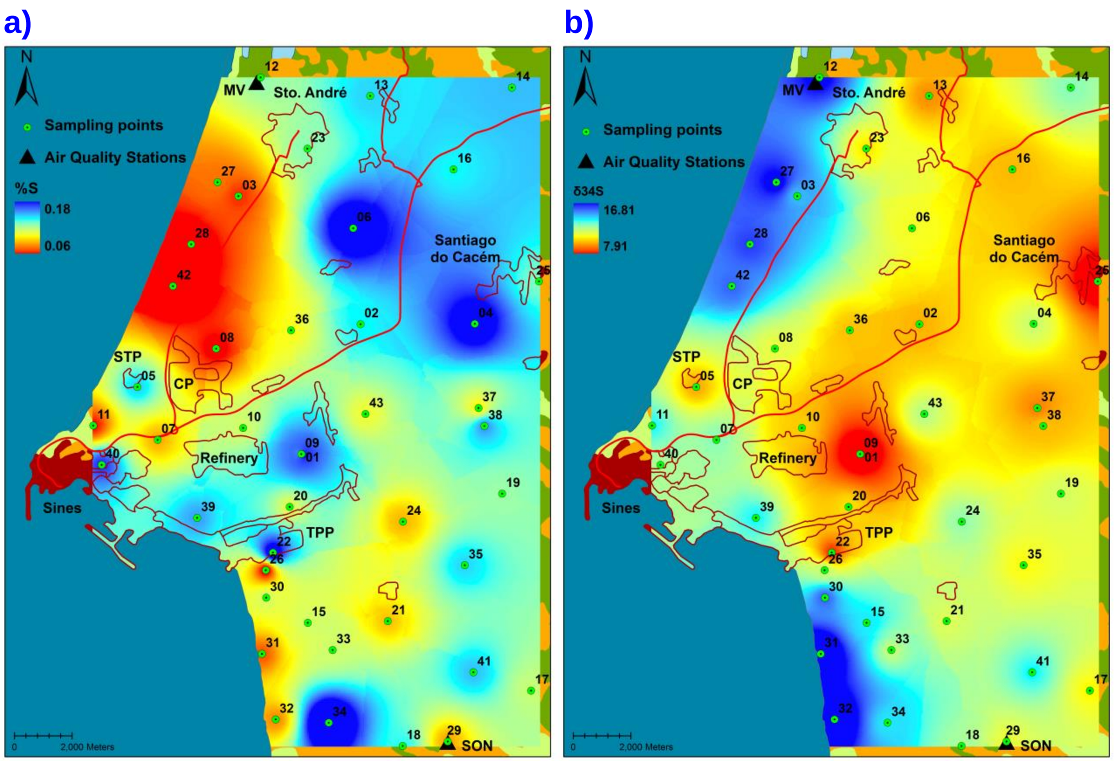
NMDS (%N & $\delta^{15}N$)



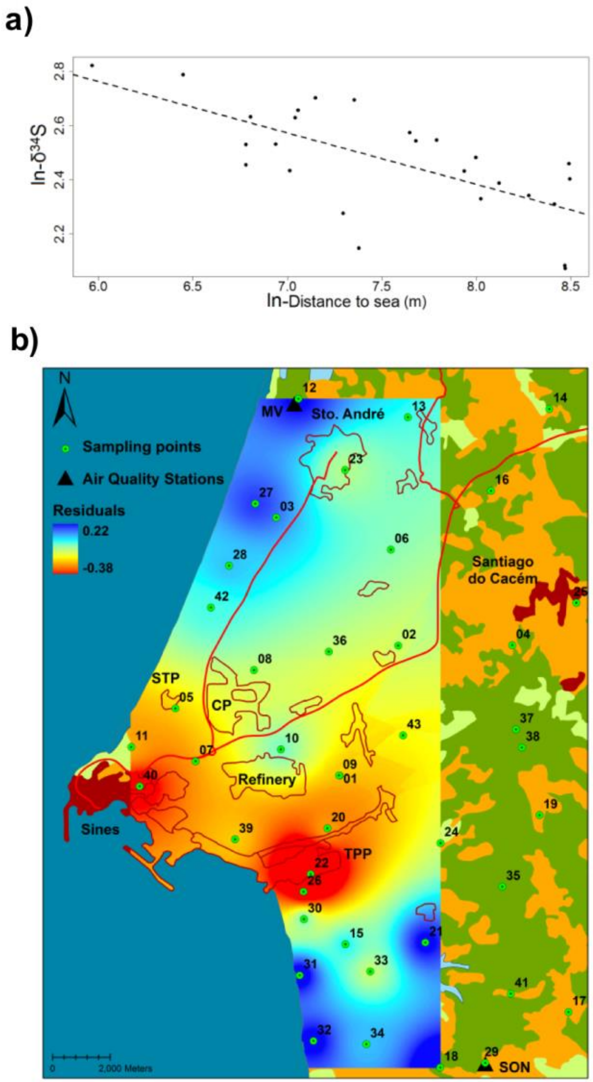
nitrogen signature of different sources based on %N and δ15N composition



Sulphur signature of different sources based on %S and $\delta^{34}S$ composition



Spatial modelling of sulphur concentrations and isotopic signatures in lichens. Interpolation of a) S concentration and b) $\delta^{34}S$ values in lichens. Artificial Areas and main roads are represented by red lines, green dots are the sampling points and main cities and industries are labelled.



Spatial model of the effect of Artificial Areas on $\delta^{34}S$. To detect the influence on $\delta^{34}S$ of other land-use types than the Ocean, we interpolated the residuals from a) the relationship between the distance to the sea and $\delta^{34}S$ (n=26; $F_{1,24}$=21.18; p-value<0.05; r=0.69), using an IDW interpolation technique. This produced a b) map showing departures from this model, or from the dominant influence of the sea on $\delta^{34}S$. Artificial Areas and main roads are represented by red lines, green dots are the sampling points and main cities and industries are labelled.

We have found an important sea influence that masked the effects of anthropogenic sources of S, which we were, nevertheless, able to detect.

- **Future…..**

- **Ecology and Environment:** ***Nitrogen deposition; Global change drivers; interactions between "traditional pollutants" and climate change; <u>Critical thresholds</u>***

- **Tools and Analysis**: ***Development of analytical tools to determine pollutants origin (i.e. stable isotopes)***

- **Public Heath:** ***Spatial and temporal analysis, using lichens as a surrogate of "more traditional sensors"; <u>critical N-loads for Human populations</u>***

- **Innovation?:** ***Bio-sensors with "poikilohydric characteristics"***

acknowledgments










- **FCTPortuguese Science and Technology Foundation: SFRH/BPD/75425/2010 and SFRH/BD/17880/ 2004**
- **DesertWarning: PTDC/AAC-CLI/104913/2008**
- **GISA: private funding**
- **SINESBIOAR- LIFE00 ENV/P/000830**
- **SERN: PTDC/BIA-BEC/ 99323/2008)**

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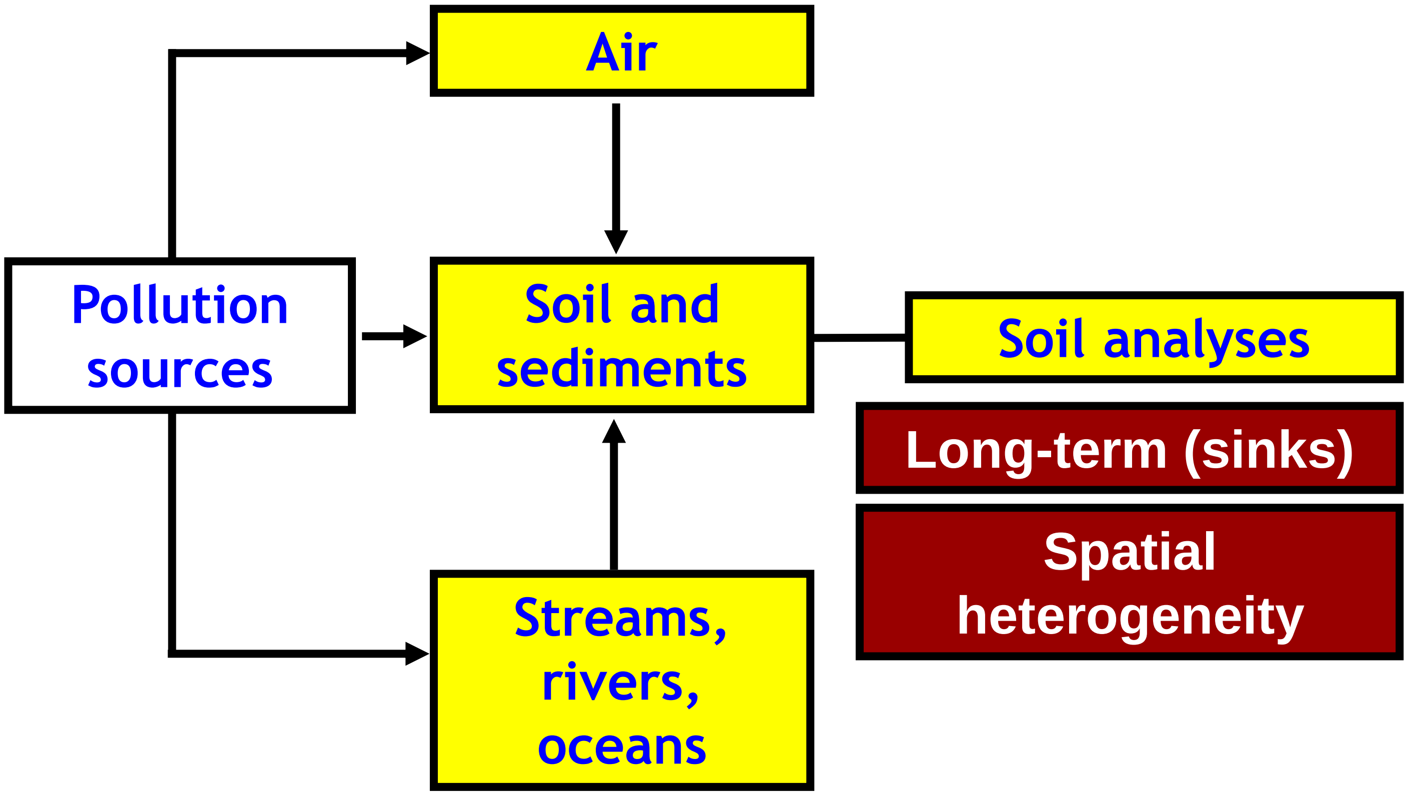
Environmental monitoring of PAHs and PCDD/Fs



Environmental monitoring of PAHs and PCDD/Fs

Air

Pollution sources

Soil and sediments

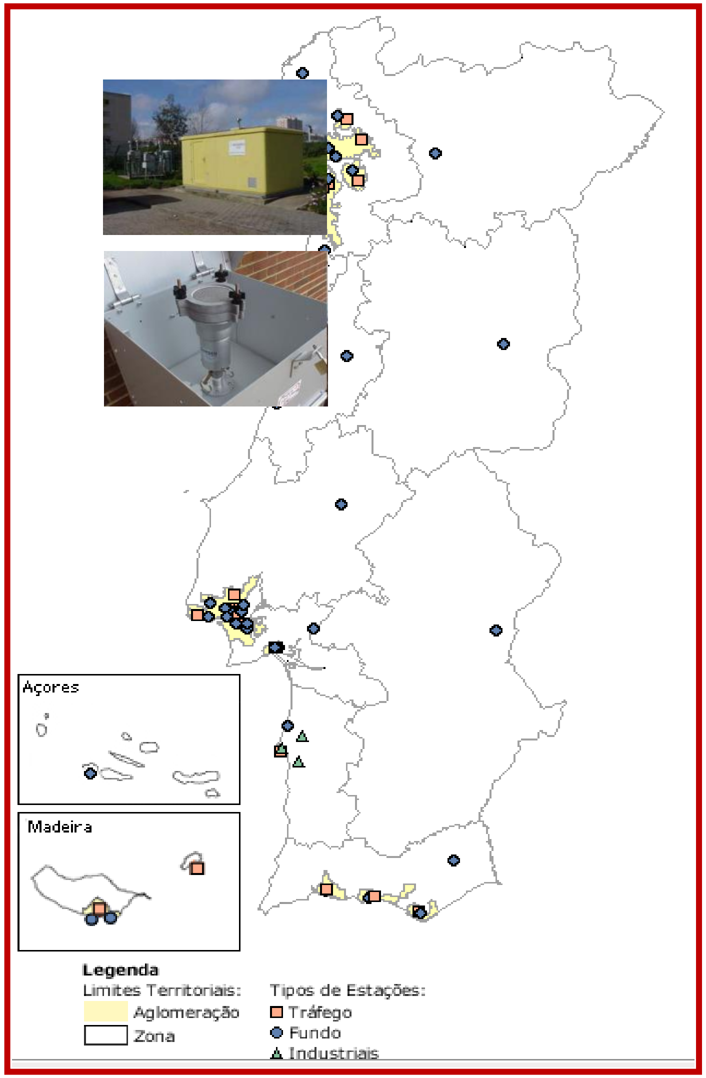
Streams, rivers, oceans

Water analyses

Short-term indicator

Lack of detection

Environmental monitoring of PAHs and PCDD/Fs



Air quality monitoring stations in Portugal – www.qualar.org

Only four air quality monitoring stations measuring PAHs in Portugal.

- **Aveiro**
  - **benzo[a]pyrene in PM10**
- **Estarreja**
  - **benzo[a]pyrene in PM10**
- **Fundão**
  - **benzo[a]pyrene in PM10**
- **Amadora**
  - **benzo[a]pyrene in PM10**
  - **benzo[b]fluoranthene in PM10**
  - **indeno[1,2,3-cd]pyrene in PM10**

Only one air quality monitoring station is currently measuring PCDD/Fs.

Biomonitoring POPs

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

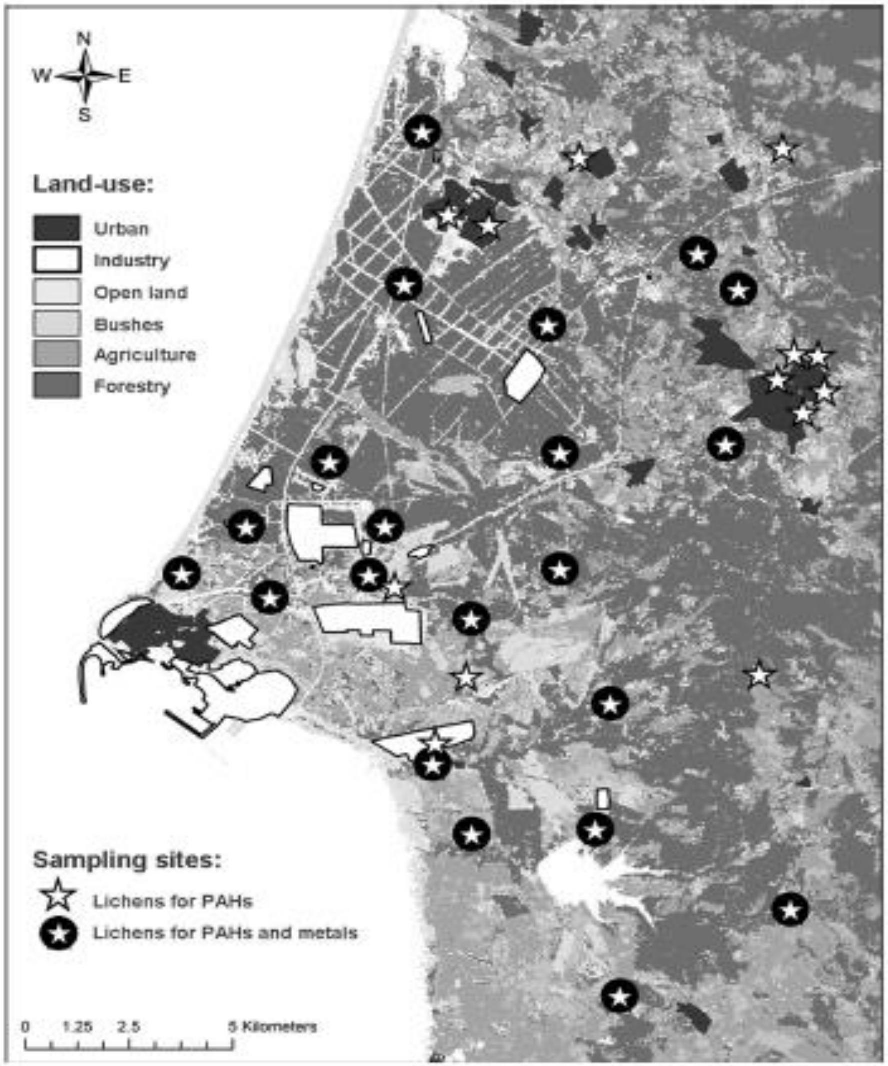
Advantages of using biomonitors/lichens to assess POP pollution

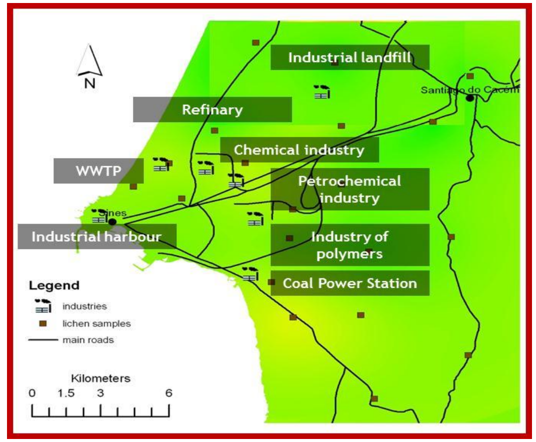
High spatial resolution (possible to obtain information at many sampling sites – low cost).

Accumulate pollutants over their lifetime, reflecting a chronic exposure.

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

Lichen sampling

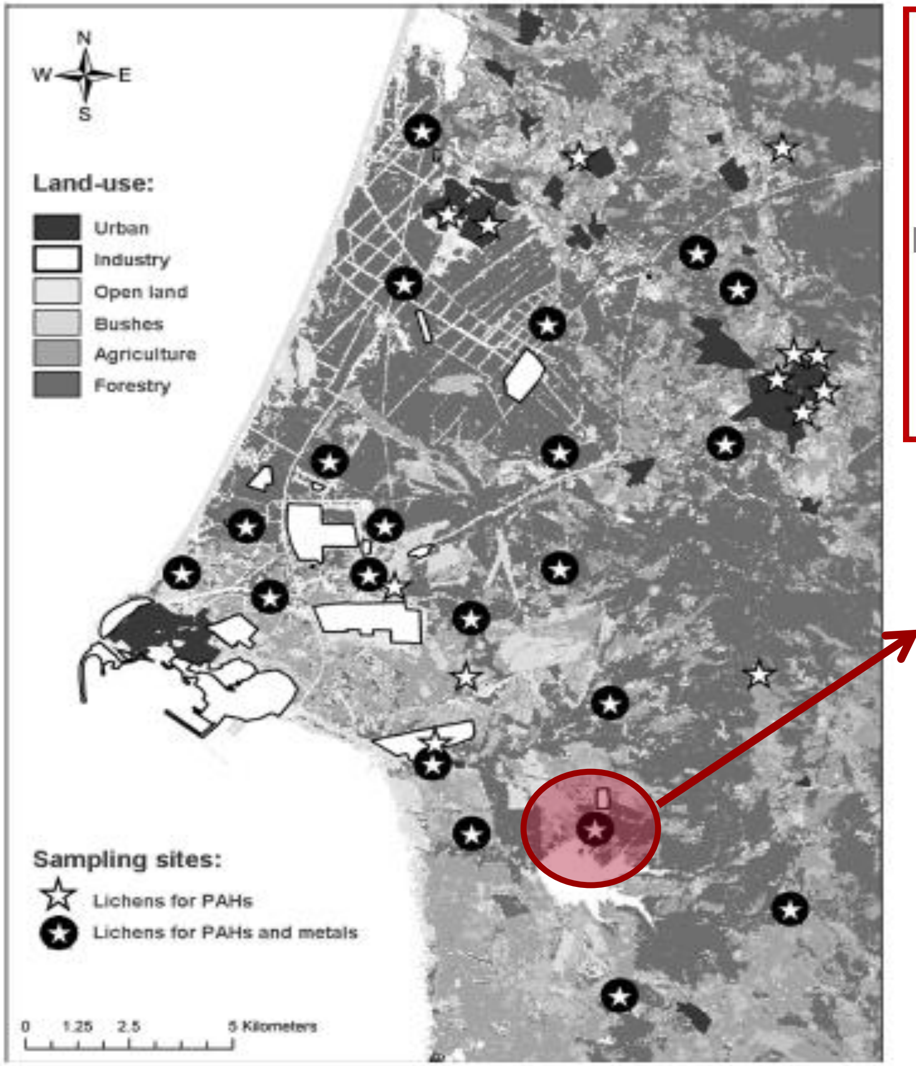


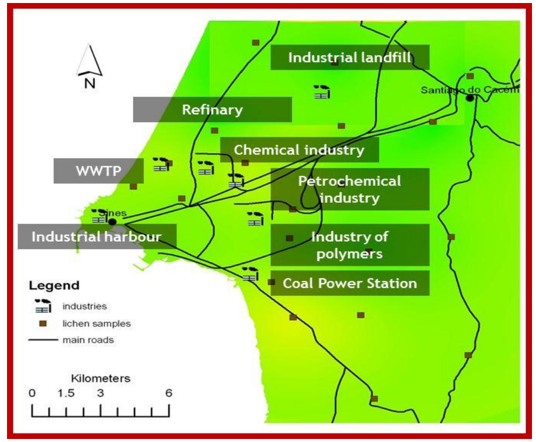


- **Collection of the foliose lichen *Parmotrema hypoleucinum* in 34 sampling sites from *Quercus suber*.**
- **Samples were placed in ambar glass bottles and stored at 4ºC in the dark until chemical analysis.**
- **Sampling was perfomed during 3 days under constant climatic conditions (no precipitation events) (Jan 2008).**

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

Characterization of land-use





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

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

Chemical analysis of the 16 EPA-PAHs

Soxhlet extraction with acetonitrile

↓

Concentration (rotavapor)

↓

Clean-up

(florisil)

↓

Concentration (N stream)

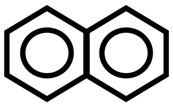
↓

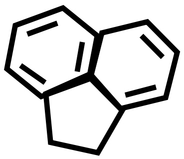
HPLC

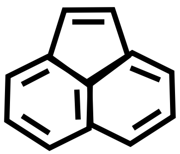
Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

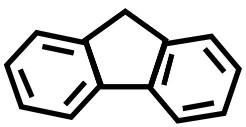
Priority 16 PAHs recommended by EPA

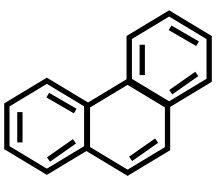
Low molecular weight PAHs (LMW) (2 and 3 rings)

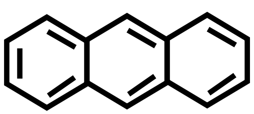

Naphthalene


Acenafteno

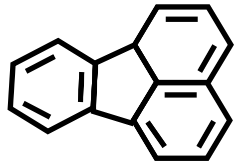

Acenaphtylene

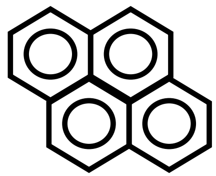

Fluorene

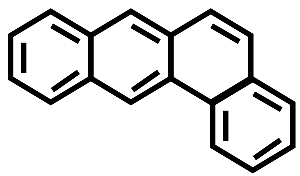

Phenanthrene

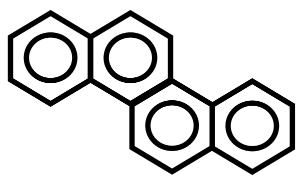

Anthracene

(4 rings)

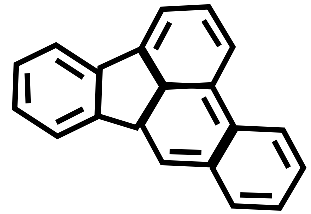

Fluoranthene

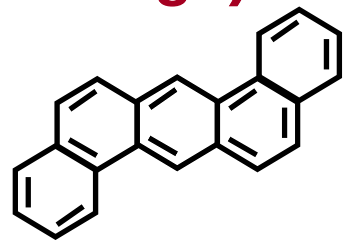

Pyrene

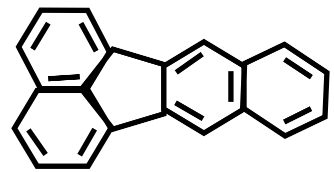

Benzo-a-anthraceno

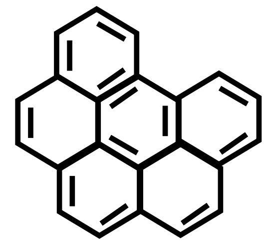

Chrysene

High molecular weight PAHs (HMW) (5 and 6 rings)

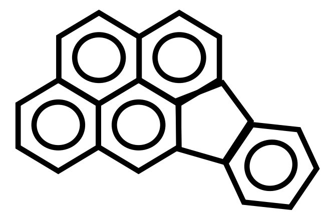

Benzo-b-fluoranthene


Dibenzo-ah-anthracene


Benzo-k-fluoranthene


Benzo-ghi-perylene


Benzo-a-pyrene


Indeno-123cd-pyrene

Using lichens to track pollution sources

TABLE 1. PAH Concentrations (ng PAH/g Lichen) Measured in Lichens Collected from Sites with Different Dominating Land-Use Classes within a Buffer of 1 km Centered at Each Sampling Site[a]

		industrial	urban	ind + urb	forest	agriculture
2-ring PAHs	average	20.9	20.1	64.0	16.4	25.1
	SD	14.5	3.8	70.2	5.6	8.0
	min	18.3	13.6	14.9	10.6	13.5
	max	58.8	25.9	175.3	25.6	33.3
3-ring PAHs	average	56.3	74.4	112.5	38.5	55.8
	SD	22.1	40.0	59.5	10.9	20.8
	min	32.3	37.5	65.2	27.7	38.9
	max	91.3	137.1	217.9	54.8	88.4
4-ring PAHs	average	75.1	180.4	226.2	58.8	91.9
	SD	35.0	133.2	77.1	20.0	21.6
	min	32.4	60.6	127.9	27.7	68.5
	max	149.0	426.2	325.9	85.3	124.4
5-ring PAHs	average	11.5	11.2	33.6	7.7	13.5
	SD	10.0	3.0	30.7	4.9	6.0
	min	2.8	6.8	11.0	4.3	5.4
	max	35.7	16.4	86.6	17.4	21.7
6-ring PAHs	average	6.9	3.7	18.3	2.1	4.6
	SD	7.6	1.3	24.9	0.8	3.8
	min	0.9	1.6	3.1	1.1	0.0
	max	24.0	4.8	66.2	3.4	8.9
16 EPA-PAHs	average	178.9	289.7	454.5	123.3	191.0
	SD	80.0	174.5	233.9	30.2	50.7
	min	93.6	126.8	232.9	90.5	128.4
	max	332.0	599.2	871.8	157.1	264.9

[a] Industrial sites (0.93 to 18.98% covered by industrial areas, $N = 9$), urban sites (0.11 to 43.87% covered by urban areas, $N = 8$), industrial and urban mixed sites (21.40 to 64.64% covered by industrial and urban areas, $N = 6$), forest sites (50.45 to 71.91% covered by wooded areas, $N = 6$), and agricultural sites (27.78 to 47.48% covered by agricultural areas, $N = 5$).

- **Mixed areas – urban and industrial – show the highest PAH concentrations (16 EPA-PAHs)**

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

Using lichens to track pollution sources

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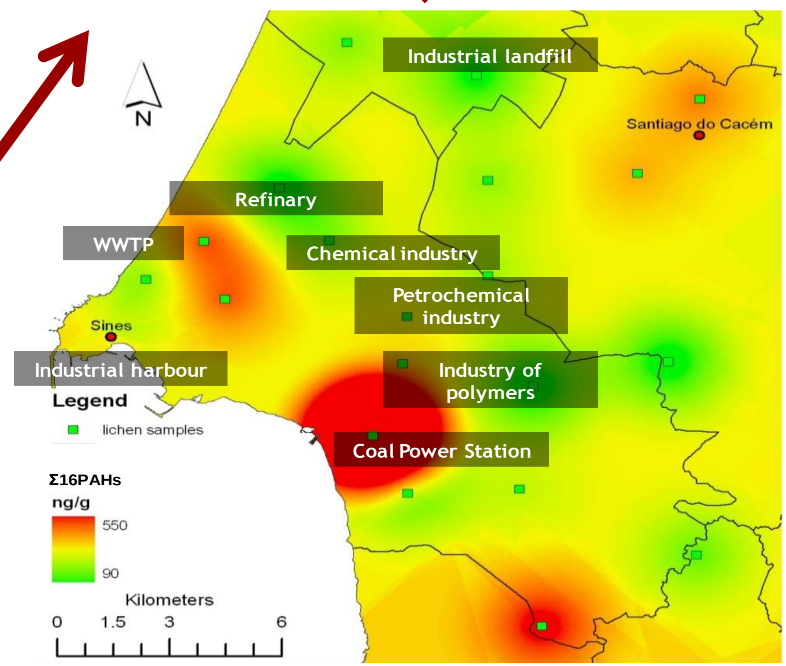
	min	18.3	13.6	14.9	10.6	13.5
	max	58.8	25.9	175.3	25.6	33.3
3-ring PAHs	average	56.3	74.4	112.5	38.5	55.8
	SD	22.1	40.0	59.5	10.9	20.8
	min	32.3	37.5	65.2	27.7	38.9
	max	91.3	137.1	217.9	54.8	88.4
4-ring PAHs	average	75.1	180.4	226.2	58.8	91.9
	SD	35.0	133.2	77.1	20.0	21.6
	min	32.4	60.6	127.9	27.7	68.5
	max	149.0	426.2	325.9	85.3	124.4
5-ring PAHs	average	11.5	11.2	33.6	7.7	13.5
	SD	10.0	3.0	30.7	4.9	6.0
	min	2.8	6.8	11.0	4.3	5.4
	max	35.7	16.4	86.6	17.4	21.7
6-ring PAHs	average	6.9	3.7	18.3	2.1	4.6
	SD	7.6	1.3	24.9	0.8	3.8
	min	0.9	1.6	3.1	1.1	0.0
	max	24.0	4.8	66.2	3.4	8.9
16 EPA-PAHs	average	178.9	289.7	454.5	123.3	191.0
	SD	80.0	174.5	233.9	30.2	50.7
	min	93.6	126.8	232.9	90.5	128.4
	max	332.0	599.2	871.8	157.1	264.9

[a] Industrial sites (0.93 to 18.98% covered by industrial areas, $N = 9$), urban sites (0.11 to 43.87% covered by urban areas, $N = 8$), industrial and urban mixed sites (21.40 to 64.64% covered by industrial and urban areas, $N = 6$), forest sites (50.45 to 71.91% covered by wooded areas, $N = 6$), and agricultural sites (27.78 to 47.48% covered by agricultural areas, $N = 5$).

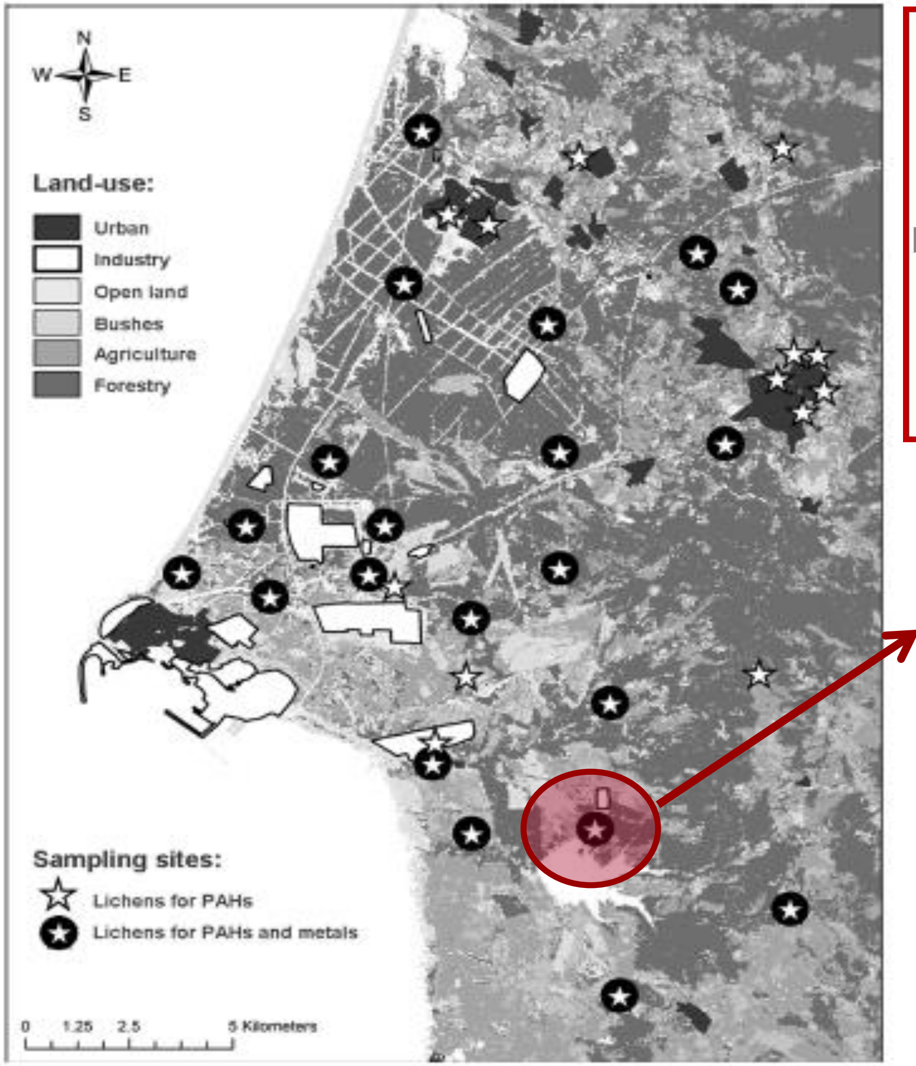
- **Mixed areas – urban and industrial – show the highest PAH concentrations (16 EPA-PAHs)**

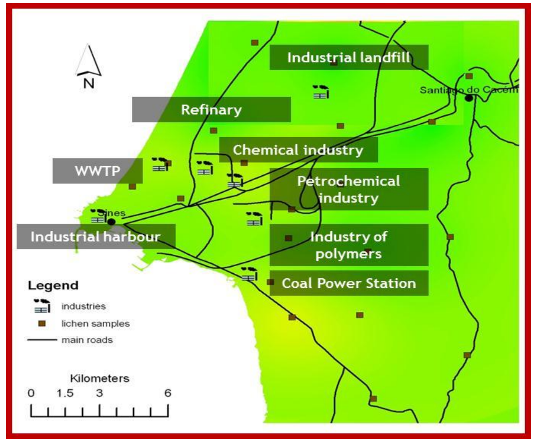


Map of the interpolattion of the concentration of the 16PAHs, using lichens as biomonitors (n=34)

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.

Using lichens to track pollution sources





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

Principal Component Analysis (PCA) using relative covers of each land-use class and PAH profiles in lichens.

Augusto et al., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environmental Science & Technoloyy 43(20):7762-7769.