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Measuring and mapping the effectiveness of the European Air Quality Directive in reducing N and S deposition at the ecosystem level

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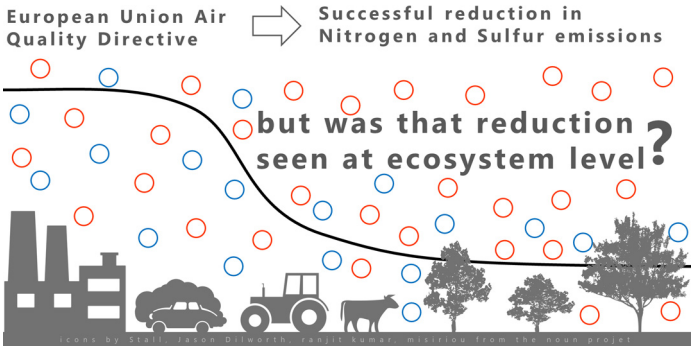
HIGHLIGHTS

- Directive 2001/81/EC accomplished the reduction of N & S from industrial emissions.
- Ecological indicators (lichens) respond to N & S deposition.
- A reduction of ~70% S was achieved both in emissions and on lichen accumulation.
- N accumulated by ecological indicators does not follow the reduction in N emissions.
- Ecosystems are still threatened by excess N from agriculture and transport.

GRAPHICAL ABSTRACT



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ABSTRACT

To protect human health and the environment (namely ecosystems), international air quality protocols and guidelines, like the Gothenburg protocol (1999) and the 2001 EU Air Quality Directive (NECD), conveyed national emission ceilings for atmospheric pollutants (Directive 2001/81/EC), including the reduction of sulfur (S) and nitrogen (N) emissions by 2010. However, to what degree this expected reduction in emissions had reflections at the ecosystem level (i.e. pollutant levels reaching and impacting ecosystems and their organisms) remains unknown. Here, we used lichens as ecological indicators, together with reported air and precipitation pollutant concentrations, to determine and map the consequences of the S and N atmospheric emission's reduction, during the implementation of the 2001 Directive (in 2002 and 2011), due primarily to the industrial-sector. The study area is a mixed-land-use industrialized Mediterranean agroforest ecosystem, in southwest Europe.

The reduction of S emissions (2002−2011) was reflected at the ecosystem level, as the same S-declining trend was observed in atmospheric measurement stations and lichens alike (−70%), indicating that most S deposited to the ecosystem had an industrial origin. However, this was not the case for N with a slight N-reduction near industrial facilities, but mostly N-deposition in lichens increased in areas dominated by agricultural land-uses.

Taken together, these results highlight the importance of going beyond emissions estimation and modeling, to assess the success of the implementation of the NECD in lowering pollutant accumulation in living organisms and their environment. This can only be achieved by measuring pollutant deposition at the ecosystem level (e.g. living

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organisms). By doing so, we were able to show that the 2001 NECD was successful in reducing S concentrations from Industry, whereas N remains a challenge. Despite the small reduction in N-emissions, deposition into ecosystems did not reflect these changes as agriculture and transport sectors must reduce NH_3 and NO_x emissions.

1. Introduction

Nitrogen and sulfur are two pollutants listed among the most important anthropogenic pressures on our planet (Rockstrom et al., 2009). Rockstrom et al. (2009) estimated boundaries that should not be exceeded as to avoid unpredictable human-induced environmental changes on a global scale. However, nitrogen's biochemical flow has already exceeded its safe boundaries and atmospheric aerosol loading (e.g. particulates, tropospheric ozone, sulfur and nitrogen oxides), which is related to atmospheric pollution, is yet to be quantified (Steffen et al., 2015). Following the Gothenburg Protocol in 1999, the European Union (EU) legislated in 2001 the national ceilings for atmospheric pollutants expected to significantly impact the environment (Directive 2001/81/EC or NECD). Efforts to reduce acidification, soil eutrophication and ground-level ozone (O_3) were a firm acknowledgement of the deleterious effects of excess nitrogen and sulfur (nitrogen oxides – NO_x; ammonia – NH_3; sulfur dioxide – SO_2) in the environment (Directive 2001/81/EC), among others. The Directive also stated that the World Health Organization (WHO) guidelines regarding those pollutants were being exceeded by all member states, thus implying potential health problems across the EU (Directive 2001/81/EC).

Portugal, a EU member state, had the 9th largest country area of the EC15, but the 4th largest "allowance" (ceiling identified in Fig. 1) for SO_2 emissions per country area, symptom of an aggravated SO_2 pollution problem (data from the Directive 2001/81/EC, European Community with 15 members, at the time). These national ceilings were in effect in Portugal until 2015, when the revision of the Gothenburg Protocol resulted in newly approved legislation (Directive EU 2016/2284) defining new goals for the reduction of atmospheric emissions of pollutants from 2020 to 2029 (−7% for NH_3, −36% for NO_2, −63% for SO_2, relatively to 2005), and after 2030 (−15% for NH_3, −63% for NO_2, −83% for SO_2; relatively to 2005).

Air pollutants such as NO_x (nitrogen oxides NO and NO_2), NH_3 (ammonia) and SO_x (sulfur oxides, mainly SO_2) are reactive forms in the atmosphere, creating NO_3^-, NH_4^+ and SO_4^{2-} compounds (Rockstrom et al., 2009). They are heavily produced by many human activities: combustion processes produce NO_x (e.g. power production, transports, combustions in industry), which is readily transformed into NO and NO_2. Ammonia, on the other hand, originates mostly from fertilizers used in agriculture (Erisman et al., 2007). Fuel combustion is the main anthropogenic generator of SO_x (SO_2), mostly from energy generation and distribution (see Fig. 1, for Portuguese emissions between 1990 and 2015). All these compounds have negative impacts on the environment, namely on soil acidification, water eutrophication, formation of particulate matter and contributing to the greenhouse effect (Erisman et al., 2007; Shibata et al., 2015; Sutton et al., 2011), with cascading outcomes on ecosystem structure and functionality (e.g. shrub/grass ratio; van den Berg et al., 2016).

Although the immediate result of the 2001 EU directive was a noticeable reduction in pollutant emissions reported to the European Environmental Agency (EEA) at the national level (−25% of NH_3, −35% of NO_2, −80% of SO_2 from 2001 to 2015 in Portugal; Fig. 1), the effective measurement of pollutant concentrations in air and precipitation, or its modeling, is limited by the number and location of the few air quality monitoring stations available (APA, 2017a). Moreover, the magnitude of the effect of the directive, i.e. its effectiveness, on several ecosystems, is often lacking local validation and was not a matter of report to the EEA (until now), although it should ultimately be the "raison d'être" of such a directive, as ecosystem health, ultimately, reflects on human health.

Ecological indicators can be used to overcome the above-mentioned problem. Ecological indicators are measurable characteristics of the structure, composition or function of ecosystems (Niemi and McDonald, 2004). Ecological indicators have been broadly used along measures of pollutants concentration data, aiming at measuring its impacts on ecosystems, e.g. looking at changes in biodiversity (Pinho et al., 2012) and pollutants accumulation within the organisms (Barros et al., 2015; Pinho et al., 2017). These ecosystem-based measures provide qualitative and/or quantitative information about pollutant deposition and allow reducing the limitations of a small regional coverage from monitoring stations. Being living organisms, ecological indicators integrate pollutant accumulation with their own physiological response to the pollutant, reflecting that of the ecosystem due to their low critical loads (Pinho et al., 2012). Lichens (symbioses of fungi with algae and/or cyanobacteria) are ubiquitous organisms that uptake their water and nutrients directly from the air, together with any pollutants present, making them excellent ecological indicators (Pinho et al., 2008b; Pinho et al., 2017; Vieira et al., 2018). In terrestrial environments, lichens have been the most used and studied biomonitors for assessing air pollutant concentrations, and for measuring

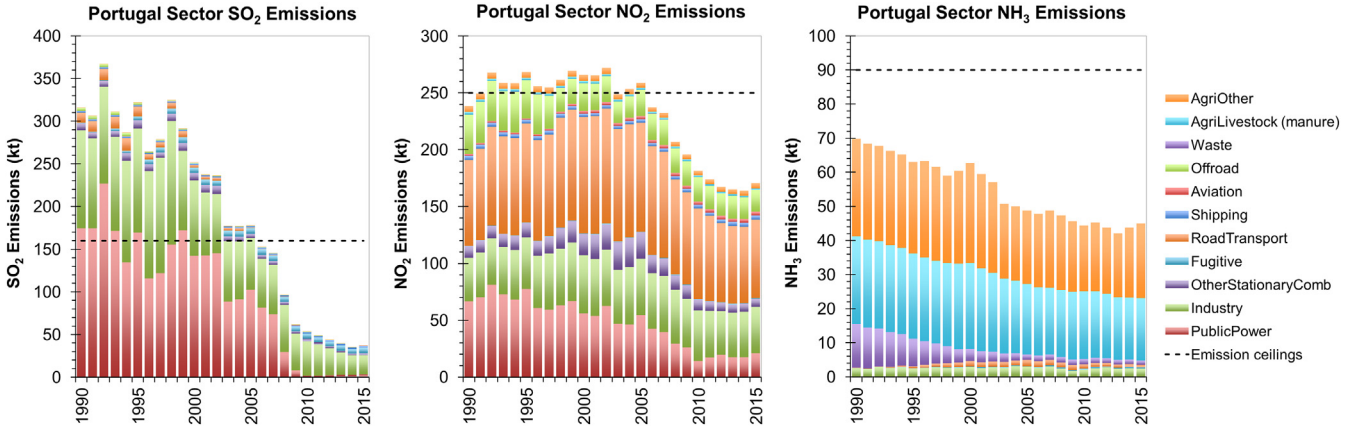

Fig. 1. Portugal National Sectorial Emissions 1990–2015, for compliance with Directive 2001/81/EC, reported to EMEP/EEA for SO_x (as SO_2), NO_x (as NO_2) and NH_3 (EEA, 2017). The horizontal lines indicate the 2010 National Ceilings (2001/81/EC).

integrated effects of pollutants on ecosystems (e.g. lichen diversity and air pollution levels, related to detection of early pollution effects; lichen pollutant accumulation related to air concentrations) and human health (Cislaghi and Nimis, 1997; Ribeiro et al., 2014).

Now under the Directive EU 2016/2284, article 9, EU agreed to fulfill direct monitoring objectives to account for the impacts of atmospheric pollution on ecosystems (notably acidification and eutrophication), although still based mostly on physicochemical measurements on indicators (soil and water) and less on ecological indicators (only for ozone or aquatic ecosystems). Considering the progresses already achieved by the implementation of the several air quality guidelines and legislation, a further step is necessary to validate the effects of the impact of those measures at ecosystem level. As such, important lessons could be learned from looking at the results of the application of the previous Directive 2001/81/EC, which will aid in defining the outcomes expected for ecosystems and to adjust the expectations for the new 2016 Directive. With this in mind, we looked at pollutant concentrations in ecological indicators in 2002 (the beginning of implementation of the 2001 Directive) and then again nine years later in 2011, when the goals defined by the national ceiling would already have been achieved. We questioned the effectiveness of the Directive for terrestrial Mediterranean ecosystems, in terms of the N and S accumulation experienced by a network of ecological indicators (lichens), covering an area exposed to intense petrochemical pollution since the 70's, and surrounded by agricultural areas, agroforestry (*Montado*) and a natural park. This work aims to answer the following questions: do the reported emissions' decreasing trends, and the trends observed in monitoring stations, reflect those detected in ecosystems (i.e. lichens)? And, are the effects of reduced emissions on pollutant deposition observed at local or regional scales?

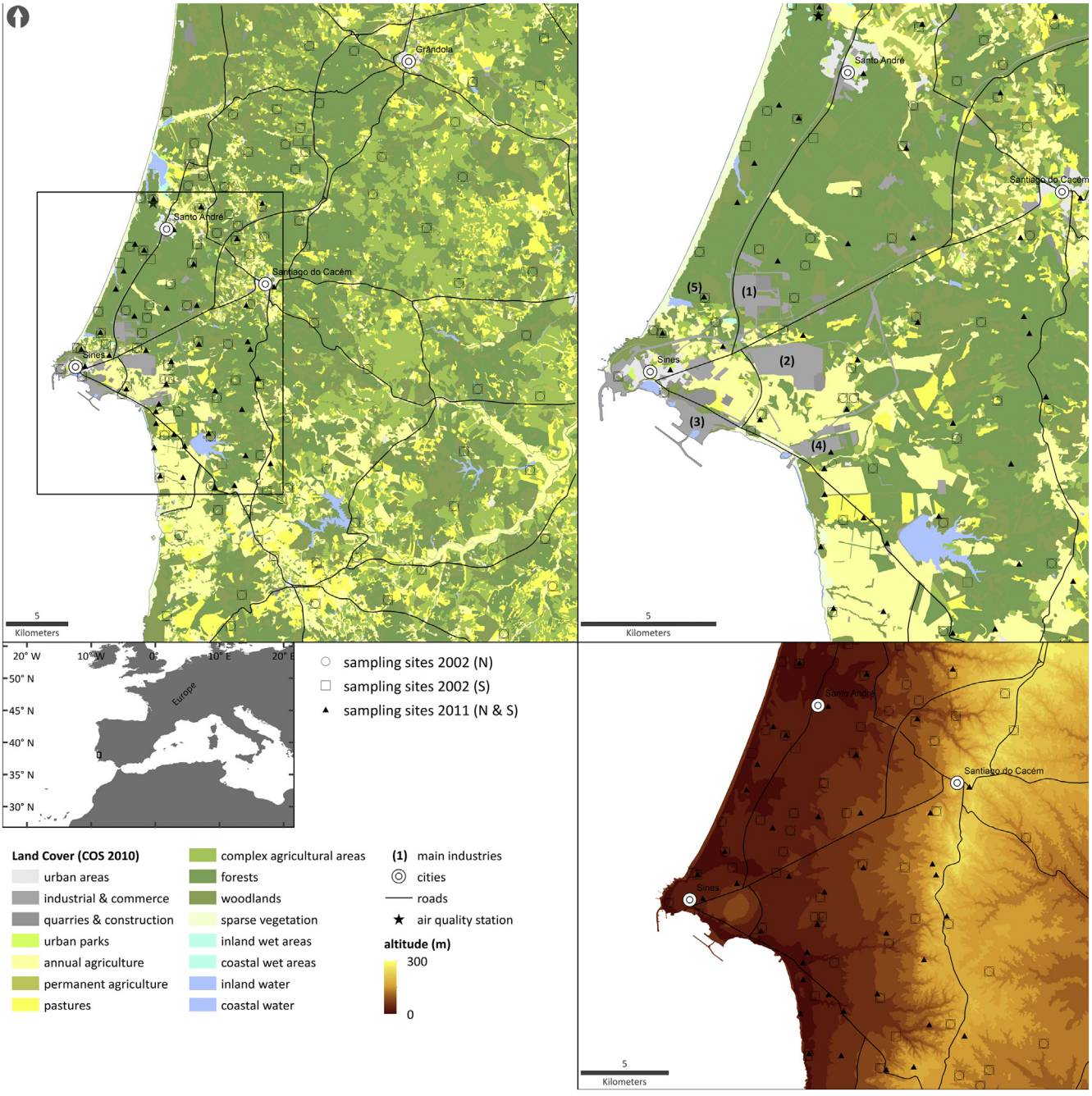

Fig. 2. Study area, evidencing sampling points (2002 and 2011), land use (COS2010; DGT, 2010) and topography (IGEOE, 2018). Main cities, urban and industrial areas: label by number: (1) petrochemical industries, (2) oil refineries, (3) industrial harbor, (4) coal power plant, (5) industrial water treatment plant.

2. Methods

2.1. Study area

This work was developed in 2002 and 2011, within a large Portuguese petro-industrial area (*Alentejo Litoral* region), active since the late 70's (Fig. 2). In the study area (ca. 25 × 15 km), there is a deep-water harbor (Sines), an important entry port at the European level, a railway, motorways, a coal-fired power plant, an oil refinery, petrochemical industry, an industrial sewage treatment plant, an industrial landfill, and many other smaller industries. Moreover, in the area there is also a natural park (*Parque Natural do Sudoeste Alentejano e Costa Vicentina*), a matrix of forested areas and shrubland (including cork oak woodlands, and pine and eucalyptus plantations), agricultural fields, mainly as non-irrigated extensive systems (cereals) or irrigated high-intensity agriculture (vegetables and rice - these heavily fertilized), but also orchards and animal production farms. The resident population changed from 37,140 to 37,316 thousand inhabitants (2001 to 2011, respectively; INE, 2018) distributed among three larger settlements (population > 6000, *Santiago do Cacém*, *Santo André* and *Sines*) and several smaller ones.

This region has a Mediterranean climate, with average annual temperature of 10.7–22.4 °C and a total annual precipitation of about 735 mm (1981–2010 average; IPMA, 2018). Winds prevail from North-Northwest, offering a strong Atlantic influence.

2.2. Emission and atmospheric concentration data

Data on atmospheric emissions (NH_3, NO_x (NO_2) and SOx (SO_2)) were collected from the European Monitoring Evaluation Programme/European Environment Agency (EMEP/EEA) and measurements of the concentration of acidifying/eutrophying compounds in the air and precipitation for Portugal were respectively collected from the Portuguese Environmental Agency (APA - Agência Portuguesa do Ambiente) and from the Norwegian Institute for Air Research (NILU) database (EBAS database). This reporting is part of the countries effort to fulfill the air pollution reduction commitments:

1) the National Sectorial Emissions between 1990 and 2015 (represented in Fig. 1; EEA, 2017); sector classes follow the Nomenclature for Reporting aggregation for Gridding and Large Point Sources (GNFR).
2) NH_3, NO_x (NO_2) and SO_x (SO_2) gridded emissions, including national emissions (by sector) and those resulting from international shipping in the North-East Atlantic Ocean (EMEP, 2018), were extracted from two grid cells overlapping the study area, from 2000 to 2015 (Fig. 3). Units refer to total pollutant mass emitted (10^9 g = 10^3 Mg = 10^3 t = 1 kilotonne (kt)), per year.
3) air concentration data reported by APA for NO_2 and SO_2 (APA, 2017a) and concentration in precipitation provided by EBAS for NH_4^+, NO_3^- and xSO_4^{2-} (sulfate corrected for sea salt contribution; EBAS, 2018; Fig. 4), from the *Monte Velho*, a background monitoring station in the study area (location in Fig. 2), between 1994 and 2016 (with gaps). Air concentration units refer to hourly average pollutant mass, per volume of air ($\mu g \cdot m^{-3}$) and units of concentration in the precipitation correspond to daily averages of pollutant mass per volume of rain ($mg\ N \cdot l^{-1}$ and $mg\ S \cdot l^{-1}$).

2.3. Deposition on ecological indicators (lichens)

Lichens were collected in sampling points distributed across the study area in two different sampling field surveys (2002 and 2011; Fig. 2). Selection criteria were similar in both: cork-oak woodlands were selected whenever possible (preferably *Quercus suber* L., cork oak, and *Pinus* spp., pine), away for the direct influence of local pollution sources (e.g. roads, industries). In 2002 a total of 106 samples for N and 111 samples for S were collected in an area of 50 × 40 km, with an average distance between sampling points of approximately 2490 m. In 2011 a total of 42 samples (both for N and S) were collected, across an area of 15 × 25 km, with an average distance between sampling sites of 1990 m. To compare N and S concentrations accumulated by lichens in 2002 and 2011, we selected the study area of 2011 (15 × 25 km) given that it was fully included in the larger area sampled in 2002. However, because sampling sites did not exactly coincide in both surveys, we interpolated N and S concentrations between the sampling points for each year. See Barros et al. (2015), Pinho et al. (2004), Pinho et al. (2008a) and Pinho et al. (2017) for further details.

We collected in situ samples of the lichen *Parmotrema hypoleucinum* (Steiner) Hale, an abundant species in the region. In-situ lichens ensure that the samples have been exposed to pollution deposition for an extended period, thus representing a temporal integration of that deposition (Barros et al., 2015). Previous works showed very significant correlation between measured or estimated air pollutants concentration and the concentration of the same pollutants measured in lichens, both over time and space (Augusto et al., 2010; Pinho et al., 2014).

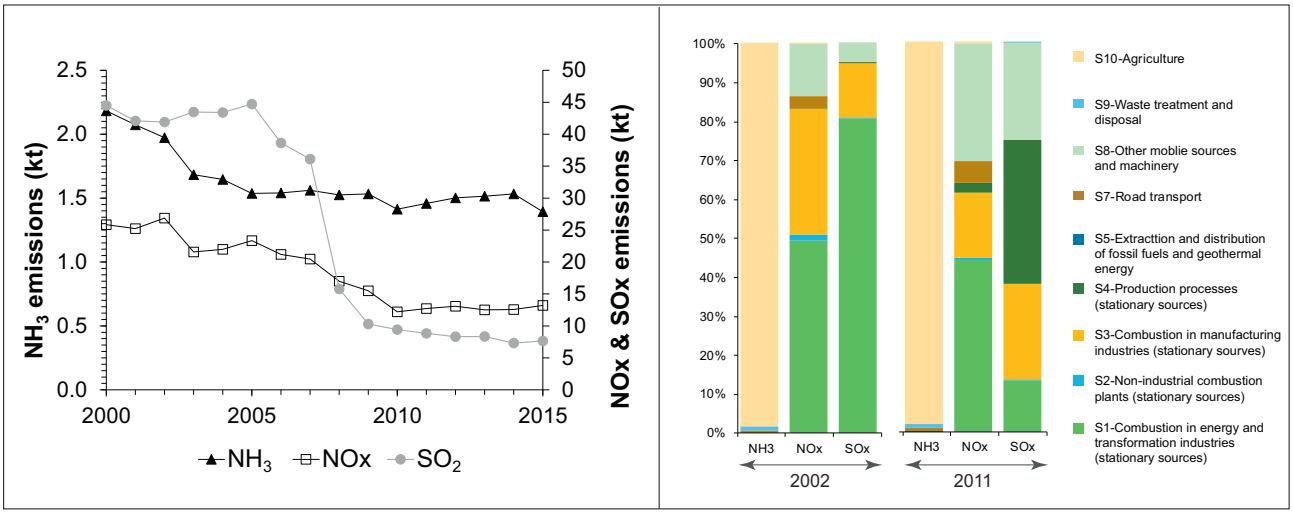

Fig. 3. Left: emissions calculated for two 50 × 50 km resolution grid-cells overlapping the study area, including contributions from international shipping in the North-East Atlantic Ocean. Right: sector contribution for local emissions in 2002 and 2011.
(Data source: EMEP (2018).)

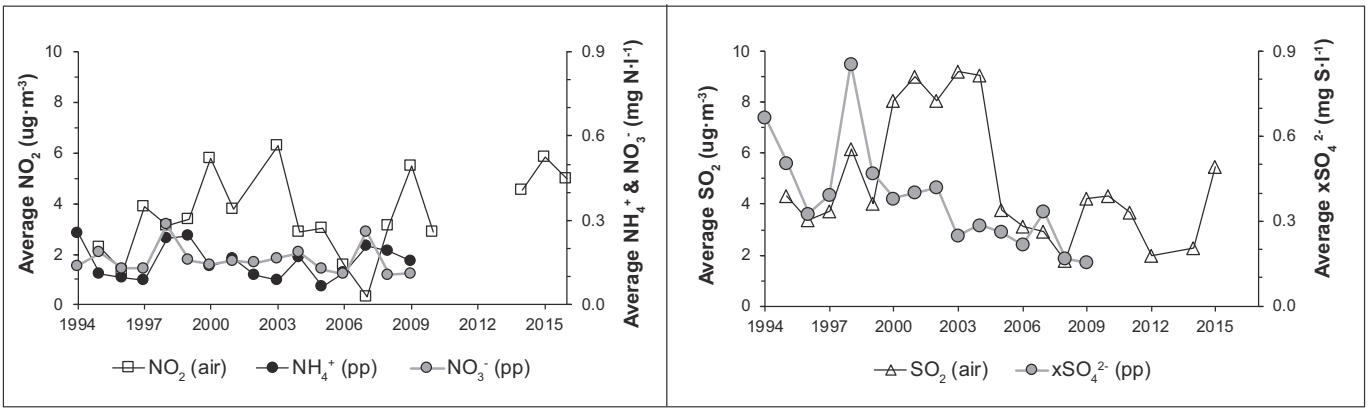

Fig. 4. Mean concentrations at the background monitoring station (Monte-Velho). (air) corresponds to concentrations in air and (pp) in precipitation. (Source APA (2017a) and EBAS (2018).)

Sampling and processing details were described elsewhere (Barros et al., 2015; Pinho et al., 2004; Pinho et al., 2008a; Pinho et al., 2017). Chemical analyses of nitrogen (N) and sulfur (S) on the cleaned, dried, and ground lichen thalli, were made by elemental mass analysis (Euro Vector CHNS-O Elemental Analyzers) (Pinho et al., 2008a). Concentrations of N and S in lichens are presented in percentage of dry weight (w/w %), or in milligram per gram of dry weight ($mg \cdot g^{-1}$).

2.4. Ecological indicator concentrations data analysis

The N and S concentration data (w/w %) from lichens were firstly interpolated within the study area, using ordinary kriging after analysis and plot of the empirical semi-variogram (Goovaerts, 1997) using all available data for each time period (Fig. 5). For all variables the nugget effect was considered zero and a spherical function was used to model

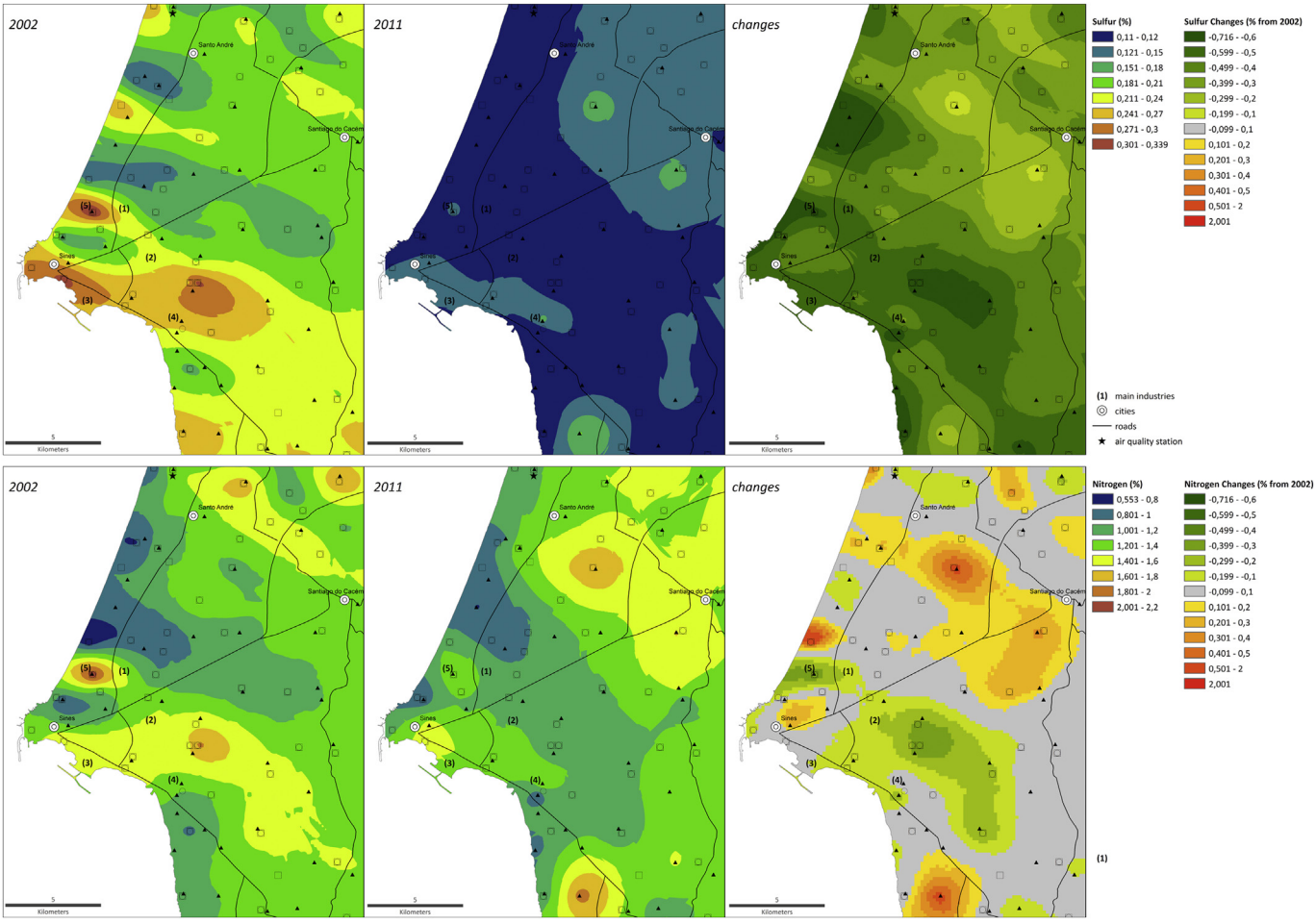

Fig. 5. Mapping the deposition of N and S to the ecosystem using lichens. Sulfur (top) and Nitrogen (bottom) concentrations (1% dry weight = 10 $mg \cdot g^{-1}$) measured in 2002, 2011 and the % difference from 2002 (changes). Increasing S and N deposition are colored in yellow to red and decreasing deposition in green, while variations under 10% are colored in grey.

the empirical variogram values. Both were found to fit the data well. Anisotropy was included in the model and the directions were automatically adjusted by the software. Ranges were adjusted manually to fit the empirical variogram values. For N (2002) the major range was 4000 m and the minor range 3000, and the direction of maximum continuity was 99°. For S (2002) the major range was 5000 m and the minor range 3000, and the direction of maximum continuity was 111°. For N (2011) the major range was 4000 m and the minor range 3900, and the direction of maximum continuity was 104°. For S (2011) the major range was 4000 m and so was the minor range (isotropic variogram). Both the absence of the nugget effect and the relatively large range (around 1/3 of the study area) indicate that the spatial structure of the data was strong. The adjusted functions were then used to estimate each variable using ordinary kriging.

To understand the overall spatial variation in concentrations and changes between 2002 and 2011, a 100 m resolution grid was used to retrieve the data (n = 30,679) and boxplots were constructed with these values across the entire study region (Fig. 6). We opted not to perform statistical analyses using p-value testing for two reasons. Firstly, sampling points did not geographically coincide between 2002 and 2011, and thus we could not use the observed values in sampling sites as samples to test for the influence of time in deposition. Secondly, we opted not to use the data retrieved for the 30,679 sites (used in boxplots) due to lack of statistical independence. In fact, because the data in both time-periods was interpolated using geostatistics, the values estimated for the region are not independent from each other, but rather depend on the values observed in nearby sites. Thus, we opted by not quantifying the statistical strength of the regional differences observed over time and focused instead in comparing the local reductions or increases observed in small areas in the study area.

3. Results

3.1. Changes in N and S measured in monitoring stations

Gridded emissions made available by EMEP within the study area (Fig. 3-left) suggest a reduction between 2002 and 2011 of 26% in NH_3 (−0.52 kt), of 53% in NO_x (−14.2 kt), and of 79% in SO_2 (−33.1 kt). There were no major shifts in the sector's sources of ammonia emissions (Fig. 3-right); but major changes were observed for NO_x and SO_2, such as the relative reduction of emissions from power production (particularly for SO_2) and relative increase in the emissions from "Other mobile sources and machinery". Still, for SO_2 it is also noticeable an increase in the contribution of emissions derived from "Stationary production processes" in 2011.

The average concentration of acidifying/eutrophying compounds registered in the *Monte Velho* monitoring station (Fig. 4) shows a reduction between 2002 and 2011 of 11% in NO_2 ($-0.35\ \mu g \cdot m^{-3}$), 36% in NO_3^- ($-0.04\ mg\ N \cdot l^{-1}$), 54% in SO_2 ($-4.37\ \mu g \cdot m^{-3}$) and 63% in xSO_4^{2-} ($-0.26\ mg\ S \cdot l^{-1}$), and a 47% increase of NH_4^+ ($+0.05\ mg\ N \cdot l^{-1}$).

3.2. Changes in N and S at the ecosystem level

Regarding deposition on ecosystems, in 2002 concentrations of sulfur (S) in lichens were higher in the industrial area, showing a dispersion in a N-NW direction (Fig. 5, values in w/w %), and an average of $2.07 \pm 0.32\ mg\ S \cdot g^{-1}$ (range 1.28–3.38 $mg \cdot g^{-1}$) across the study area. In the case of N, concentrations were also higher in the industrial area and similar dispersion direction, but some higher values were found up north, further inland. The average N concentration for the total area was $12.8 \pm 1.8\ mg\ N \cdot g^{-1}$ (range 6.19–21.3 $mg \cdot g^{-1}$) (Fig. 6, values in w/w %).

Nine years later in 2011, the panorama changed considerably for S, showing a significant decrease in concentrations measured in lichens ($1.14 \pm 0.19\ mg\ S \cdot g^{-1}$, range 0.59–1.81 $mg \cdot g^{-1}$). A reduction of up to 72% was observed in lichens along most of the industrial area and smaller reductions were observed in northern inland areas (overall range 16% to 72% reductions). On the other hand, N concentrations measured in lichens sampled in 2011 were lower in the industrial areas but increased in many inland areas. Between 2002 and 2011, lichen N concentrations in industrial areas showed up to 40% decreases in some cases, but about half of the study area shows an increase in lichen N concentrations that reached 71%. On average, N concentrations in 2011 were $12.7 \pm 1.7\ mg \cdot g^{-1}$ (8.0–18.8 $mg \cdot g^{-1}$). Across the sampling area, we detected an average decrease of 44 ± 11% in S and increase of 0.9 ± 15% in N between 2002 and 2011 (Fig. 6).

4. Discussion

The deposition of nitrogen and sulfur (here represented by their accumulation in lichens), in the studied ecosystem was monitored in 2002 and 2011, within an area with large known petro-chemical industries since the 70's. This study coincided with the application of the Directive 2001/81/EC that committed EU countries to specific national emission ceilings for air pollutants. Overall, we observed a strong reduction in sulfur, but not in nitrogen deposition.

Due to the enforcing of the directive, local companies changed their operation procedures (e.g. power production from just coal to a mix of systems with hard-coal and fuel-oil) and further introduced desulfurization of emissions after 2008 (APA, 2017b). This resulted in large reductions of S emissions (−79%), which were also observed in the concentrations of S measured in the nearby background air monitoring station (−54% in the air and −63% in the precipitation). This trend was similar in the S deposition on ecosystems, which we monitored here using lichens sampled near industrial areas (>−72%), thus confirming the success of the implementation of the directive at the ecosystem

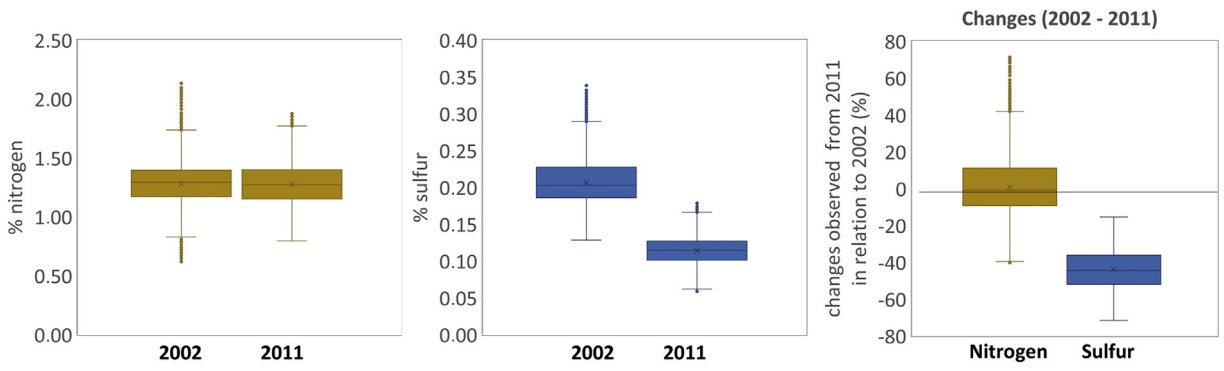

Fig. 6. Regional deposition of S and N. Box-plots for the region's S (blue) and N (yellow) measured in lichens, in 2002, 2011 and their difference (%). Mean (cross), median (line), 0.25 and 0.75 quartiles, and outliers (interquartile range ×1.5). Values obtained from interpolation maps (n = 30,679).

level. The overall reduction of S deposition on ecosystems across the study area suggests it had an overwhelming contribution of industrial S. In fact, at the national level (Fig. 1), the reduction of SO_2 emissions in the power production and industry sectors (the largest contributors) was of 99% (144 kt) and 47% (33 kt), respectively. Considering just the study region, the emissions reduction trend contributed to a ~18% reduction at the national level (Fig. 1; national totals −79% or −187 kt SO_2), which represented around less 190 M€/year in damages during the period of 2002–2011, corresponding to a 6–16 k€ per tonne of SO_2 for health and crop impacts (AEAT, 2005).

Reductions in N deposition on ecosystems of up to 40% were detected in the area near industries (Fig. 5), following a 53% decrease in NO_x emissions, mostly originating from combustion in energy and transformation industries and from manufacturing industries (this area representing 14% of the national reduction 2002–2011). Thus, the reduction of N deposition to ecosystem in areas near industries seems to match the reduction of industrial NO_x emissions. However, the overall picture of the study area is quite different, with some areas showing an increase of N deposition. This patchy pattern of changes in N concentrations suggests that multiple sources of N are contributing to N deposition. The reduction of ammonia emissions (in the order of tonnes) is much less impressive than that of NO_2 (in the order of kilotonnes). Ammonia is mostly emitted by agriculture, livestock and waste (at national level these sectors combined represent 96% of ammonia emissions; Fig. 1). In fact, it is in inland agricultural areas that we find the most striking increases in N deposition to ecosystems, as well as near a sewage treatment plant (coastal N hotspot in Fig. 5). This suggests that although the Air Quality Directive did result in a reduction of N emissions, mostly due to reductions of NOx, it had only marginal effects in the reduction of N deposition to ecosystems (measured by lichens) due to the prevalence of ammonia in the emissions. The reduction of N emissions in the years considered and in the study area generated a significant economic impact of ca. 11–31 k€/t for NH_3 and ca. 4–12 k €/t for NO_x (AEAT, 2005), amounting to less ~11 M€/year due to NH_3 damages and less ~116 M€/year due to NO_x damages. These results suggest that for N, efforts for reduction are still lower than what would be desirable for the environment and for the economy, mainly due to the lack of reduction of ammonia emissions from agriculture.

5. Conclusion

To conclude, the air quality protocols and the Directive 2001/81/EC were successful in reducing the deposition of S to ecosystems, due the reduction of SO_2 emissions from industries, its main source. For N, although a decrease of NO_2 and NH_3 were reported in emissions, this reduction was not observed at the ecosystem level, except near industrial areas. This was likely caused by the intensification of agricultural practices, which locally increased the NH_3 emissions. This reveals the challenge still posed by calculating ammonia emissions from agriculture, highlighting that further efforts must be directed beyond the industrial sectors to effectively reduce the impact of N deposition to ecosystems and on human health.

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