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FIRST FIELD/MODELLING ASSESSMENT OF THE ATMOSPHERIC DISTRIBUTION OF D5 IN PORTUGAL

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Introduction

The combination of field work and modelling approaches to allow a more comprehensive study of the atmospheric behaviour of emerging pollutants was used to define and validate the spatial and temporal patterns of the siloxanes D5 in Portugal. An integrated system of third-generation models that represent the current state of knowledge in air quality modelling, and yields simulations of high spatial and temporal resolution was employed. The justification for such an effort lies in the low awareness existing still today about the life cycles of emerging contaminants and even more if we consider its model validation against experimental data.

In terms of siloxanes, some studies already employed modelling strategies such as the BETR (Berkeley-Trent) model to assess their atmospheric distribution, mainly for D5^{1,2}. But these works involve regional and global domains and do not rely so much on a climatic perspective. Hence the idea to associate chemistry transport models (CTMs) with a strong climatic approach, and apply it to a local scale, as can be a domain covering Portugal and Galicia. And for this project the Weather Research and Forecast (WRF) model^{3,4} was coupled to the CTM CHIMERE⁵.

The modelling approach suffered from the scarcity of data currently available for the emissions of siloxanes into the environment and the respective emission factors⁶. For Portugal this information does not exist, but some simulations could be done adapting data from literature. Results show a seasonal pattern of the presence of D5 in Portugal, related with meteorological parameters and a general overestimation of the D5 concentrations, especially in the winter, comparing to those measured in the field with sorbent-impregnated polyurethane foam disks (SIPs) in eight sampling points. However, in the summer the modelled levels are closer to the field data, except for a remote area where the model overestimates D5. Therefore, it can be considered that this first field/modelling approach for siloxanes in Portugal is a very promising work that makes way for future related studies.

Materials and methods

Field data

Two pre-cleaned SIP disks impregnated with XAD-4 sorbent (14 cm diameter; 1.35 cm thick; surface area, 365 cm²; mass, 4.40 g; volume, 207 cm³; density, 0.0213 g cm⁻³) were placed in each site (duplicates), and another one acted as field blank at the moment of the deployment. A total of 16 samplers were successfully exposed over two periods of 3 months (one campaign in the summer and another in the winter) in 8 sites covering different land uses and urban stresses (Figure 1). Further detail on these campaigns can be found elsewhere⁷. At the end of the deployment period, the samplers were retrieved, re-sealed in their original containers, and taken to the lab in the appropriate conditions.

Figure 1. Passive air sampling sites.

Analytical methodology

SIP disks were stored at -20 °C until extraction, which was performed using 200 mL Soxhlet extractors. The SIPs, spiked with 75 ng of internal standard (M4Q), were extracted overnight with DCM/Hex 1:1. Then, the extract was passed through a glass column containing Na₂SO₄. The eluate was then reduced to approximately 1 mL by rotary evaporation, transferred to glass vials, evaporated to near-dryness by N₂ and redissolved in 150 µL of Hex. Samples were then quantified by chromatographic analysis in a Varian

4000 GC/MS system (Walnut Creek, CA, USA), with the conventional CP-1177 split/splitless injector adapted with a Merlin Microseal System and a special low-bleed Agilent DB-5 ms ultra-inert column (30 m x 0.25 mm I.D., 0.25 μm film thickness) to minimise siloxane bleeding from the instrument. With helium as the carrier gas at 1 mL min⁻¹, the GC oven temperature program was as follows: start at 35 C (hold for 5 min), then raised to 160 C at 10 C min⁻¹. The injector was at 200 C with a liner without glass wool and the injection volume was 1 μL in splitless mode. The detection of the target compounds was performed using the ion-trap mass spectrometer operating in electron ionization mode (70 eV) and time-scheduled selected ion storage (SIS) acquisition. All analytical procedures were monitored using strict QA/QC measures.

Modelling parameters

The WRF+CHIMERE modeling system, coupled to the estimated D5 emissions, was run and evaluated for the nested domain (Portugal and Galicia with a resolution of 3 km), during a simulation covering the year 2014. Figure 2 shows the main parameterisations used and the outlook of the terrain height, land use index and vegetation fraction included.

Figure 2. Main parameterisations for WRF and CHIMERE tools and values for terrain height, land use index and vegetation fraction included for the domain.

Results and discussion

The field data revealed that the concentrations of D5 varied from 0.1 mg m⁻³ in the remote area of Midões in the summer to almost 2 mg m⁻³ in the industrial area of Z. I. Mota in the summer. The ratio between the winter and the summer campaigns vary according to the site, but there is a clear predominance of D5 in the summer in the beach sites, particularly in the Praia da Luz site, where the D5 concentration ratio from summer to winter is above 4. For the modelling approach, data for D5 emissions in Portugal (a crucial input parameter for the model) was inexistent, so the option was to find emission rates available in literature, all from northern latitudes. The differences are considerable, with the lowest rate being less than half the highest one. So it was decided to use the extreme values: 135 mg capita⁻¹ d⁻¹ and 310 mg capita⁻¹ d⁻¹.

The simulations for the D5 concentrations show a predominant distribution along the more densely populated coastal areas and with a hotspot in Galicia, where levels rise over 20 ng m⁻³. Also, the more interior areas to the north of Portugal have more incidence than for the whole south. The winter concentrations are higher than in the summer for both emission factors. As mentioned previously, this last evidence is in line with the literature^{1,9,10} but it does not account for the local emission and population variations which were suggested as reasons for the higher levels found in the field measurements⁷. Still, for the southernmost coastal areas of Portugal, the simulated concentrations increase slightly. This is an indication that this modelling strategy has a solid base.

Results were validated against the field data and, for the simulations with the McLachlan et al (2010) emission factor, it can be seen that in general the model overestimates the D5 concentrations, especially in the winter, but the differences are acceptable considering the aforementioned limitations. In fact, in the summer the modelled levels are very close those of the passive samplers, except for Midões, a remote area where there is a higher overestimation of D5 by the model.

Overall, this first modelling approach for siloxanes in Portugal yielded very promising results. The main drawbacks are identified and will be object of further study in the future. These issues and the inclusion of other scenarios (not possible at this time due to the computational effort needed) are already projected for follow-up studies.

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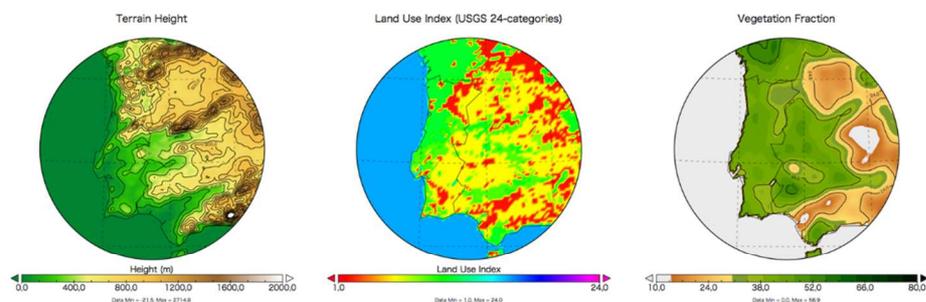
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Figure 1



Figure 2



WRF parameterisations:

Microphysics → **WSM3**
 PBL → **Yonsei University**
 Radiation → **CAM**
 Soil → **Noah LSM**
 Cumulus → **Kain-Fritsch**

CHIMERE parameterisations:

Chemical Mechanisms → **MELCHIOR2**
 Aerosol chemistry → Inorganic (thermodynamic equilibrium with **ISORROPIA**)
 and organic (**MEGAN SOA** scheme) aerosol chemistry
 Natural aerosols → **dust, re-suspension and inert sea-salt**
 Boundary Conditions → **LMDz-INCA+GOCAR**