MODELLING HEAVY METALS CONCENTRATIONS OVER ITALY: COMPARISON WITH OBSERVATIONS AND SOME SENSITIVITY TESTS

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Abstract This study shows the spatial distribution of As, Cd, Ni and Pb concentrations simulated with atmospheric modelling system of the MINNI project (AMS-MINNI). The simulations have been performed for the year 2005 with spatial resolutions of 20 km over Italy and 4 km over Northern Italy. Both anthropogenic and natural emissions have been taken into account. The simulated concentrations generally agree with available observations. The influence on heavy metal concentrations of boundary conditions, emissions from surrounding countries and horizontal resolution have been evaluated, evidencing a significant relevance of both boundary conditions and horizontal resolution.

Key words: Heavy Metals, Air Quality Modelling, Sensitivity analysis

INTRODUCTION
Some heavy metals (HMs) are toxic pollutants both for human health and environment. They are persistent and ubiquitous in the environment, as a result of both natural and anthropogenic activities. Adverse impacts on humans become evident only after several years of exposure since these pollutants are subject to bioaccumulation. European Commission has imposed air concentration target values of 6, 20 and 5 ng m\textsuperscript{-3} for arsenic (As), nickel (Ni) and cadmium (Cd), respectively, in Directive 2004/107/EC and a limit value of 500 ng m\textsuperscript{-3} for lead (Pb) in Directive 2008/50/EC.

HMs exist in atmosphere as fine particles, therefore their concentrations depend on several interactive processes such as emissions, advection/diffusion, dry and wet removal that are included in air quality models. Many studies based on experimental data have been published in literature but only few numerical modelling studies are currently available. Therefore, the knowledge of spatial and temporal distribution of these pollutants over Europe is still poor. In order to simulate the pollutants considered by the above Directives, the air quality model FARM (Silibello et al., 2008), part of AMS-MINNI, has been upgraded to take into account HMs, mercury and polycyclic aromatic hydrocarbons (PAHs) (Silibello et al., 2012). Several simulations have been carried out for the year 2005 over Italy with the upgraded version of FARM. This work shows annual mean concentrations simulated for As, Cd, Ni, Pb and their sensitivity to changes in horizontal spatial resolution and to the presence of boundary conditions and of emissions from surrounding countries.

Model description and simulation setup
The AMS-MINNI (Mircea et al., 2014) includes components such as the meteorological model RAMS (Regional Atmospheric Modelling System, Version 6.0, Cotton et al., 2003), SURFpro (SURFace-atmosphere interface PROCessor, ARIA/ARIANET, 2011) and the emission processor EMMA (EMission MANager, ARIA/ARIANET, 2006).

FARM accounts for pollutant transformations by considering gas-phase chemistry (SAPRC99, Carter, 2000), aerosol dynamics (AERO3, Binkowsky, 1999) and chemistry (ISORROPIA, Nenes et al., 1998 and SORGAM, Shell et al. 2001), as well as wet and dry deposition of gases and aerosol. The AERO3
module has been upgraded as described in Silibello et al. (2012) in order to take into account polycyclic aromatic hydrocarbons and heavy metals regulated by the EU legislation. Meteorological fields have been computed with RAMS model over Italy at 20 km resolution using initial and boundary conditions from ECMWF analysis. These fields have been downscaled over Northern Italy at 4 km resolution using LAPS (Local Analysis and Prediction System, http://laps.noaa.gov/)

The National Emissions Inventory has provided the anthropogenic emissions over the national territory. For the foreign countries included in the domain of simulations, the emissions have been based on official data received from the EMEP Centre on Emission Inventories and Projections (CEIP) [http://www.ceip.at]. Natural HMs emissions associated to soil dust and sea-salt aerosols have been computed following Travnikov and Ilyin (2007) approach. Wind re-suspension of particles from land and sea has been estimated using the approach of Vautard et al. (2005) and Zhang et al. (2005). Initial and boundary conditions have been provided by EMEP/MSC-E model output for HMs and from EMEP/MSC-W model output for the other pollutants.

Four simulations, summarized in Table 1, have been carried out with the above-mentioned setup. IT0, IT1 and IT2 experiments cover the Italian domain at 20 km horizontal spatial resolution. The first takes into account boundary conditions, national and emissions from surrounding countries, the second excludes the boundary condition and the latter does not take into account emissions from surrounding countries. NI simulation covers the Northern part of Italy and uses the IT0 boundary conditions and emissions for 4 km spatial resolution.

<table>
<thead>
<tr>
<th>NAME</th>
<th>Boundary Condition</th>
<th>Emissions</th>
<th>Model domain/Resolution</th>
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</thead>
<tbody>
<tr>
<td>IT0</td>
<td>EMEP MSC-W (other pollutants)</td>
<td>Inside Italy (National Inventory)</td>
<td>Italy 20x20 km²</td>
</tr>
<tr>
<td></td>
<td>EMEP MSC-E (HMs)</td>
<td>Outside Italy (EMEP MSC-W,E)</td>
<td></td>
</tr>
<tr>
<td>IT1</td>
<td>EMEP MSC-W (other pollutants)</td>
<td>Inside Italy (National Inventory)</td>
<td>Italy 20x20 km²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outside Italy (EMEP MSC-W,E)</td>
<td></td>
</tr>
<tr>
<td>IT2</td>
<td>EMEP MSC-W (other pollutants)</td>
<td>Inside Italy (National Inventory)</td>
<td>Italy 20x20 km²</td>
</tr>
<tr>
<td></td>
<td>EMEP MSC-E (HMs)</td>
<td>Outside Italy (EMEP MSC-W,E)</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>From IT0 simulation</td>
<td>Inside Italy (National Inventory)</td>
<td>Northern Italy 4x4 km²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outside Italy (EMEP MSC-W,E)</td>
<td>(EMEP)</td>
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**Results**

Figure 1 shows the annual mean concentration for arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb) obtained in experiment IT0. Simulated concentrations are comparable with Gonzalez et al. (2012) results, who carried out a simulation for 2008 with CHIMERE model at 0.2° spatial resolution over Europe, and they are in quite good agreement with observations (dots). Highest concentrations are found in Po Valley and in major Italian cities. However, it can be observed that the concentrations are below the limit and target values expressed in EC directives for the simulation with 20 km spatial resolution.
Figure 1. Annual mean concentration (ng m$^{-3}$) for arsenic (c$_{As}$), cadmium (c$_{Cd}$), nickel (c$_{Ni}$), lead (c$_{Pb}$) estimated from IT0 experiment. Dots are annual mean concentration from observations.

Percentage differences between IT1 and IT2 with respect to IT0 are shown in Figure 2. For all pollutants, it can be noted that the influence of boundary conditions is higher than the influence of emissions from surrounding countries over the Italian territory. Major islands (Sardinia and Sicily) experience the highest influence since they are closer to the boundaries. Northern Italy is less influenced by long-range transport and more by the high local emissions (see Figure 1).
Comparing the results of IT0 (20 km) (Figure 1) with the experiment NI (4 km) (Figure 3), it can be noted that the increase of the spatial resolution of simulation leads to a decrease of the areas with high concentrations and to an increase of the maximum concentration in the domain. The comparison between NI and IT0 experiments (Figure 3) also indicates that the spatial distributions of concentrations and emissions are correlated: maximum emission and concentration differences are located in the same areas. This is probably due to several concomitant factors such as low dispersive conditions (low winds), long atmospheric persistence of fine aerosol particles containing heavy metals and lack of chemical transformation. NI experiment shows better agreement with observations (not shown) since it estimates higher concentration with respect to IT0, which exhibits usually a negative bias with respect to measurements.

Conclusions
This numerical modelling study presents the distribution of heavy metal (As, Cd, Ni, Pb) concentrations for the year 2005 over Italy. It explores the impact of horizontal spatial resolution, of boundary conditions and of emissions from surrounding countries on annual concentration values. Results are consistent with previous modelling works and show quite good agreement with observations. The increase of concentrations in high-resolution experiment improves the agreement with observations; a higher horizontal spatial resolution would be necessary to adequately simulate heavy metal concentrations. The close relation between heavy metal concentrations and local emissions suggest that an important part of the uncertainties is related to the emission inventories. This study also shows the importance of boundary conditions in areas with low emissions.

REFERENCES


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