16th International Conference on
Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes
8-11 September 2014, Varna, Bulgaria

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

Mario Adani[1], Mihaela Mircea[1], Camillo Silibello[2] Massimo D'Isidoro[1], Luisella Ciancarella[1], Lina Vitali[1], Antonio Piersanti[1], Gino Briganti[1], Andrea Capelletti[1],Gaia Righini[1], Giuseppe Cremona[1], Gabriele Zanini[1]

[1]ENEA, National Agency for New Technologies, Energy and Sustainable Economic Development, via Martiri di Monte Sole 4, 40129, Bologna, Italy
[2]ARIANET Srl, Via Gilino, 9, 20128, Milan, Italy

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^{-3} for arsenic (As), nickel (Ni) and cadmium (Cd), respectively, in Directive 2004/107/EC and a limit value of 500 ng m^{-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, Binkownsky, 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 1. List of the experiments

NAME	**Boundary Condition**	**Emissions**	**Model domain/ Resolution**
IT0	EMEP MSC-W (other pollutans) EMEP MSC-E (HMs)	Inside Italy (National Inventory) Outside Italy (EMEP MSC-W,E)	Italy 20x20 km^2
IT1	EMEP MSC-W (other pollutans)	Inside Italy (National Inventory) Outside Italy (EMEP MSC-W,E)	Italy 20x20 km^2
IT2	EMEP MSC-W (other pollutans) EMEP MSC-E (HMs)	Inside Italy (National Inventory)	Italy 20x20 km^2
NI	From IT0 simulation	Inside Italy (National Inventory) Outside Italy (EMEP MSC-W,E) (EMEP)	Northern Italy 4x4 km^2

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.

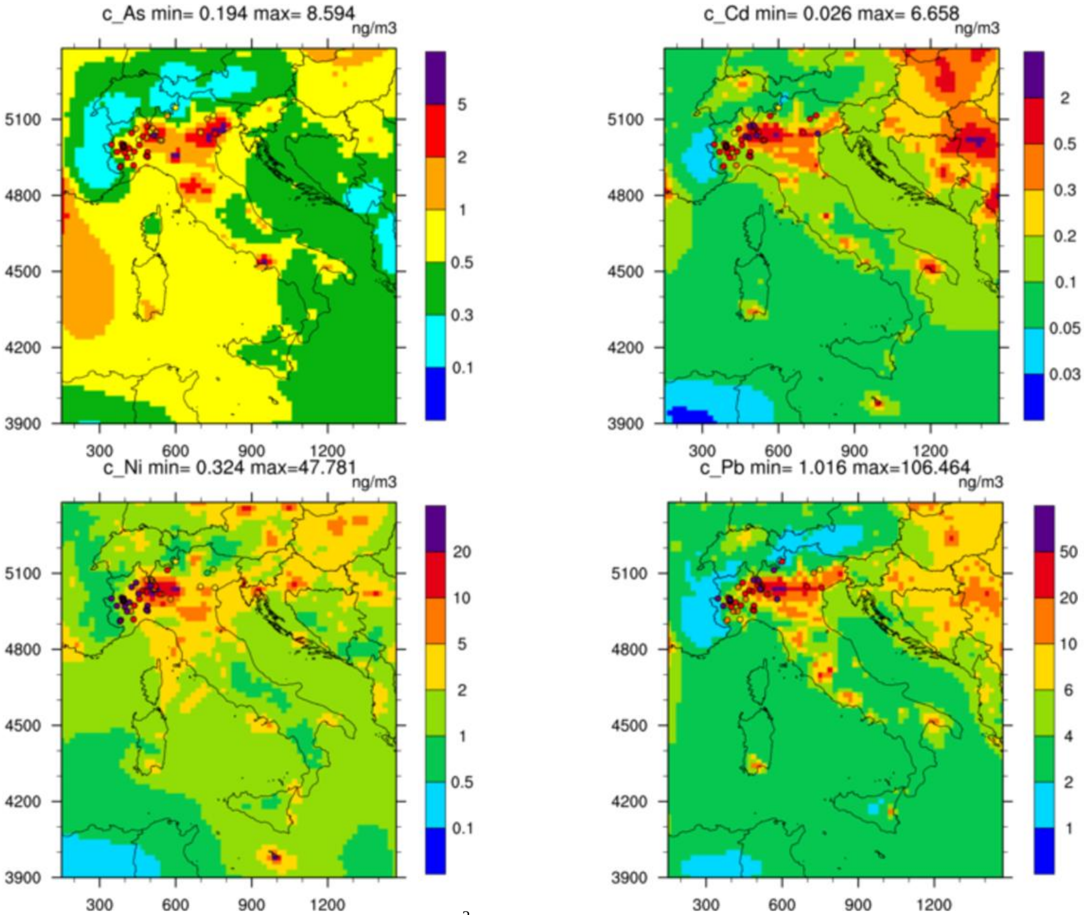

Figure 1. Annual mean concentration (ng m^{-3}) for arsenic (c_As), cadmium (c_Cd), nickel (c_Ni), lead (c_Pb) estimated from IT0 experiment. Dots are annual mean concentration from observations.

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**).

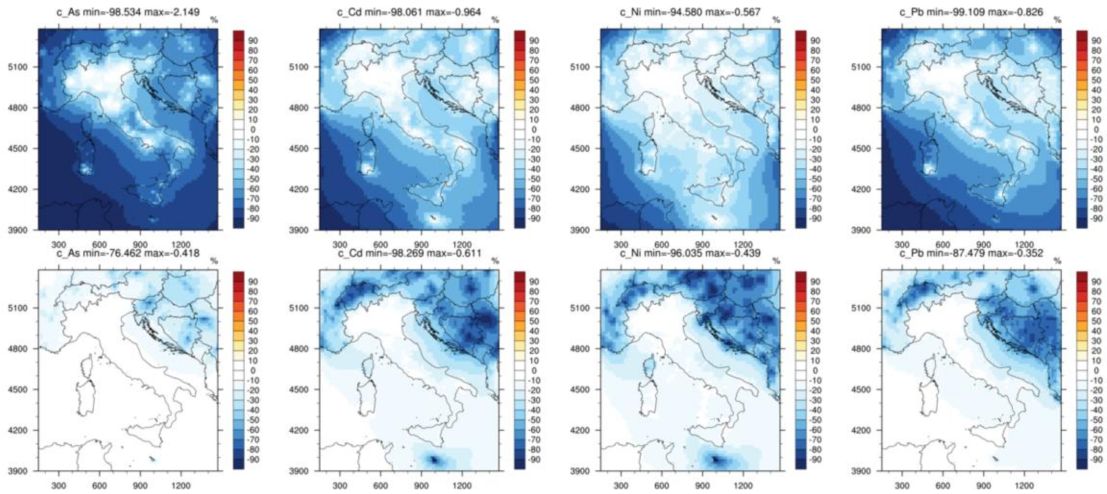

Figure 2. Annual mean percentage difference: top panels (IT1 - IT0)/IT0 and bottom panels (IT2 - IT0)/IT0. From left to right the pollutants are arsenic, cadmium, nickel and lead.

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.

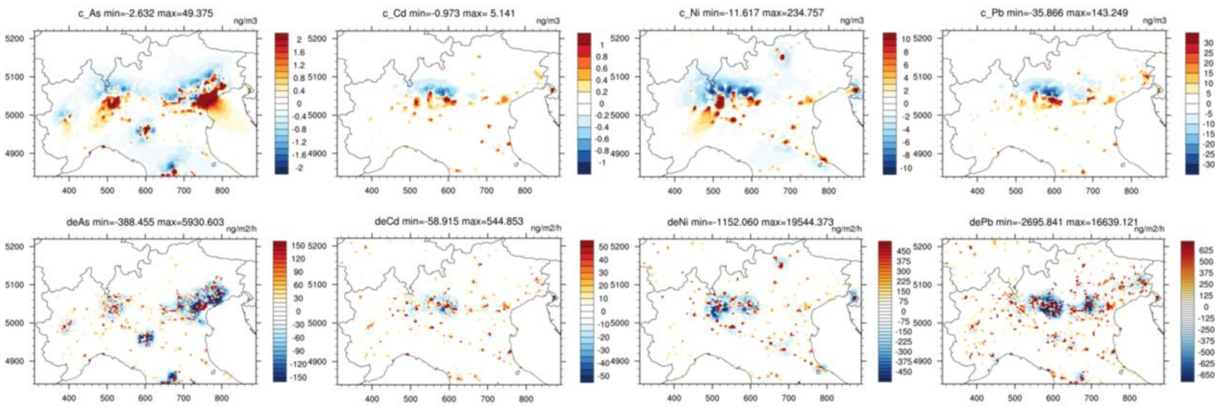

Figure 3. Annual mean differences between NI and IT0 experiments: concentrations (ng m^{-3}) and emissions (ng m^{-2} h^{-1}) are shown in the top and bottom panels, respectively. From left to right the pollutants are arsenic, cadmium, nickel and lead.

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 suggests 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

ARIANET, 2011: SURFPRO3 User's guide (SURFace-atmosphere interface PROcessor, Version 3)-Release 2.2.0. Arianet report R2011.31.

ARIANET, 2006: EMMA (EMGR/make) - User's guide - Version 4.0. Arianet report R2006.38..

Binkowski F. S., 1999: The aerosol portion of Models-3 CMAQ. In Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. Part II: Chapters 9-18. D.W. Byun, and J.K.S. Ching (Eds.). EPA-600/R-99/030, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, 10-1-10-16.

Carter, W.P.L., 2000. Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment. Final Report to California Air Resources Board, Contract 92-329 and 95-308, SAPRC, University of California, Riverside, CA.

Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008: On ambient air quality and cleaner air for Europe (The Framework Directive). From the Official Journal of the European Communities, 11.06.2008, En. Series, L152/51.

Council Directive 2004/107/EC of the European Parliament and of the Council of 15 Dicember 2004: Relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air (Fourth Daughter Directive). From the Official Journal of the European Communities, 26.1.2005, En. Series, L 23/3.

Cotton, WR, Pielke, RA, Walko, RL, Liston, GE, Tremback, CJ, Jiang, H, McAnelly, RL, Harrington, JY, Nicholls, ME, Carrio, GG, McFadden, JP. RAMS 2003: Current status and future directions. *Meteorology and Atmospheric Physics* 2003; 82: 5-29.

Gonzalez M. A., Vivanco M. G., Palomino I., Garrido J. L., Santiago M., Bessagnet B., 2012: Modelling Some Heavy Metals Air Concentration in Europe. *Water Air Soil Pollut.*, 223, 5227-5242.

Mircea, M., Ciancarella, L., Briganti, G, Calori, G, Cappelletti,G., Cionni, I., Costa, M., Cremona, G., D'Isidoro, M., Finardi, S., Pace, G., Piersanti, A., Righini, G., Silibello, C., Vitali, L., Zanini, G., 2014: Assessment of the AMS-MINNI system capabilities to simulate air quality over Italy for the calendar year 2005. *Atmospheric Environment, 84, 178-188*.

Nenes A., Pandis S.N., Pilinis C., 1998: ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. *Aquat. Geoch.*, 4, 123-152.

Schell B., Ackermann I. J., Hass H., Binkowski F. S., Abel A., 2001: Modeling the formation of secondary organic aerosol within a comprehensive air quality modeling system. *J. Geophys. Res.*, 106, D22, 28275-28293.

Silibello, C, Calori, G, Brusasca, G, Giudici, A, Angelino, E, Fossati, G, Peroni, E, Buganza, E.,2008: Modelling of PM10 concentrations over milano urban area using two aerosol modules. *Environmental Modelling and Software*, **23**, 333-343.

Silibello C., Calori G., Costa M.P., Dirodi M.G., Mircea M., Radice P., Vitali L., Zanini G., 2012: Benzo[a]pyrene modelling over Italy: comparison with experimental data and source apportionment. *Atmospheric Pollution Research*, 3, 4, 399-407.

Travnikov O. Ilyin I., 2007: Modelling of heavy metals atmospheric dispersion in Europe. Meteorological Synthesizing Centre East of EMEP.

Vautard R., Bessagnet B., Chin M., Menut L., 2005: On the contribution of natural Aeolian sources to particulate matter concentrations in Europe: Testing hypotheses with a modeling approach. *Atmospheric Environment*, 39, 3291-3303.

Zhang KM., Knipping EM., Wexler AS., Bhave PV., Tonnesen GS., 2005: Size distribution of sea-salt emissions as a function of relative humidity. *Atmospheric Environment*, 39, 3373-3379.