Modelling the fine and coarse fraction of Pb, Cd, As and Ni air concentration in Spain

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Abstract
Lead, cadmium, arsenic and nickel are present in the air due to natural and anthropogenic emissions, normally joined to particles. Human health and ecosystems can be damaged by high atmospheric levels of these metals, since they can be introduced in organisms via inhalation or ingestion. Small particles are inhaled and embebed in lungs and alveolus more easily than coarse particles. The CHIMERE model is a eulerian air quality model extensively used in air quality modelling. Metals have been recently included in this model in a special version developed in the CIEMAT modelling group (Madrid, Spain). Vivanco et al. (2011) and González et al. (2012) showed an evaluation of the model performance for some metals in Spain and Europe. In these studies, metals were considered as fine particles. Nevertheless there is some observational evidence of the presence of some metals also in the coarse fraction. For this reason, a new attempt of modelling metals considering a fine (<2.5 μm) and coarse (2.5-10 μm) fraction has been done. Measurements of metal concentration in PM10, PM2.5 and PM1 recorded in Spain were used to obtain the new metal particle distribution size. On the other hand, natural emissions, not considered in the above mentioned studies, were implemented in the model, by considering metal emissions associated to dust resuspensiont. An evaluation of the new version is presented and discussed for two domains in Spain, centered on Barcelona and Huelva respectively.
Key words: Heavy Metals, Air Quality Modelling, Particulate Matter, Pb, Cd, As, Ni.

Modelización de las fracciones gruesa y fina de Pb, Cd, As y Ni en el aire en España

Resumen
Metales como el plomo, cadmio, arsénico y niquel son emitidos a la atmósfera por diversas fuentes naturales y antropogénicas, normalmente como componente de la fracción partículada. La incorporación de partículas vía inhalación o ingestión a los organismos vivos puede provocar graves problemas de salud y daños a ecosistemas, especialmente cuando se trata de las partículas más finas, ya que penetran con mayor facilidad en los pulmones y alvéolos. CHIMERE es un modelo euleriano de calidad del aire empleado por numerosos grupos de modelización, especialmente en Europa. Algunos metales pesados fueron incluidos como partículas finas no reactivas en una versión especial del modelo desarrollada por el Grupo de Modelización de la Contaminación Atmosférica de CIEMAT (Vivanco et al., 2011; González et al., 2012). Sin embargo, estudios sobre medidas de metales en aire indican que algunos metales pueden también formar parte de partículas más gruesas. Por ello, se ha incorporado en la versión v2013 de CHIMERE la posibilidad de diferenciar entre la fracción fina (<2.5 μm) y gruesa (2.5-10 μm) de cada metal, basándose en medidas de estos metales en PM10, PM2.5 y PM1. Por otro lado, se han incorporado al modelo las emisiones de metales de tipo natural, en concreto las producidas por la resuspensión de polvo. En esta publicación se incluye una evaluación del modelo para dos dominios en España en los que se dispone de medidas

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de metales en PM10 y PM25, uno de ellos localizado en Cataluña y el otro centrado en Huelva. Se presentan los principales resultados y conclusiones.
Palabras clave: Metales Pesados, Modelización de la Calidad del Aire, Material Particulado, Pb, Cd, As, Ni.

Contents: 1. Introduction. 2. The CHIMERE model. 3. Model setup. 4. Model performance evaluation methodology. 5. Results. 6. Conclusions. Acknowledgment. References.

Normalized reference
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1. Introduction

Metals in the atmosphere are present in very low concentrations. According to WHO (2006) more than 2 million premature deaths each year can be attributed to the effects of urban outdoor and indoor air pollution (WHO, 2006). Diseases, such as cancer, neurotoxicity or cardiotoxicity, can be potentially linked to high levels of metal particles in the atmosphere (HEI 1998; US EPA 1999). Organisms can assimilate particles via inhalation, since they settle into the bronchial regions of the lungs; the risk of inhalation of these metals increase for smaller particle diameters. Also atmospheric deposition of these metals constitutes a potential risk, since metals can accumulate in soils or water and move to the organisms by ingestion. To protect human health and ecosystems air quality standards for ambient air levels of a number of metals are considered in European Directives since 1999. Directive 1999/30/CE, more recently updated by Directive 2008/50/CE, sets an annual limit value of 500 ng/m^3 for Pb. Annual target levels for As (6 ng/m^3), Cd (5 ng/m^3) and Ni (20 ng/m^3) are regulated by the Directive 2004/107/CE. Simulations including these pollutants in regional models are not very common; for some of these metals, there is not an updated emission inventory in Europe. EMEP (European Monitoring and Evaluation Programme, http://www.emep.int/) emission database includes Pb and Cd (besides Hg), but not As or Ni (or other non reactive metals). TNO has also developed an emission inventory for Pb and Ni, but for As, Ni and other heavy metals TNO inventory dates from 2000 (Dutch Organisation for Applied Scientific Research, Van der Gon et al., 2005). These limitations in the emission information add a large uncertainty to model exercises and avoid a correct evaluation of model results. In Spain, the Ministry of Agriculture, Food and Environment has prepared an emission inventory at the EMEP grid (that means, with a horizontal resolution of 50x50 km^2) for Pb, Cd, As and Ni, as well as for other metals and pollutants. The spatial resolution of this database limits the evaluation of model performance, forcing the use of measurements at background sites. On the other hand the emissions inventories normally provide annual totals, being necessary an estimation of the temporal disaggregation. This is generally done by applying some temporal profiles, becoming consequently difficult to correctly represent specific real situations.

Traditionally, models have implemented metals as fine particles (Bartnicki and Olendrzynski, 1996; Ilyin et al., 2010, 2011; Gusev et al., 2008, 2009; Travnikov and Ilyin, 2005; Hutzel and Luecken, 2008; Mircea et al., 2013). Monitoring sites have started to measure metals in PM10, PM2.5 and PM1. Some studies, such as Allen et al. (2001), Kuloglu and Tuncel (2005) and Witt et al. (2010) show that metals can be also present in the coarse fraction of particles. In this work we have included a coarse and a fine component of metals in the CHIMERE model; for this purpose we have estimated a contribution of the coarse fraction in the anthropogenic emissions based on the coarse/fine ratio found in observed concentration values, assuming that observed concentration values can provide an idea of emissions for days with a low natural contribution. Besides he have assigned a size profile to the fine and coarse components for each metal, taking into account studies such as Allen et al. (2001), Kuloglu and Tuncel (2005) and Witt et al. (2010).

On the other hand, natural emission contribution can be as large as the anthropogenic one (Nriagu, 1989; Richardson et al., 2001; Pacyna and Pacyna, 2001). For this reason, metal resuspension, the main source of natural emissions, was also included in the model. The dust resuspension parametrization included in CHIMERE was used to calculate metal resuspension, taking into account the metal-content in soils (Richardson et al., 2001; Navas and Machín, 2002).

Not many eulerian air quality models include the representation of both fine and coarse fractions of metals. Table 1 shows a summary of the studies focused on heavy metals modelling. Only Chen et al. (2013) and Fallah Shorshani et al. (2014) using lagrangian models and direct measurements of metal emissions from sources have considered metal sizes for high resolution applications. Regarding natural emissions, only references based on the EMEP heavy metals model (Travnikov and Ilyin, 2005; Ilyin et al., 2010, 2011; Gusev et al., 2008, 2009; Shatalov et al., 2013) and Mircea et al. (2013) include them in their simulations.

Observations recorded at some Spanish sites were used to evaluate the CHIMERE results for the new modelling features: size metallic particle differentiation and natural resuspensión.

2. The CHIMERE model

CHIMERE is a eulerian off-line chemistry-transport model (Menut et al., 2013). External forcings (meteorological fields, emissions and boundary conditions) are required by the model, giving atmospheric concentrations of gas-phase and aerosol species. The CHIMERE model has been extensively applied in Europe over the past years (Hodzic et al. 2005; Bessagnet et al. 2004, 2005; Monteiro et al. 2005; Vivanco et al. 2008, 2009a, b). In Spain, the CHIMERE model has been applied to model gas and particle pollutants, and more recently, to model heavy metals (Vivanco et al. 2011; González et al., 2012), with an special version developed in the CIEMAT modelling group (Madrid, Spain). In that version Pb, Cd, As, Ni, Cu, Cr, Zn and Se were included as non reactive fine particles. For this paper, a new development has been implemented in the model in order to distinguish a fine and coarse fraction of metals.

Table 1. Summary of the characteristics of models that include heavy metals

References	**Model**	**Metals**	**Fine/ Coarse**	**Natural Emissions**
Bartnicki and Olendrzynski (1996)	HMET-50	As, Cd, Pb, Zn	No	No
Travnikov and Ilyin(2005) Ilyin et al. (2010,2011) Gusev et al. (2008,2009) Shatalov et al. (2013)	MSCE-HM	Pb, Cd, Hg	No	Yes
Hutzell and Luecken (2008)	CMAQ	Pb, Cd, Ni, Cr, Mn	No	No
Mircea et al. (2013)	FARM	Pb, Cd, As, Ni	No	Yes
Chen et al. (2013)	HYSPLIT	Cr, Co, Ni, La, Zn, Mo	Yes	No
Fallah Shorshani et al. (2014)	Polyphemus	Pb, Cd, Zn	Yes	No
González (2014)	CHIMERE	Pb, Cd, As, Ni, Cu, Cr, Zn, Se	Yes	Yes

CHIMERE considers a sectional aerosol module (Bessagnet et al., 2004). The aerosol density of each heavy metal was discretized in some size sections using a log-normal distribution. The mass fraction M_l in each interval depends on the mass median diameter D_g and the geometric standard deviation σ_g (Eq. 1). It is calculated by taking into account the minimum and maximum interval diameters $d_{min,l}$ and $d_{max,l}$, and using the *erf* error function (it follows a normal distribution). In this work 6 sizes or bins were used for the following diameter intervals: 0, 0.039, 0.156, 0.625, 2.5, 10 and 40 µm. For each metal, a discretized size distribution was estimated for the fine and coarse fraction, taking into account the PM10, PM2.5 and PM1 concentration measured at the Barcelona monitoring site from 2005 to 2010 (recorded by IDÆA-CSIC group), as well as some studies over Europe (Allen et al., 2001; Kuloglu & Tuncel, 2005; Witt et al., 2010). The concentration vs. size for each metal at Barcelona site is shown in Fig. 1.

$$M_l = 0.5\left|\mathrm{erf}\left(\frac{\ln\frac{d_{max,l}}{D_g}}{\sqrt{2}\ln\sigma_g}\right) - \mathrm{erf}\left(\frac{\ln\frac{d_{min,l}}{D_g}}{\sqrt{2}\ln\sigma_g}\right)\right| \qquad (1)$$

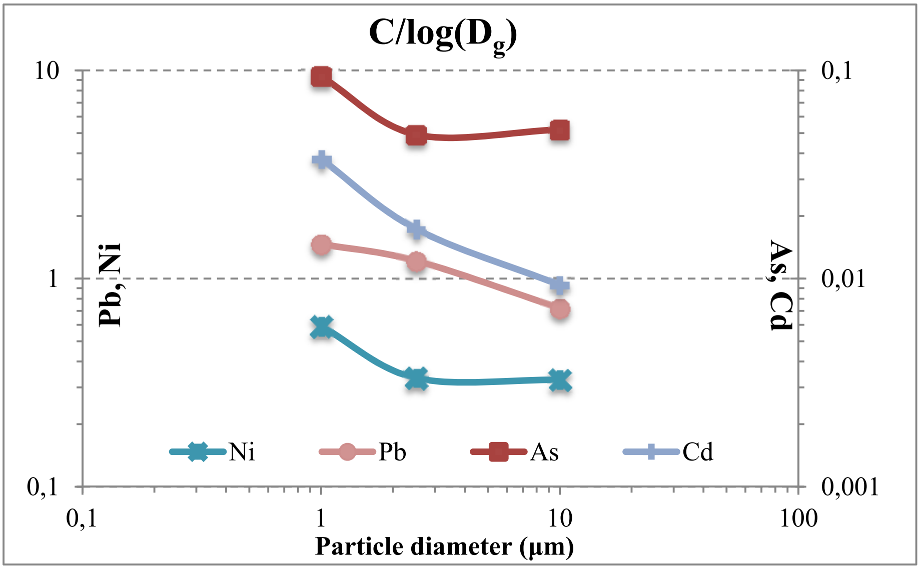

Figure 1. Size distribution for Pb, Cd, As and Ni (Barcelona), considering he concentration of each metal (C) in PM10, PM2.5 and PM1. Size distribution is plotted by considering two separate logarithmic y-axis, one for Pb and Ni and another one for As and Cd.

The new values for the diameter (D_g) and geometric standard deviation (σ_g) (Table 2) were included in the CHIMERE aerosol module; Fig. 2 shows the mass percentage in each bin for the different metal species, in consistency with these new values for D_g and σ_g. Table 3 shows the size intervals in the CHIMERE discretized distribution.

Table 2. New values for mass median diameter and geometric standard deviation.

	Metal	D_g (m)	σ_g
Coarse species	Pb_C, Cd_C, As_C, Ni_C	$4.00 \cdot 10^{-6}$	1.1
Fine species	Pb_F, Cd_F, As_F	$0.14 \cdot 10^{-6}$	2.1
	Ni_F	$0.40 \cdot 10^{-6}$	0.4

Table 3. Size intervals in 6-bins CHIMERE distribution

Bin 1	$9.8 \cdot 10^{-3}$ - $3.9 \cdot 10^{-2}$ µm
Bin 2	$3.9 \cdot 10^{-2}$ - $1.6 \cdot 10^{-1}$ µm
Bin 3	$1.6 \cdot 10^{-1}$ - $6.3 \cdot 10^{-1}$ µm
Bin 4	$6.3 \cdot 10^{-1}$ - 2.5 µm
Bin 5	2.5 - 10 µm
Bin 6	10 - 40 µm

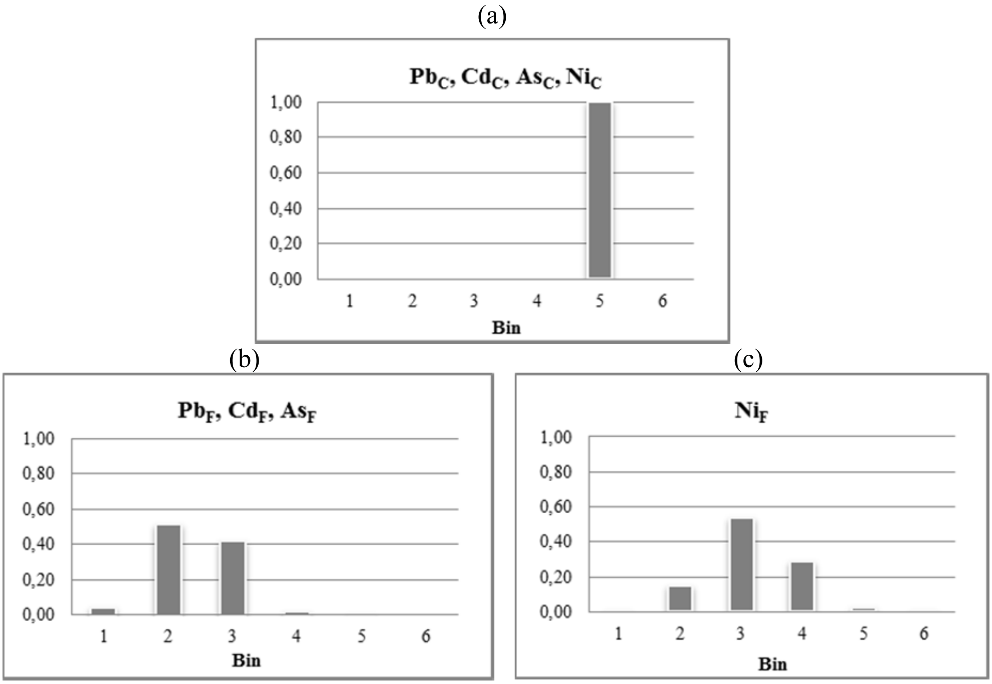

Figure 2. Mass percentage in each bin for the different metal species (coarse and fine). For the coarse species Pb_C, Cd_C, As_C, Ni_C, total mass is confined in bin 5 (2.5 - 10 µm) (a); for the fine species mass distribution is presented in (b) for Pb_F, Cd_F, As_F and in (c) for Ni_F.

To estimate the contribution of both coarse and fine fractions, a correspondence between emissions and measured concentrations was assumed when natural contribution was low. Therefore, only days with low Al_2O_3 concentration in the coarse fraction were used in order to select data with significant anthropogenic contribution (this compound has a natural origin and it mostly exists in nature in the coarse fraction, according to Kuloglu and Tuncel, 2005). 21 Spanish monitoring sites (IDÆA-CSIC and CIQSO data) were used for this purpose. The coarse/fine fraction found from observations was applied to anthropogenic emissions as a first approach. This fraction was also adjusted according to the specific conditions of SNAP activities (EMEP-CORINAIR Emission Inventory Guidebook).

Metal resuspension was the second development implemented in the CHIMERE model. Natural emissions fraction can be as large as anthropogenic one (Nriagu, 1989; Richardson et al., 2001; Pacyna and Pacyna, 2001). As a first approach, metal resuspension due to dust flow was included in the model. A parametrization suggested by Richardson et al. (2001) was implemented in CHIMERE (v2013) dust module to calculate metal resuspension, taking into account the metal content in soils. For this work, mean values for metal content measured in Europe and published by Richardson et al. (2001) were selected: 38.0 mg/kg for Pb, 0.75 mg/kg for Cd and 29.0 mg/kg for Ni; for As, we selected the value presented by Navas and Machín (2002) for Spanish soils, 11.8 mg/kg (there was no As value in Richardson et al. 2001).

3. Model setup

The CHIMERE model coupled to the WRF meteorological model in an off-line way, was applied to simulate metal concentration over the full year 2009 for 6 domains EU05, SP02, CAT075, CAT025, HU075 and HU025 (Fig. 3, Table 4). Two of them (CAT075 and CAT025) are centered on Barcelona, and two other (HU075 and HU025) on Huelva. These regions were selected due to their high pollution levels and because there are measurements of metal air concentration in PM10 and PM25 available. Three simulations were done:

1. Basic configuration, [B], with metals as a unique fine specie.
2. Fine/Coarse configuration, [F+C], with metals defined with a fine and coarse fraction.
3. Fine/Coarse configuration, [F_N+C_N], with metals defined with a fine and

coarse fraction, and considering metal resuspension as natural emissions.

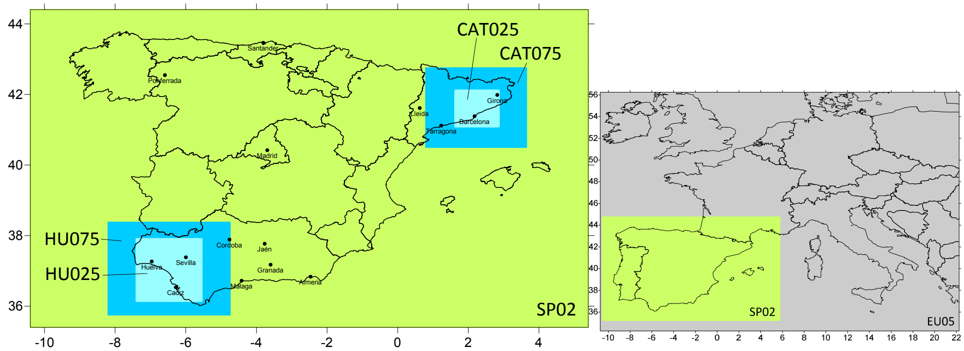

Figure 3. Location of CHIMERE domains

Anthropogenic emissions in the Spanish area were obtained from the Spanish Ministry of Agriculture, Food and Environment (MAGRAMA); for the rest of the European domain we took EMEP (for Pb and Cd) and TNO (for As and Ni) emission database. These emissions were spatially and temporally disaggregated, considering land use information and seasonal/hourly profiles. No boundary condition for metals was used for the coarsest European domain.

Table 4. Resolution of CHIMERE domains*

EU05	SP02	CAT075	CAT025	HU075	HU025
0.5º	0.2º	0.075º	0.025º	0.075º	0.025º
* *8 vertical levels up to 500 hPa was considered for all the domains*					

4. Model performance evaluation methodology

CHIMERE estimates were evaluated with metal daily concentrations measured at some Spanish monitoring sites from MAGRAMA, EMEP, IDÆA-CSIC and CIQSO networks. First, thirteen background stations (Niembro, Campisábalos, San Pablo de los Montes, Víznar, Els Torms, Mahón, Montseny, Alcalá de Guadaira, Carranque, Lepanto, Príncipes, Ronda del Valle and San Fernando) were used for a general evaluation of SP02 simulations, by using metal concentration in PM10 (Table 5).

Then, a deeper evaluation was carried out for the highest resolution domains (CAT025 and HU025), using metal concentration in PM10 and PM2.5 at background and industrial monitoring sites (Barcelona, Montseny, Alcalá de Guadaira, Príncipes, San Fernando and Campus del Carmen, Table 6); these data come from IDÆA-CSIC and CIQSO networks. Some time series and statistics values for Pb, Cd, As and Ni for the general and detailed evaluations are presented.

Table 5. Monitoring background sites used in first evaluation

SP02	LAT(º)	LON(º)	SOURCE
San Pablo de los Montes	39.548	-4.349	EMEP
Mahón	39.875	4.322	EMEP
Víznar	37.237	-3.534	EMEP
Niembro	43.439	-4.849	EMEP
Campisábalos	41.274	-3.142	EMEP
Els Torms	41.394	0.735	EMEP
Montseny	41.779	2.358	IDÆA-CSIC
Alcalá de Guadaira	37.342	-5.833	CIQSO
Carranque	36.721	-4.429	CIQSO
Lepanto	37.894	-4.768	CIQSO
Príncipes	37.377	-6.004	CIQSO
Ronda del Valle	37.784	-3.781	CIQSO
San Fernando	36.463	-6.202	CIQSO

Table 6. Monitoring sites used in second evaluation (considering fine/coa fractions) (B is for Background monitorign sites and I is for Industrial)

CAT025	LAT(º)	LON(º)	SOURCE
Barcelona (I)	41.387	2.116	IDÆA-CSIC
Montseny (B)	41.779	2.358	IDÆA-CSIC
HU025	**LAT(º)**	**LON(º)**	**SOURCE**
Alcalá de Guadaira (B)	37.342	-5.833	CIQSO
Príncipes (B)	37.377	-6.004	CIQSO
San Fernando (B)	36.463	-6.202	CIQSO
Campus del Carmen (I)	37.271	-6.924	CIQSO

A statistical analysis was done for each metal metal and for each type of simulation. As statistical parameters we considered Bias, MFB (Mean Fractionan Bias), MFE (Mean Fractional Error) and RMSE (Root Mean Squared Error) (Table 7). MFB and MFE (with ranges of values between -200% to 200% and 0 to 200%, respectively), are suggested by Boylan & Russell (2006). The authors suggest that the model performance criteria has been met when both MFB and MFE are less than or equal to approximately ±60% and 75%, respectively.

Table 7. Statistical parameters used in evaluation of the CHIMERE simulations

Bias	$Bias = \frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)$
Mean Fractional Bias	$MFB = \frac{1}{N}\sum_{i=1}^{N}\frac{M_i - O_i}{(M_i + O_i)/2}$
Mean Fractional Error	$MFE = \frac{1}{N}\sum_{i=1}^{N}\frac{\lvert M_i - O_i\rvert}{(M_i + O_i)/2}$
Root Mean Squared Error	$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)^2}$
$\bar{M} = \frac{1}{N}\sum M_i \quad \bar{O} = \frac{1}{N}\sum O_i$	M: Modelled values O: Observed values

5. Results

Fig. 4-7 show some time series for the general evaluation (metals in PM10 obtained for the SP02 domain) for all the simulations ([B] in grey, [F+C] in blue and [F_N+C_N] in pink). Although time series were prepared for all the stations included in Table 5, only Niembro and Campisábalos are shown in this paper. These are background sites, so concentrations measured at them are representative of an area large enough to be consistent with the simulation resolution. Statistics values (Tables 8-11) were calcualated by considering all the stations available (Table 5). Only basic simulation [B] and complete simulation [F_N+C_N] results are shown. Time series indicate an aceptable agreement between model and observations, although there are some discrepancies.

For Pb (Fig. 4) at Niembro, a quite good correspondence between model and observations can be seen for most of the year. However, some of the high values (above 10 ng/m^3) measured are not captured by the model. Not many differences exist among the three simulations, and sometimes [F+C] and [F_N+C_N] present lower values than [B]; this fact is due to the higher dry deposition rate of coarse particles in both [F+C] and [F_N+C_N] simulations, with no effect in [B] where just fine particles for metals are considered. At Campisábalos, with lower metal concentrations, Pb is well reproduced by CHIMERE, and only a few values at the end of the year are underestimated. Statistics shown in Table 8 confirm the better results for [F_N+C_N] simulation, with values for MFB and MFE of -48% and 74%, respectively, both under the model performance criteria set by Boylan and Russell (2006). However, for the basic configuration MFE is above 75%. Negative values for MFB show an underestimation by the model for both configurations.

Table 8. Statistical values for Pb simulations

SIMULATION	BIAS ($ng \cdot m^{-3}$)	MFB (%)	MFE (%)	RMSE ($ng \cdot m^{-3}$)
SP02 [B]	-4.019	-59	85	8.7
SP02 [F_N+C_N]	-4.211	-48	74	8.6
CAT025 [B]	-2.970	-35	63	6.2
CAT025 [F_N+C_N]	-2.638	-24	58	6.0
CAT025 [F_N]	-2.352	-30	57	4.9
CAT025 [C_N]	-0.770	-16	69	2.3
HU025 [B]	11.900	29	96	27.0
HU025 [F_N+C_N]	13.676	38	89	28.5
HU025 [F_N]	11.616	29	86	20.4
HU025 [C_N]	-1.238	24	102	13.8

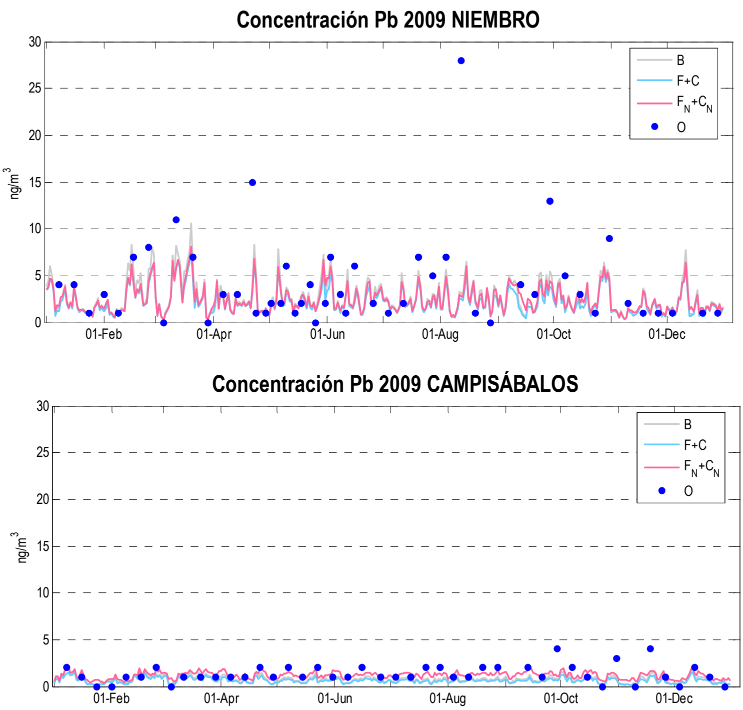

Figure 4. Time series showing modelled (lines) and observed daily values (dots) of Pb at Niembro (upper graphic) and Campisábalos (bottom graphic) monitoring sites.

For Cd (Fig. 5), the model is overestimating concentrations during the most part of the year at Niembro. While model results exceed 0.1 ng/m^3 in most of the cases measured values are almost always below 0.1 ng/m^3. Measurements taken at Niembro confirm the presence of some high Cd daily values above 0.15 ng/m^3, but not as often as the model suggests. In this station, the highest velocity of coarse particles dry deposition rate drives to higher values in [B] than in the fine/coarse model configurations for the major part of the year. On the other hand, air concentrations at Campisábalos are well reproduced by CHIMERE model, regarding both temporal variability and concentration values. Table 9 showing statistics results indicates that both MFB and MFE are under the target model performance criteria, with better results in [F_N+C_N] (-32% for MFB and 70% for MFE).

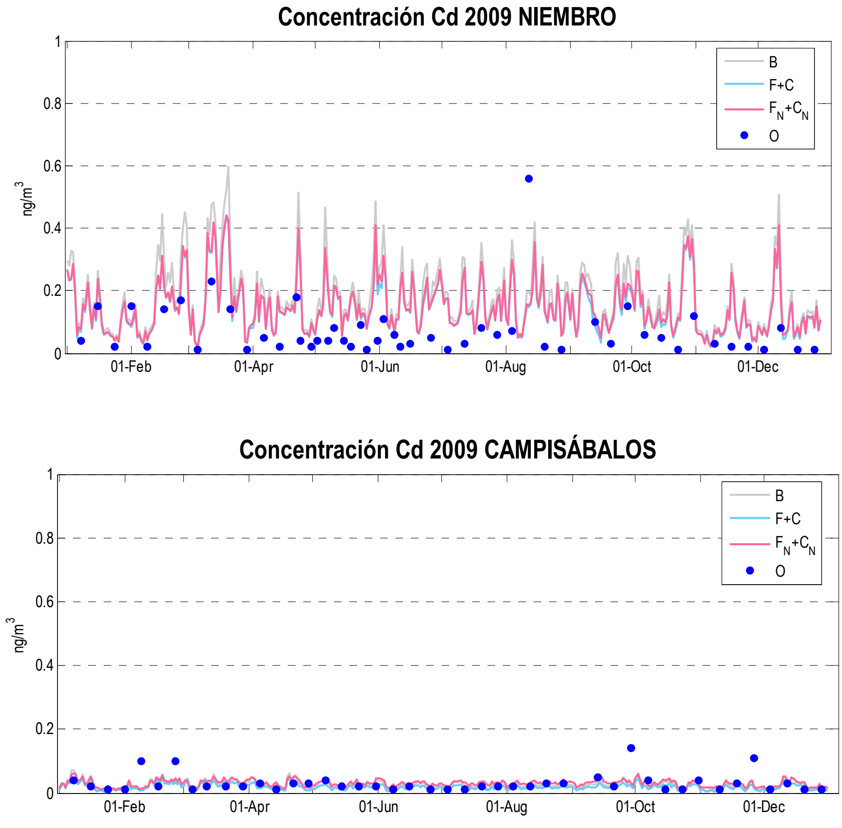

Figure 5. Time series showing modelled (lines) and observed daily values (dots) of Cd at Niembro (upper graphic) and Campisábalos (bottom graphic) monitoring sites

Table 9. Statistical values for Cd simulations.

SIMULATION	BIAS ($ng \cdot m^{-3}$)	MFB (%)	MFE (%)	RMSE ($ng \cdot m^{-3}$)
SP02 [B]	-0.054	-38	73	0.2
SP02 [F_N+C_N]	-0.069	-32	70	0.2
CAT025 [B]	0.038	23	54	0.2
CAT025 [F_N+C_N]	0.032	22	52	0.2
CAT025 [F_N]	-0.018	-36	52	0.1
CAT025 [C_N]	0.034	62	86	0.1
HU025 [B]	0.601	35	89	1.0
HU025 [F_N+C_N]	0.667	37	88	1.1
HU025 [F_N]	0.485	15	88	0.8
HU025 [C_N]	0.067	3	97	0.3

Natural contribution of the complete simulation [F_N+C_N] provides a great improvement for As (Fig. 6). The basic model configuration underestimated As concentration values at Niembro and Campisábalos (specially in the second one); after including natural emissions in [F_N+C_N], most of the high observed values that were not well reproduced before, are now better captured. Nevertheless, CHIMERE results are closer to observations in [B] and [F+C] at the beginning of the year at Campisabalos, where [F_N+C_N] overestimates observations. The general improvement of [F_N+C_N] for As is also found when analyzing the statistics results. Table 10 shows a large difference between the basic and complete model configurations. MFB and MFE in [B] are -120% and 136%, respectively, indicating a high underestimation. For [F_N+C_N] including size and natural emissions these metrics have changed to -38% and 75%, significantly correcting the underestimation.

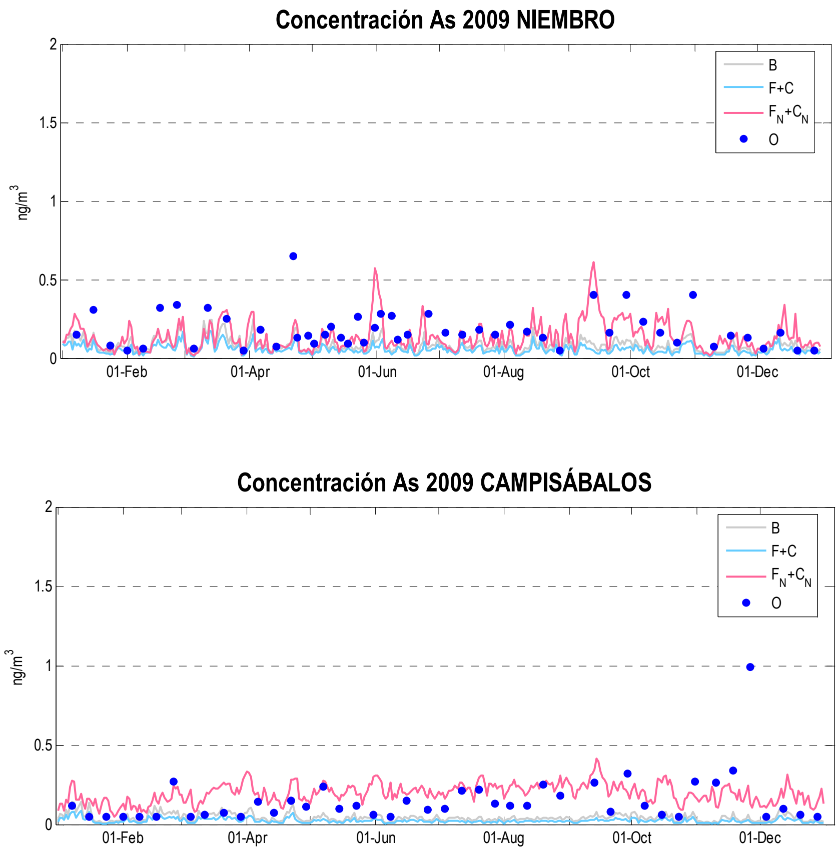

Figure 6. Time series showing modelled (lines) and observed daily values (dots) of As at Niembro (upper graphic) and Campisábalos (bottom graphic) monitoring sites.

Table 10. Statistical values for As simulations

SIMULATION	BIAS ($ng \cdot m^{-3}$)	MFB (%)	MFE (%)	RMSE ($ng \cdot m^{-3}$)
SP02 [B]	-0.403	-120	136	0.6
SP02 [F_N+C_N]	-0.265	-38	75	0.5
CAT025 [B]	-0.368	-121	123	0.4
CAT025 [F_N+C_N]	-0.194	-32	60	0.3
CAT025 [F_N]	-0.125	-26	59	0.2
CAT025 [C_N]	-0.099	-58	78	0.2
HU025 [B]	2.266	-44	128	5.0
HU025 [F_N+C_N]	1.238	-1	91	3.8
HU025 [F_N]	-0.659	1	88	3.0
HU025 [C_N]	0.942	-29	123	2.4

For Ni (Fig. 7), the temporal behavior is quite well reproduced by all the model configurations, specially at Campisábalos monitoring site, where natural emissions in [F_N+C_N] have driven to a better model performance and only few observations in November are above model estimates. At Niembro, in spite of a quite good agreement for a large part of the year, data above 3 ng/m^3 are not captured by the model. Statistical results in SP02 domain (Table 11) show an underestimation for both simulations, although better scores in [F_N+C_N]; MFB and MFE are -21% and 66% respectively, both under the model performance criteria set by Boylan and Russell (2006).

Table 11. Statistical values for Ni simulations

SIMULATION	BIAS ($ng \cdot m^{-3}$)	MFB (%)	MFE (%)	RMSE ($ng \cdot m^{-3}$)
SP02 [B]	-0.580	-40	77	2.5
SP02 [F_N+C_N]	-0.554	-21	66	2.4
CAT025 [B]	-1.111	-24	52	2.4
CAT025 [F_N+C_N]	-0.957	-12	52	2.4
CAT025 [F_N]	-0.903	-13	61	2.0
CAT025 [C_N]	-0.256	-2	68	0.9
HU025 [B]	6.432	13	108	11.6
HU025 [F_N+C_N]	7.556	27	98	12.6
HU025 [F_N]	5.028	19	94	8.8
HU025 [C_N]	1.360	-4	114	5.1

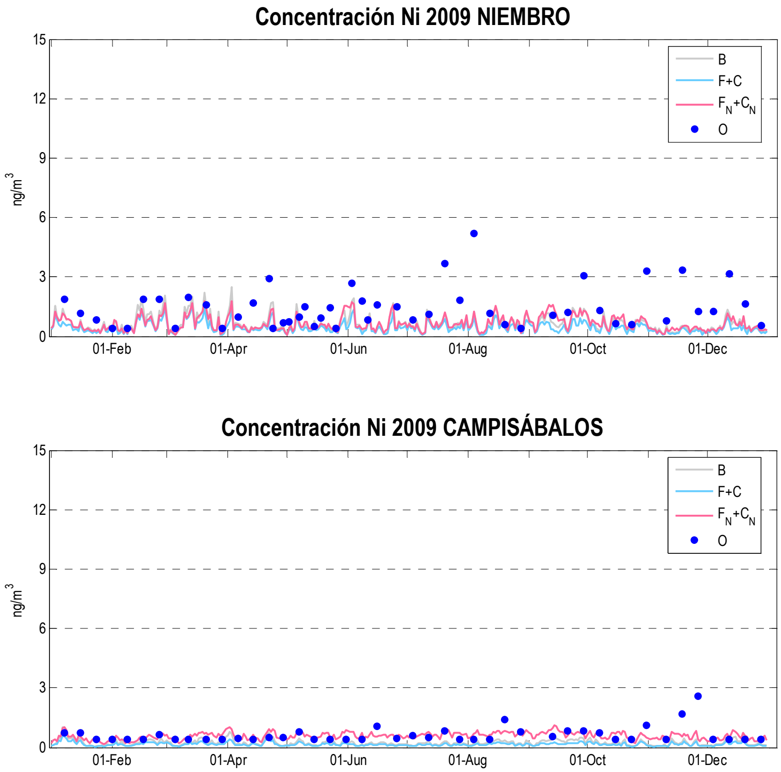

Figure 7. Time series showing modelled (lines) and observed daily values (dots) of Ni at Niembro (upper graphic) and Campisábalos (bottom graphic) monitoring sites.

As we have mentioned, we perfomed a second evaluation, by analyzing the simulations at the highest resolution domains, CAT025 and HU025. Total levels of each metal (figures 8-11) were analysed for the basic ([B] in grey) and most complete simulation ([F_N+C_N], in pink); also fine (F_N, in purple) and coarse (C_N, in orange) fractions were separately analysed. Six monitoring sites (Table 6) were used for this evaluation, although only Montseny (for the CAT025 domain) and Príncipes (HU025) are illustrated in figures 8-11. However, statistical evaluation includes all the rural and industrial sites. Observations at Príncipes are higher than at Montseny, and the model reproduces quite reasonably this variation of concentration values for Pb, Cd, As and Ni. Also, the fine and coarse fractions are well reproduced: levels calculated by CHIMERE of coarse particles are lower than fine levels, consistently with measures. For Pb (Fig. 8), observed and modelled temporal behaviour are in a good concordance, except for some days in April in the case of Príncipes, where the coarse fraction is highly underestimated.

Something similar happens to Cd (Fig. 9), with low concentration values at Montseny and higher values at Príncipes. Modelled time series at both monitoring sites are in a quite good agreement with air concentration levels, in spite of a slight underestimation of the fine fraction at Príncipes at the beginning of the year. For As (Fig. 10), observations are better reproduced at Montseny, while at Príncipes both coarse and fine fractions are underestimated. However, temporal variability at the end of the year is in a good concordance. Fig. 11 shows a good agreement between observations and model results for Ni at Montseny, while at Príncipes some underestimation is found during the first half of the year, especially for the coarse fraction.

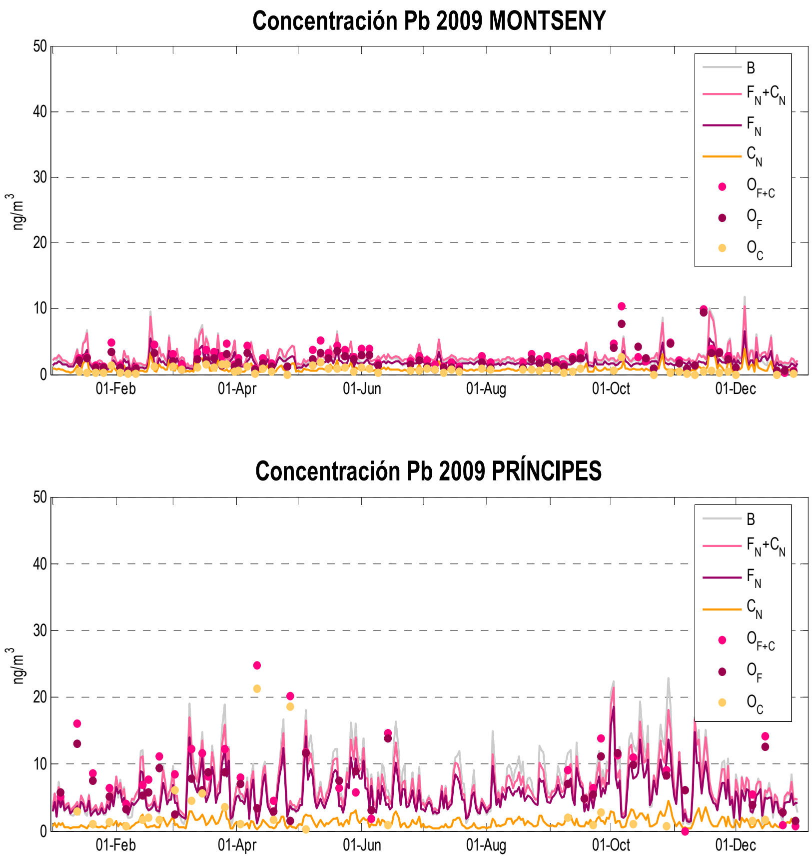

Figure 8. Time series showing modelled (lines) and observed daily values (dots) of Pb at Montseny (upper graphic) and Príncipes (bottom graphic) monitoring sites.

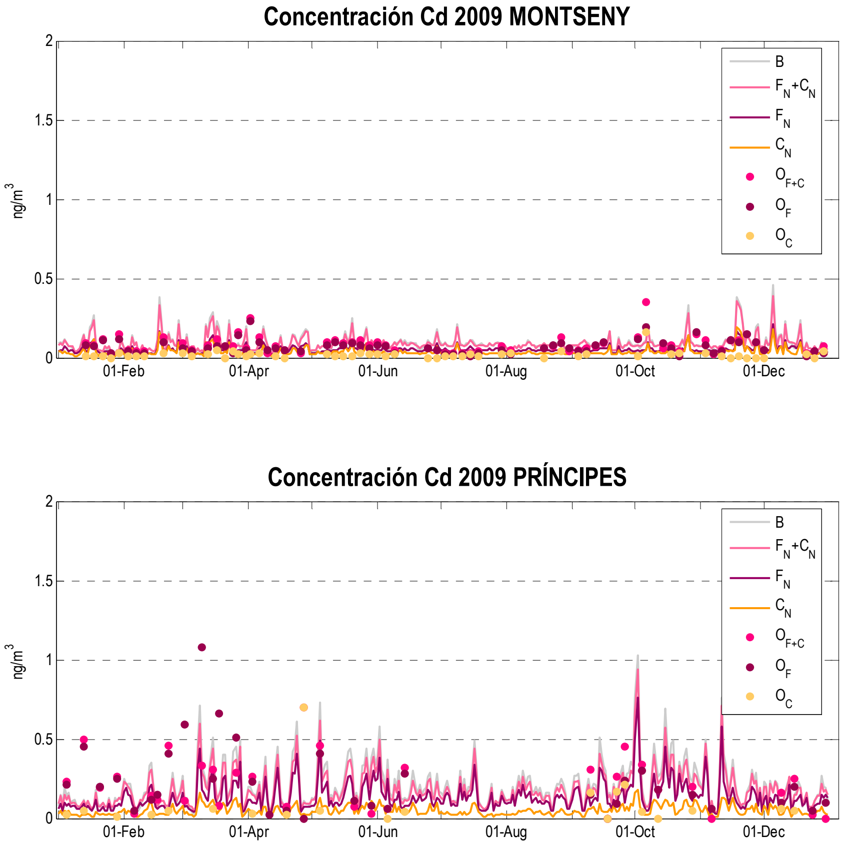

Figure 9. Time series showing modelled (lines) and observed daily values (dots) of Cd at Montseny (upper graphic) and Príncipes (bottom graphic) monitoring sites.

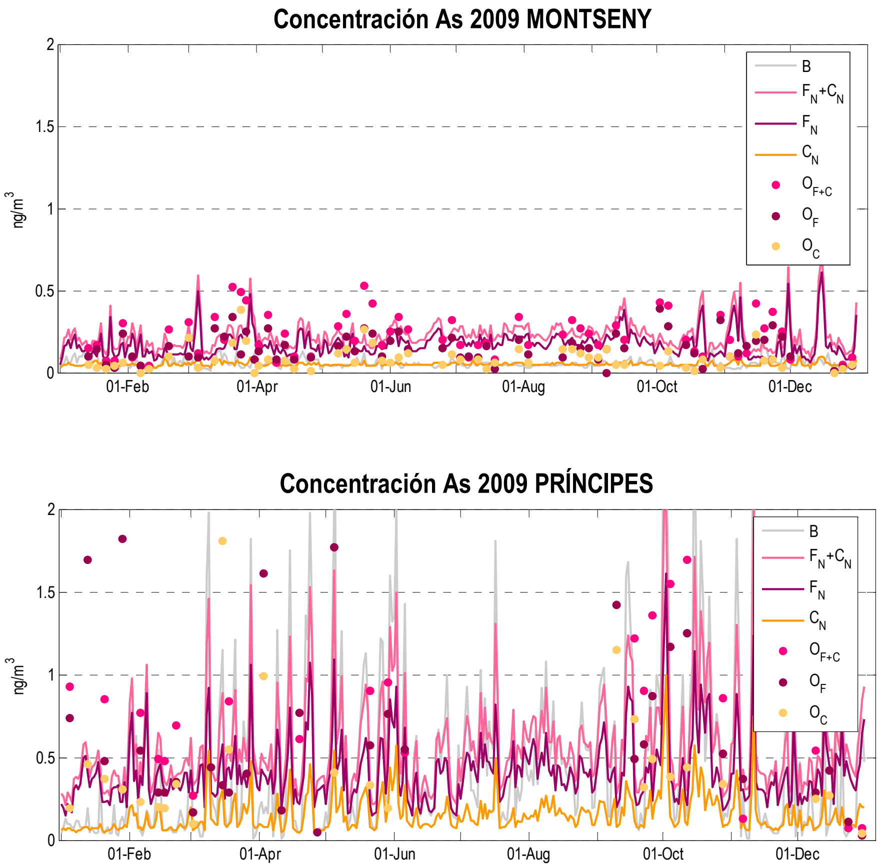

Figure 10. Time series showing modelled (lines) and observed daily values (dots) of As at Montseny (upper graphic) and Príncipes (bottom graphic) monitoring sites

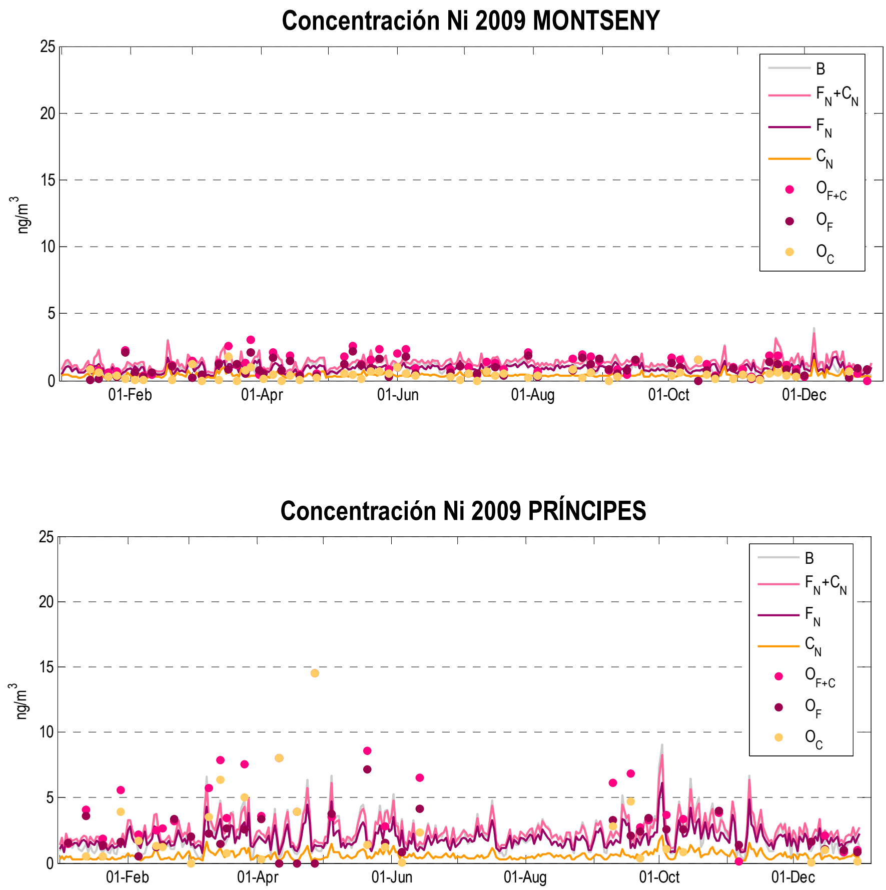

Figure 11. Time series showing modelled (lines) and observed daily values (dots) of Ni at Montseny (upper graphic) and Príncipes (bottom graphic) monitoring sites.

Statistical values in Tables 8-11 also include the evaluation of the CAT025 and HU025 domains. For Pb (Table 8), good values for MFB (below −35%) and for MFE (below 70%) are found for CAT025; nevertheless, for HU025 MFE values are above 75% for all the simulations. Some underestimation is present for CAT025 and overestimation for HU025, with positive MFB values. CHIMERE has the best behavior in CAT025 for the most complete simulation [F_N+C_N]. In the case of Cd (Table 9), there is some overestimation for CAT025 and HU025, (not for SP02, as explained before), and an underestimation of the fine fraction in CAT025 (MFB, -36%). MFE values exceed the 75% critical limit in most of the cases, except for F_N in CAT025, where MFE is equal to 52%. For As (Table 10), the improvement of [F_N+C_N] found for SP02 is also observed for the two highest resolution domains, with better results for CAT025 and worse for HU025, especially for the coarse fraction (MFE above 100%). Table 11 shows the results for Ni; an underestimation for CAT025 and an overestimation for HU025 can be observed, except for the coarse fraction. However, MFE values are very high in HU025 (next 100%), with a worse behavior of the coarse fraction. In CAT025, both [B] and [F_N+C_N] have statistical values below Boylan and Russell (2006) model performance criteria.

6. Conclusions

In this study we have implemented in the CHIMERE model the possibility of distinguishing between the coarse and fine fraction of metal concentration in atmospheric particles. Also we have improved the heavy metal version of the model by including metal resuspension. In an overall evaluation of the model performance, metal concentration obtained for a domain covering the Iberian Peninsula (SP02) at a 0.2º of horizontal resolution were compared to measurements at background monitoring sites (metal in PM10). CHIMERE showed the best behaviour for the most complete version of the model [F_N+C_N]. A second evaluation of the fine and coarse fractions was done for two domains at a higher resolution, by comparing model results to measurements of metal concentration in PM10 and PM25. Metal resuspension due to dust flux included in [F_N+C_N] configuration improved the model estimates and corrected some underestimation, especially for As. The treatment of heavy metals as fine and coarse particles (not only fines) has improved model results, with a good agreement between model and observations for the fine fraction. The fact that fine particles are more dangerous for human health becomes interesting this modeling development, as this fraction can now be estimated.

Taking into account the statistical values obtained for these domains, CHIMERE results were found to be better for CAT025 than for HU025. Metal size distribution was set in CHIMERE by considering their concentration in PM10, PM2.5 and PM1 measured at one monitoring site located in CAT025 (Barcelona) and thus this could have some positive effect over this area. On the other hand, statistic results showed in this paper for HU025 are negatively affected by one industrial site, Campus del Carmen, where the model presented an important overestimation.

One of the factors driving to discrepances between model and observations is related to the emission uncertainties. Besides the limitations associated to the estimation methodology itself, spatial resolution for emissions was 50x50 km^2 on an annual basis, being necessary to apply different approaches to convert this original information to model requirements. On the other hand, the contribution of the fine and coarse fraction in the anthropogenic emissions for each metal was calculated with PM10 and PM2.5 concentrations in some Spanish stations, using only days with significant anthropogenic contribution. Al_2O_3 indicator was used for this purpose, and thus some overestimation of the coarse fraction could occur. Also some uncertainty can be linked to the fact that we have assumed a similar coarse/fine contribution in measurements and emissions. A better resolution in emissions inventories and better knowledge of the coarse and fine fractions for each metal would reduce the input errors and improve heavy metal modelling.

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References

1999/30/CE, Directiva del Consejo Europeo relativa a los valores límite de dióxido de azufre, dióxido de nitrógeno y óxidos de nitrógeno, partículas y plomo en el aire ambiente. 22 abril 1999. L 163, p. 41-60.

2004/107/CE, Directiva del Parlamento Europeo y del Consejo relativa al arsénico, el cadmio, el mercurio, el níquel y los hidrocarburos aromáticos policíclicos en el aire ambiente. 15 diciembre 2004. L 23, p. 3-16.

2008/50/CE, Directiva del Parlamento Europeo y del Consejo relativa a la calidad del aire ambiente y a una atmósfera más limpia en Europa. 21 mayo 2008. L 152, p. 1-44.

ALLEN, A.G., E. NEMITZ, J.P. SHI, R.M. HARRISON AND J.C. GREENWOOD (2001). Size distribution of trace metals in atmospheric aerosols in the United Kingdom. *Atmos. Environ., 35,* 4581-4591.

BARTNICKI, J. AND K. OLENDRZYNSKI (1996). Modeling Atmospheric Transport of Heavy Metals Over Europe in the 50 km Grid System (IIASA Working Paper WP-96-141).

BESSAGNET, B., A. HODZIC, R. VAUTARD, M. BEEKMANN, L. ROUIL, R. ROSSET (2004): Aerosol modelling with CHIMERE – preliminary evaluation at the continental scale. *Atmos. Environ., 38,* 2803-2817.

BESSAGNET B., A. HODZIC, O. BLANCHARD, M. LATTUATI, O. LE BIHAN, H. MARFAING AND L. ROUIL (2005). Origin of particulate matter pollution episodes in wintertime over the Paris Basin. *Atmos. Environ., 39,* 6159-6174.

BOYLAN, JW. AND AG. RUSSELL (2006). PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models. *Atmospheric Environment, 40,* 4946-4959.

CHEN B, AF. STEIN, PG. GUERRERO MALDONADO, AM. SANCHEZ DE LA CAMPA, Y. GONZALEZ---CASTANEDO, N. CASTELL AND JD. DE LA

ROSA (2013). Size distribution and concentrations of feavy metals in atmospheric aerosols originating from industrial emissions as predicted by the HYSPLIT model. *Atmos. Environ., 71*, 234–244.
FALLAH SHORSHANI, M., C. BONHOMME, G. PETRUCCI, M. ANDRÉ AND C. SEIGNEUR (2014). Road traffic impact on urban water quality: a step towards integrated traffic, air and stormwater modelling. *Environ. Sci. Pollut. Res., 21,* 5297–5310.
GONZÁLEZ, MA (2014). Mejora de la modelización de metales pesados en la atmósfera. Aplicación a la Península Ibérica. Thesis. Universidad Complutense de Madrid.
GONZÁLEZ, MA., MG. VIVANCO, I. PALOMINO, JL. GARRIDO, M. SANTIAGO AND B. BESSAGNET (2012). Modelling some heavy metals air concentration in Europe. *Water, Air, Soil Pollut., 223,* 5227-5242.
GUSEV A., I. ILYIN, V. SHATALOV AND V. SOKOVYCH (2008). Modelling of transboundary atmospheric pollution by heavy metals and POPs in Europe and Central Asia (EMEP/MSC-E Report #1/2008).
GUSEV A., I. ILIYN, O. ROZOVSKAYA, V. SHATALOV, V. SOKOVYCH AND O. TRAVNIKOV (2009). Modelling of heavy metals and persistent organic pollutants: New developments (EMEP/MSC-E Report #1/2009).
HEI. (1998). Health Effects Institute. Attachment A: Summary of a Workshop on Metal-Based Fuel Additives and New Engine Technologies.
HODZIC, A., R. VAUTARD, B. BESSAGNET, M. LATTUATI AND F. MORETO (2005). On the quality of long-term urban particulate matter simulation with the CHIMERE model. *Atmos. Environ., 39,* 5851-5864.
HUTZELL, WT. AND DJ. LUECKEN (2008). Fate and transport of emissions for several trace metals over the United States. Sci. Tot. Environ., 396, 164-179.
ILYIN, I., O. ROZOVSKAYA, V. SOKOVYH, O. TRAVNIKOV, M. VARYGINA, W. AAS AND H.T. UGGERUD (2010). Heavy Metals: Transboundary Pollution of the Environment (EMEP/CCC Report #2/2010).
ILYIN, I., O. ROZOVSKAYA, O. TRAVNIKOV M. VARYGINA, W. AAS AND H.T. UGGERUD, (2011). Heavy Metals: Transboundary Pollution of the Environment (EMEP/CCC Report #2/2011).
KULOGLU, E. AND G. TUNCEL (2005). Size distribution of trace elements and major ions in the eastern Mediterranean atmosphere. *Water, Air, Soil Pollut., 167,* 221-241.
MENUT, L., B. BESSAGNET, D. KHVOROSTYANOV, M. BEEKMANN ET AL (2013). CHIMERE 2013: a model for regional atmospheric composition modelling. *Geosci. Model Dev., 6,* 981-1028.
MIRCEA, M., C. SILIBELLO, G. CALORI ET AL (2013). A Study of Heavy Metals Pollution in Italy with the Atmospheric Modelling System of the MINNI project. E3S Web of Conferences 1, 03003.
MONTEIRO, A., R. VAUTARD, C. BORREGO AND A. I. MIRANDA (2005). Long-term simulations of photo oxidant pollution over Portugal using the CHIMERE model. *Atmos. Environ., 39,* 3089–3101.

NAVAS, A AND J. MACHÍN (2002). Spatial distribution of heavy metals and arsenic in soils of Aragón (northeast Spain): controlling factors and environmental implications. *Applied Geochem., 17*, 961-973.

NRIAGU, JO. (1989). A global assessmet of natural sources of atmospheric trace metals. *Nature 338:* 47-49.

PACYNA, JM., AND E.G. PACYNA (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev., 9*, 269–298.

RICHARDSON, GM., R. GARRETT, I. MITCHELL, M. MAH-PAULSON AND T. HACKBARTH (2001). Critical review on natural global and regional emissions of six trace metals to the atmosphere. *Risklogic Scientific Services*.

SHATALOV V., I. ILYIN, A. GUSEV, O. ROZOVSKAYA, V. SOKOVYKH AND O. TRAVNIKOV (2013). Heavy Metals and Persistent Organic Pollutants: Model Assessment of Pollution and Research Activities (EMEP/MSC---E Report #2/2013).

TRAVNIKOV, O. AND I. ILYIN (2005). Modelling of heavy metal airborne pollution in Europe: evaluation of the model performance (EMEP/MSC-E Report #8/2005).

US EPA (1999). National Air Toxics Program: The Integrated Urban Strategy (1999). U.S Environmental Protection Agency, Washington, DC.

VAN DER GRON, H.A.C., VAN HET BOLSCHER, M., VISSCHEDIJK, A.J.H., ZANDVELD, P.Y.J. (2005).Study to the effectiveness of the UNECE Heavy Metals Protocol and costs of possible additional measures. Phase I: Estimation of emission reduction resulting from the implementation of the HM. Protocol. TNO-Report B&O-A, R 2005/193.

VIVANCO, MG., M. CORREA, O. AZULA, I. PALOMINO, F. MARTÍN (2008). Influence of model resolution on ozone predictions over Madrid area (Spain). ICCSA 2008.

VIVANCO, MG., I. PALOMINO, R. VAUTARD, B. BESSAGNET, F. MARTIN, L. MENUT AND S. JIMENEZ (2009a). Multi-year assessment of photochemical air quality simulation over Spain. *Environ. Model. & Soft*., *24,* 63–73.

VIVANCO, MG., I. PALOMINO, F. MARTÍN, M. PALACIOS, O. JORBA, P. JIMÉNEZ, JM. BALDASANO, AND O. AZULA (2009b). An Evaluation of the Performance of the CHIMERE Model over Spain Using Meteorology from MM5 and WRF Models. ICCSA 2009.

VIVANCO, MG., MA. GONZÁLEZ, I. PALOMINO, J.L. GARRIDO, X. QUEROL, B. BESSAGNET, J. DE LA ROSA AND A. SÁNCHEZ DE LA CAMPA (2011). Modelling arsenic, lead, cadmium and nickel ambient air concentrations in Spain. ICCSA 2011.

WHO (2006). Air quality guidelines: Global update 2005, Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. World Health Organization Regional Office for Europe. WHO regional publications.

WITT, MLI., N. MEHERAN, TA. MATHER, JCM. DE HOOG AND DM. PYLE (2010). Aerosol trace metals, particle morphology and total gaseous mercury in the atmosphere of Oxford, UK. *Atmos. Environ., 44*, 1524–1538.