Primary aerosols and secondary inorganic aerosols budget over the Mediterranean basin during 2012 and 2013

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Abstract. In the frame of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx), we analyse the budget of primary aerosols and secondary inorganic aerosols over the Mediterranean basin during the years 2012 and 2013. To do this, we use a two-years long numerical simulation with the Chemistry-Transport Model MOCAGE validated against satellite and ground based measurements. The budget is presented on an annual and a monthly basis on a domain covering $29°$ North to $47°$ North latitude and $10°$ West to $38°$ East longitude.

The years 2012 and 2013 show similar seasonal variations. The desert dust is the main contributor to the annual burden in the Mediterranean region with a peak in spring. The secondary inorganic aerosols, taken as a whole, also contribute significantly as well as sea salts. Sulphate aerosols have a maximum in summer and sea salts in winter, while nitrate and ammonium aerosols do not exhibit large seasonal changes. The results show that all the considered types of aerosols, except for sea salt aerosols, have a net import/export term that is negative, meaning that aerosols emitted and chemically produced within the domain are transported out, with high values for some of them. For example, around 40% of the emitted black carbon are exported. The main sources of changes between 2012 and 2013 are wind variations acting on the desert dust emissions and the import of aerosols from North American fires.

In order to assess the importance of the emissions of the marine and the coastal areas, we made a sensitivity test simulation. This simulation is similar to the first one but with the removal of the anthropogenic emissions over the sea and over a 50km wide band inland along the coast. It shows that about a third of the aerosols emitted and chemically produced and about a half of the exported part in the Mediterranean basin originate from the marine and coastal area, meaning that anthropogenic air pollution from primary aerosols and secondary inorganic aerosols in this region mainly comes from local emissions.

1 Introduction

Atmospheric pollution is an environmental problem our modern societies have to face with. It has impacts on human health (WHO, 2013), agriculture (Agrawal et al., 2003), ecosystems (Bytnerowicz et al., 2007) and even on buildings (Grossi and Brimblecombe, 2002). It also has an impact on meteorology and climate (Stocker et al., 2013).

The Mediterranean basin region is a sensitive region to atmospheric pollution, especially for air quality issues (Rodríguez et al., 2006) because of the high population density on the Mediterranean coast. The emission sources are various with most of the anthropogenic and biogenic sources in the northern part of the basin and large mineral dust emissions in the south. The

Mediterranean basin is also subject to biomass burning related emissions. The geography of this area with an abrupt topography associated with the synoptic scale flows also favours the accumulation of pollutants. Moreover, this region is especially sensitive to global climate change. Climate simulations predict dryer and warmer conditions, especially during the summer (Giorgi and Lionello, 2008).

5   In this context, the ChArMEx project aims at acquiring knowledge about the present and the future air chemical composition of the Mediterranean area and its various impacts (Dulac, 2014). In the framework of ChArMEx, three intensive observation periods took place in summer between 2012 and 2013. In 2012, the TRAQA campaign (transport and air quality above the Mediterranean basin) aimed at characterising the dynamical processes exporting polluted air mass from sources region of the Mediterranean basin. During the TRAQA campaign, 20 June – 13 July 2012, meteorological conditions were mainly favouring

10 continental outflow from different source regions of the basin (Di Biagio et al., 2015). Two intensive campaigns, ADRIMED and SAFMED, were conducted in 2013. The first one, ADRIMED (Aerosol Direct Radiative impact on the regional climate in the MEDiterranean region) took place between the 11 June and the 5 July 2013 (Mallet et al., 2016). The first part of this campaign is characterized by the displacement with time of synoptic elements such as lows and ridges leading to changes in the synoptic flux: easterly (16 June), southerly (19 June), north-westerly (29 June) for example. The SAFMED campaign

15 (Secondary Aerosol Formation in the MEDiterranean) took place between 24 July and 1 August (Di Biagio et al., 2015). The meteorological conditions during this campaign can be divided into two periods. The first period corresponds to a stable anticyclone located on the western part of the basin until the 26 July possibly privileging an accumulation of pollutants in the area. Then, the basin was affected by a cyclonic system on 28-29 July leading to very clean conditions.

    The data collected during these campaigns, together with model simulations, have been used to analyse the aerosols in the

20 Mediterranean basin during summer. The aerosol contributions during summer 2012 were analysed by Rea et al. (2015) using the Chemistry-Transport Model (CTM) CHIMERE (Menut et al., 2013). They show that the Euro-Mediterranean region was largely influenced by mineral dust. Indeed, surface PM_{10} were composed at 62% of mineral dust while anthropogenic aerosols being the second contributor (19%). For $PM_{2.5}$, the anthropogenic emissions were the major part with 52% of the surface $PM_{2.5}$ composition. The mineral dust were the second contributor with 17%. Biogenic sources played also a significant role

25 in $PM_{2.5}$. As for the Aerosol Optical Depth (AOD), being an indicator of the total column of aerosols, anthropogenic sources accounted for 34% of the total AOD, while mineral dust 23% and biogenic sources 14%. Menut et al. (2015) analysed the ozone and aerosol variability between the 1 June and the 15 July 2013. They show this period was not very polluted, mainly due to several precipitation events. Aerosols in the boundary layer, were predominated by sea salt, sulphate and mineral dust. The column of aerosols was mainly composed of mineral dust.

30   These past studies focused on the particular season that is summer. Here we go a step further by analysing the aerosol budget based on a two-years long simulation (2012 and 2013) in order to characterize the seasonal variability of the primary aerosols and the secondary inorganic aerosols over these two years. We choose these two years because they correspond to an intensive period of measurements during the ChArMEx campaign and therefore are well documented. This study is based on the chemistry-transport model MOCAGE (Josse et al., 2004; Sič et al., 2015; Guth et al., 2016) and the use of a wide range of

35 observations.

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The paper is organised as follows. Section 2 presents the MOCAGE model and the simulation set up. The simulation is then evaluated in section 3. In Section 4, we analyse the budget and the variability of the aerosols over the Mediterranean basin. This analysis is done over a smaller domain that is presented by the red squares in the figures of this paper and especially in Fig. 1. Section 5 presents the results of a sensitivity test aiming at quantifying the impact of the anthropogenic emissions from

5 the Mediterranean sea and its coast. Finally, section 6 concludes this article.

2 Configuration of the MOCAGE simulation

This section presents the MOCAGE model used in this study and the set up of the simulation discussed in sections 3 and 4.

2.1 The MOCAGE model

MOCAGE (Modele de Chimie Atmospherique à Grande Echelle) is an off-line global chemistry transport model with grid-
10 nesting capability used for research at Météo-France in a wide range of scientific studies on tropospheric and stratospheric chemistry, at various spatial and temporal scales. MOCAGE has been used for example for studying the impact of climate on air composition (Teyssèdre et al., 2007; Lacressonnière et al., 2012; Lamarque et al., 2013) or tropospheric-stratospheric exchanges using data assimilation (Barré et al., 2014). MOCAGE is also used for daily operational air quality forecasts in the framework of the French platform Prev'Air (Rouil et al., 2009, http://www2.prevair.org/) and in the European CAMS project
15 (Copernicus Atmospheric Monitoring Service). In CAMS, the MOCAGE model is one of the seven models contributing to the regional ensemble forecasting system over Europe (Marécal et al., 2015, http://macc-raq-op.meteo.fr/index.php).

The version of MOCAGE used in this study is fully detailed in Sič et al. (2015) and Guth et al. (2016). Two chemical schemes are implemented in order to represent both the tropospheric and the stratospheric air composition into MOCAGE. The Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997) is used in the troposphere. For the stratosphere, it is the
20 REPROBUS scheme (REactive Processes Ruling the Ozone BUdget in the Stratosphere) which is implemented (Lefèvre et al., 1994). Regarding aerosols, the version of the model used in the present study includes desert dust, sea salt, primary organic aerosols, black carbon and Secondary Inorganic Aerosols (SIA) managed through the ISORROPIA module (Fountoukis and Nenes, 2007).

The version of MOCAGE model used in this study does not include Secondary Organic Aerosols (SOA). SOA are currently
25 in development in MOCAGE and are not yet validated. In winter, carbonaceous aerosols are mainly composed of primary aerosols from biomass burning and fossil fuel combustion (Gelencsér et al., 2007). Menut et al. (2013) showed by a regional model simulation that in summer, PM_{10} aerosols are dominated by dust and secondary inorganic aerosols over the Mediterranean basin. The fraction of SOA varies between 3 and 16% of the total PM_{10} mass. Yet, SOA can be a significant contributor to aerosols. However, organic aerosol made up about a half of the measured PM_1 fine aerosol at Cape Corsica Michoud et al.
30 (2017) during the SOP2 field experiment in summer 2013. Nevertheless, our study analyses the mass budget of aerosol of all sizes in which the fine mode aerosol contribution is low. From all these studies we can expect that SOA contribution to the mass of total aerosol is small but non negligible and could lead to negative biases compared to observations.

2.2 Set up of the simulation

For this study, the model is run using a global domain at $2° \times 2°$ resolution and a nested domain over the Mediterranean basin at $0.2° \times 0.2°$ resolution. This second domain extends from $16°$ North to $52°$ North and from $20°$ West to $40°$ East. The domain simulated is larger than the zone of interest and in order to focus on the basin, we use a sub-domain centred on the Mediterranean basin represented in the Fig. 1 by the red square. This domain covers the $29°$ North to $47°$ North latitude and $10°$ West to $38°$ East longitude region and will be called "budget domain".

The MOCAGE model uses 47 vertical levels, in σ-pressure coordinates, from the surface up to $5\,\text{hPa}$. Simulations are run with a spin-up period of 3 months and are driven by the meteorological fields from ARPEGE operational analyses (Courtier et al., 1991).

2.3 Emissions

At the global scale, anthropogenic emissions used are the MACCity emissions representative for 2013 given at a $0.5° \times 0.5°$ resolution (van der Werf et al., 2006; Lamarque et al., 2010; Granier et al., 2011; Diehl et al., 2012). The biogenic emissions are based on Sindelarova et al. (2014) for the volatile organic compounds. They are at a $0.5° \times 0.5°$ resolution, monthly and representative for 2010 . NO_x emissions by the soil come from the GEIA dataset (Yienger and Levy, 1995) while nitrous oxides from lightning are taken into account following Price et al. (1997). GFAS emissions (Global Fire Assimilation System, Kaiser et al. 2012) giving daily biomass burning emissions based on satellite data are used here. The natural aerosols emissions are dynamically computed using Marticorena and Bergametti (1995) for mineral dust and Gong (2003) for sea salt.

The anthropogenic emissions used at the regional scale are from the MACC-III project emission inventory representative for the year 2011. It corresponds to the latest update of the MACC-II emission inventory (Kuenen et al., 2014). This emission inventory, at a $7 \times 7\text{km}$ resolution, covers the European continent and the Mediterranean sea. It is completed over the African continent by the MACCity emissions that are also used at the global scale. The other types of emissions are the same as those used at the global scale.

3 Evaluation of the simulation

Before analysing the simulation results, their evaluation has been performed against various observations sources and is presented in this section. Unfortunately, the few ChArMEx measurements over long periods of time were not available at the time of the present study for use of the model evaluation. The statistical indicators used in this section are defined and explained in the Appendix.

3.1 Comparison with MODIS aerosol optical depth

MODIS daily mean AODs were used to evaluate the model simulations. For this purpose, we select both the daily MODIS and Deep Blue data level 3 (L3, collection 6) for the year 2012 and 2013 and perform an additional quality control and screening as presented in Sič et al. (2015) and Guth et al. (2016).

AODs in MOCAGE are calculated at $550\,nm$ using Mie theory with refractive indices taken from Global Aerosol Data Set (Köpke et al., 1997) and extinction efficiencies derived with Wiscombe's Mie scattering code for homogeneous spherical particles (Wiscombe, 1980).

Figure 1 presents the maps of the annual MNMB of the AOD simulated with the MOCAGE model against the MODIS and the Deep Blue AODs for the years 2012 and 2013. The simulated AOD shows a good agreement with the MODIS AOD with a MNMB close to 0 in a large area, especially over the Mediterranean sea.

The MNMB is lower, between -0.5 and -1, over the Red sea, the north of Africa and off the African Atlantic coast, meaning a slight underestimation by the model. It is higher, between 0.5 and 1, north of the Black sea. The MNMB is slightly negative over the Mediterranean sea for the year 2013, but not for the year 2012. The negative bias over the North of Africa can be due to an underestimation of desert dust aerosols and to a lack of secondary organic aerosols, especially for the coastal regions. Indeed, organic aerosols can represent a significant part of the fine mode aerosols (Michoud et al., 2017) hence have a noteworthy contribution to AOD in the visible.

Tables 1 and 2 present the statistics for the comparison between the MODIS AOD data and the MOCAGE simulations for 2012 and 2013 over the whole simulated domain and the budget domain, respectively. They show that the model is able to simulate well the aerosol optical depth over this period and region. The statistical indicators are similar between the two domain considered here. Hence the following discussion will focus on the whole simulated domain comparison (Table 1).

There is a slightly different behaviour between the two years. MNMB and FGE are lower for the 2012 simulation, but the correlation is better for the 2013 simulation. These numbers are consistent with those of Rea et al. (2015) for the summer 2012, despite a lower correlation (0.39 for 2012 in this study versus 0.68). This could be explained by the fact that Rea et al. (2015) only simulates the three summer months while we consider the whole year 2012.

3.2 Comparison with AERONET data

AERONET (AErosol RObotics NETwork) measures ground-based AOD from automated stations with an accuracy of ±0.01 (Holben et al., 1998). The AERONET data are used here for the simulation evaluation as in Sič et al. (2015). In this comparison, we used 33 AERONET stations for 2012 et 40 for 2013.

Figure 2 presents the comparison between the annual aerosol optical depth simulated by MOCAGE and the annual aerosol optical depth measured by the aeronet stations for the years 2012 and 2013. It shows a good agreement. This figure exhibits generally similar patterns on the mean AODs simulated by the model in 2012 and 2013. AODs are highest in 2012 over North Africa and are higher in 2013 than in 2012 over the north-east of the domain, especially over Romania and Ukraine.

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Table 3 presents the statistics of the comparison between the MOCAGE simulated AODs and the AERONET observed AODs. The model compares very well to this observation sets, with very low MNMB for both years (0.10 and 0.02) and high correlations (0.69 and 0.67). These number here are coherent with those of Rea et al. (2015) and Menut et al. (2016).

As for the MODIS AODs, this comparison shows a good agreement between the model simulation and the AERONET AOD measurements. Also both comparisons reveal coherent patterns such as an underestimation of the modelled AOD over the east coast of the Mediterranean basin.

3.3 Comparison with AIRBASE/AQeR databases

A dense measurement network is used for air quality monitoring in Europe. Data are gathered into a database named AIRBASE. It is managed by the European Topic Centre on Air Pollution and Climate Change Mitigation on behalf of the European Environment Agency (EEA). AIRBASE data are used in this study to evaluate the performance of the model for PM_{10} and $PM_{2.5}$. From 2013, EEA changed the format of their observation database. This database is now called Air Quality e-Reporting (AQeR) and there is one release of validated data for each year.

For this study, we use the latest version (version 8) of the AIRBASE database for the year 2012, and the AQeR database for the year 2013. For simplicity, we will use AQeR to designate both databases.

Monitoring stations from the AQeR database are located on various sites being representative of rural, periurban or urban conditions. In order to compare the model simulations to the observations, we select the stations which are representative of the model resolution. Following Joly and Peuch (2012), each station is characterized by a class between 1 and 10 according to its statistical characteristics. 1 corresponds to a fully rural behaviour and 10 to a highly polluted station. Then, as in Guth et al. (2016), only the stations corresponding to classes 1 to 5 are kept to remove stations that are not representative of the simulation resolution.

Table 4 presents the statistics for the comparison between MOCAGE simulations and AQeR hourly data for the year 2012 and 2013, and for PM_{10} and $PM_{2.5}$. This table shows a similar behaviour between the results for both years. Aerosols are underestimated, MNMB for PM_{10} are -0.64 and -0.59, respectively for 2012 and 2013 with correlation of 0.48 and 0.45. $PM_{2.5}$ are better represented with lower MNMB (-0.40 and -0.38) and higher correlations (0.55 and 0.53). The aerosol underestimation can be explained, at least partly by the lack of secondary organic aerosols in the model MOCAGE, but also by uncertainties in the anthropogenic emission inventories particularly on the eastern part of the Mediterranean region.

Table 5 presents the same statistics as Table 4 but over the budget domain. In terms of bias, the results are very similar with a negative bias of about $-10\mu gm^{-3}$ for PM_{10} and $-4\mu gm^{-3}$ for $PM_{2.5}$. The errors and the correlation are slightly less good than for the statistics over the whole modelled domain with for example a correlation of 0.49 for PM_{10} in 2012 against a correlation of 0.62. We should note that for $PM_{2.5}$ there are only 24 and 29 stations in the budget domain for the year 2012 and 2013, respectively. Therefore the statistics are not as solid for the budget domain as for the whole simulation domain.

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3.4 Comparison with EMEP database

In order to characterise the model behaviour against aerosol composition, we use the database made available by HTAP which includes data from several measurement networks: EMEP, IMPROVE, NAtChem, EANET, CREATE, EUSAAR, NILU and the WMO-PCSAG global assessment precipitation data set (http://www.htap.org/, http://ebas.nilu.no). Here we will only use

5   data from the EMEP program.

From this set of measurements, we use the aerosol composition in order to check the behaviour of the model regarding the simulated components of secondary inorganic aerosols. We only give the results for the year 2013 since there are too few stations available in 2012 to be statistically significant. Nevertheless, results for 2012 on this limited set of data are similar to those for 2013. Figure 3 represents the location of the stations used in this study. This figure highlights the lack of this type of

10   measurements outside Europe.

Table 6 presents the statistics for the comparison between the EMEP measurements and the MOCAGE simulation for the year 2013. Secondary inorganic aerosol compounds are slightly underestimated, with MNMBs of -0.11 for sulphate, -0.17 for nitrate and -0.19 for ammonium. Correlation is slightly better for sulphate (0.58) than for ammonium (0.53) and nitrate (0.49). The results presented here are similar to Guth et al. (2016) on MOCAGE simulation over the whole European continent.

15   This shows the ability of the model to represent the composition of the SIA, over the European part of the domain.

3.5 Conclusion on the evaluation

In this section, we used different sets of observations to evaluate the results of the model. Firstly we used aerosol optical depth measurements which provide vertically integrated measurements over a large part of the simulated domain. The model shows good results with respect to the MODIS and AERONET observations. When comparing to AERONET data, we show for

20   example very low biases (MNMB of 0.10 for 2012 and 0.02 for 2013) and good correlations (0.69 for 2012 and 0.67 for 2013). However, as shown by Michoud et al. (2017) for summer, organic aerosols can represent up to half of the PM_1 aerosols. They can then play a significant role for the visible AOD. The fact that the bias is low here can be a sign of compensations of errors since the SOA are not taken into account in this study.

Secondly, we compared the simulations to *in situ*, surface, observations. These comparisons show a fair agreement. Nev-

25   ertheless, there are large regions, especially in North Africa, where we do not have measurements available to evaluate the model.

4 Aerosol budget and variability over the Mediterranean basin

The simulation presented and evaluated in Section 3 is now used to characterize the budget of the aerosols over the Mediterranean basin.

4.1 Methodology

Over the domain considered, using hourly outputs, for a given aerosol species, we define its budget for a chosen time period
by the equation:

$$\Delta_{burden} = Em + Pr - Loss - Dep + Tran, \tag{1}$$

with Δ_{burden} is the difference of the atmospheric burden between the end and the beginning of the time period. Em is
the emission, Pr the chemical production, $Loss$ the chemical loss, Dep the deposition terms (dry and wet deposition, and
sedimentation) and $Tran$ the import/export of the aerosol in the budget domain. This last term is positive when aerosols are
imported into the domain and negative when exported. All terms are prognostic or directly computable from the simulation
outputs. For the advection, the MOCAGE model uses a semi-Lagrangian transport scheme. It means that for each model
gridpoint, the transport over a time-step is done by determining the location from which the air mass originated at the beginning
of the time-step and the associated concentration of aerosol species at this location. This approach is used in order to be able
to use long time-steps for the transport. For the MOCAGE model, the transport time-step is set to one hour. Because of the
use of a semi-Lagrangian approach in MOCAGE, the $Tran$ term cannot be directly estimated since there is no Eulerian flux
computed in the transport scheme. We therefore use an indirect estimation of the $Tran$ term by calculating the difference of
the burden before and after the transport into the budget domain at each time-step. Note that the separation between the inward
flux and the outward flux of particulate matter transported cannot be done in the $Trans$ term.

From this definition, the $Trans$ term implicitly includes the transport but also the model errors due in particular to possible
mass imbalance. Since mass conservation is insured on the global domain that serves to force the boundaries of the regional
domain, the model error due to mass imbalance is expected to be small compared to transport.

Using all these terms the residual mass, corresponding to the error made is computed using:

$$Resid = Em + Pr - Loss - Dep + Tran - \Delta_{burden}. \tag{2}$$

We have calculated this residual model error term. It is about 1% of Em or Pr for black carbon and primary organic carbon
and sulphate, about 4% of Em for desert dust and sea salt, and about 0.1% of Pr for ammonium and nitrate. Therefore it is
small and does not affect our budget analysis.

4.2 Results of the aerosol budget over the Mediterranean basin

In this subsection, we present the aerosol budget over the two year period 2012-2013, on an annually and monthly basis in
order to discuss the seasonal variability. All the following results are presented on the budget domain.

4.2.1 Annual budget

Tables 8 and 9 present the annual budget of the aerosols for the year 2012 and 2013, respectively. Note that the unit of the
burden term is Tg while the other terms unit is Gg. One can see the similar behaviour between both years, especially for black

carbon. Desert dusts and sea salts are the most important aerosols of the region with a burden of about 900Gg for desert dust and 150Gg for sea salt. Other aerosols have a mean burden between 13 and 75Gg. But altogether the SIA (sulphate, nitrate and ammonium) provide a burden similar to the sea salts. The year 2012 shows higher concentrations of carbonaceous aerosols and secondary inorganic aerosols, while the year 2013 is characterized by more natural aerosols (desert dust and sea salt). For both

5 years, one can see that all types of aerosols are exported, except for sea salt. One can note that the chemical destruction term for the sulphate is equal to zero. This is due to the hypothesis of ISORROPIA which is to condense all the sulfuric acid into the aerosol phase whatever the thermodynamic conditions are. Then, there can only be a sulphate production, no chemical loss.

Tables 10 and 11 present the annual budget of the aerosols for the year 2012 and 2013, respectively, as a percentage of the emission or the production. This allows us to easily identify which proportion of the aerosol goes preferentially to each term

10 of the budget. For natural aerosols, most of the emitted matter, about 85% for desert dusts and 95% for sea salts, is deposited in the budget domain. This is due to the size of the emitted aerosol which is larger than for the other types of aerosols. The sedimentation is thus more effective. Concerning the export, we can note that 11% of the desert dust are exported, while this percentage raises to about 30 to 40% for the carbonaceous aerosols and the sulphate, 9% for the ammonium and 2% for the nitrate. For the sea salt it is 0.7% for 2012 and 2% for 2013, but the residual mass in the budget calculation is of the same

15 order as the $Tran$ term. We can then consider the global behaviour of sea salt is that there is almost no flux. Nitrate aerosols exportations are low compared to ammonium and sulphate. It can be explained by the fact that nitrate and sea salt are linked by the ISORROPIA module. Indeed, our domain being largely over maritime surface, there are a lot of sea salts on which nitrate condense rapidly due to the thermodynamic equilibrium assumption.

To analyse the import/export of the aerosols, Figs. 4 and 5 present the yearly mean of the total column of the different

20 aerosols for the year 2012 and 2013, respectively. These panels also present the red square representing the budget domain. Figure 6 depicts the precipitation rate and the wind fields at 200m above the surface for the years 2012 and 2013. One can see the mark of the desert dust emissions north of the southern boundary of the domain (top left panel), that are transported with the dominant Easterly and North-Easterly winds, thus explaining the general export behaviour of the desert dusts. We observe the same phenomenon with carbonaceous aerosols and sulphate which concentrations are maximum in the eastern part of the

25 basin and associated with Westerly winds, exporting the aerosols by the east boarder.

By comparing the precipitation rates and the wind fields, we can note differences in the meteorology between the two years. On the Western part of the basin, the year 2013 presents higher wind speed values, especially over the gulf of Lion and North Africa. This explains the higher values of desert dust and sea salt aerosols in this region in 2013 compared to 2012. On the Eastern part of the basin, the year 2012 presents higher wind speed values over the sea, explaining here higher sea salt aerosol

30 values. Desert dust presents higher total column concentrations in 2013 and a bigger extent towards the north-east of the domain. Associated to fewer precipitation in this region in 2013, it explains the lower wet deposition of desert dust aerosols in 2013 compared to 2012 despite larger emissions. In this region, we can also see higher concentrations of carbonaceous aerosols, in 2012, which can be explained by this higher wind values exporting the pollution, from the coast of Aegan sea over the basin.

4.2.2 Monthly budget

In this subsection, we examine the aerosol budget at the monthly temporal scale. Figure 7 represents the monthly budget for the primary aerosols while Fig. 8 represents the monthly budget for the secondary inorganic aerosols. In Fig. 7, sea salt aerosols present very similar monthly variations between the two years. Sea salts show a slight annual cycle with more emissions in

5 winter months, related to higher wind speeds. Desert dusts have a similar behaviour between both years, with a very active season between January and June and less activity during the second half of the year. Nevertheless, we can note the large differences of desert dust emissions between the year 2012 and 2013, also seen on other budget terms. The 2012 season starts and finishes earlier, while the season 2013 presents higher emissions, and thus more deposition, export and burden. For 2013, we can explain this phenomenon by looking at the winds during the preferential dust season (not shown). In 2013, the average

10 low level winds are stronger on North Africa, leading to higher desert dust emissions, and thus to higher values for all the terms of the budget.

Concerning anthropogenic aerosols, black carbon presents a very similar behaviour between the two years, with a slight annual cycle having higher emissions in autumn and winter than in summer. This is consistent with the monthly variations of the emission inventory used. Organic carbon presents also a similar behaviour for both years, except in summer when there

15 is a higher burden in 2013 despite lower emissions. This comes from the import of aerosols from outside the budget domain. Figure 9 presents the total column and the biomass burning emissions for July 2012 and 2013. This panel illustrates that there were more fires during summer 2013 in North America compared to summer 2012. These fires exported a large amount of aerosols from the North American continent into the budget domain, explaining the difference of behaviour for organic carbon aerosols in summer between 2012 and 2013.

20 The budget for secondary inorganic aerosols is presented in Fig. 8. There is a similar behaviour for all secondary inorganic aerosols for both years. Nitrate and ammonium show small seasonal variations. The burden of sulphate aerosols has a strong annual cycle which is maximum in summer despite a lower production during this season. The reason for the increase of the burden is the lower deposition in summer than in winter.

4.2.3 Conclusion on the aerosol budget

25 To conclude this section on the aerosol budget over the Mediterranean basin, we highlight several points. Firstly, there is a large discrepancy in the aerosol burden according to their nature. The burden of desert dust and sea salt is much higher than that of other aerosols not only in summer as already shown by Rea et al. (2015) and Menut et al. (2015) but also throughout the whole year, leading to their predominance in the annual budget. Secondly, we find that all aerosols are exported on average from the domain of study, except for sea salt. This comes from the large emissions and the meteorological conditions within

30 the domain but also from the domain boundaries chosen for the budget calculation, especially for desert dust which northern African emissions are located within the domain.

The monthly budget shows an annual cycle that is more (desert dust) or less pronounced (sea salt, carbonaceous aerosols) depending on the type of aerosols. Desert dust are very sensitive to wind conditions. Another source of the variability is brought

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by import of aerosols such as the biomass burning from the North American continent in summer 2013 on primary organic
carbon.

5 Sensitivity study: impact of sea and coastal anthropogenic emissions

The Mediterranean basin shows a large population density on the coastal areas and high maritime traffic. In this section, we
5 assess the impact of the anthropogenic emissions in the coastal and marine Mediterranean area. To address this, we made a
second simulation where we removed the anthropogenic emissions over the sea and over a $50\mathrm{km}$ wide band along the coast.
All the other parameters of the simulation remain the same. Figure 10 presents the mask used to remove the anthropogenic
emissions for this sensitivity test along with the budget domain. in red that is the same as in Section 4. Since the natural aerosols
are not impacted by the changes made, we will not analyse them.

10 Tables 12 and 13 present the annual budget for the sensitivity simulation for 2012 and 2013, respectively. Concerning the
black carbon aerosol, we can note a similar behaviour between the two years simulated, which is consistent with what we found
in Section 4. Concerning primary organic carbon, we can still see the impact of the biomass burning from North America in
summer 2013 on this aerosol. Secondary inorganic aerosols present a similar behaviour between the two years.

In order to compare the results between the two simulations, Table 14 and 15 present the relative differences, between
15 the reference simulation and the test simulation, respectively for the year 2012 and 2013. These relative differences, for the
parameter A, are computed as follows:

$$\mathrm{A}_{diff} = \frac{\mathrm{A}_{sen} - \mathrm{A}_{ref}}{\mathrm{A}_{ref}}, \tag{3}$$

with A_{ref} the value of the parameter A in the reference simulation and A_{sen} the value of A in the sensibility test simulation.
A negative value means the parameter is lower in the test simulation than in the reference simulation. As for the import/export
20 terms, the values are always negative or null, a negative value of the difference means the exportation is less pronounced in the
test than in the reference.

For the black carbon aerosols, we see a similar behaviour between 2012 and 2013. The mean burden is reduced by about
17% while the emissions are reduced by 30% and the export by 35 to 40%. This is due to the high black carbon emissions in
the eastern part of the domain in the highly populated areas near the coast that are largely exported.

25 Primary organic carbon aerosols have a mean burden reduced by about 7.5% while the emissions are reduced by a bit less
than 30% for both 2012 and 2013. Here we can see the impact of the high aerosol concentration coming from the biomass
burning in North America. The difference in the imported term, between the reference simulation and the test simulation, are
very similar with $0.15\mathrm{Tg}$ for 2012 and $0.14\mathrm{Tg}$ 2013. It represents the reduction of the exportation of aerosols from local
sources. The reference simulation presents an export of $0.32\mathrm{Tg}$ for 2012 and $0.24\mathrm{Tg}$ for 2013. Then when calculating the
30 relative difference, the year 2013 gives a higher number.

Concerning SIA, both years are similar with a decrease in the mean burden of about 16% for ammonium, 12% for nitrate
and 17% for sulphate. The decrease in SIA formation is between 23.2% for ammonium and 36.4% for sulphate and the export

reaches about 55% for sulphates and ammonium. Figure 11 presents the total annual emission for the SIA precursors, computed over the budget domain, in the reference simulation and the sensitivity test simulation. This figure presents the numbers for 2013, but they are very similar for the year 2012. We can see that the SO_2 emissions are reduced by approximately 40%, which is coherent with the 36.4% sulphate formation decrease. The decrease of the NO_x emissions is about 50%, while the formation

5 of nitrate aerosol is lowered by only 26.7%. The precursor of nitrate aerosols is nitric acid but there are different chemical pathways NO_x can take, explaining the difference between the NO_x emission reduction and the nitrate formation decrease. Ammonium formation is lowered by 23.2% while ammonia emission are only lowered by about 20%. This is explained by the fact that ammonium is condensed onto sulphate and nitrate particle to neutralize the solution. The decrease of sulphate and nitrate becomes then a limiting factor for the formation of ammonium aerosols.

10 As a conclusion we can note the high importance of the coastal area in this region. Indeed, our sensitivity test shows that more than 20% to 30% of the emission or production of anthropogenic primary aerosols and secondary inorganic aerosols in the Mediterranean are originated from the marine or coastal area. Also, they account for more than 40% to 50% of the exported aerosols outside the budget domain. We do not show the monthly budgets here since they do not give additional information.

6 Conclusions

15 This study aimed at establishing the budget of the primary aerosols and secondary inorganic aerosols on the Mediterranean basin based on numerical simulations of the years 2012 and 2013 using the MOCAGE model. Firstly we compared the simulation to observations in order to do an evaluation of the simulation. We showed the model was able to well represent the aerosols on the Mediterranean basin. Nevertheless, this comparison shows a lack of observations in the southern part of the domain, especially in North Africa to fully evaluate the model using *in situ* surface measurements.

20 Secondly we use the two year-long simulation to compute the aerosol budget over the Mediterranean basin on a annual and monthly basis. We showed that all aerosols taken into account in this study are generally exported out of the Mediterranean domain. Nevertheless, this result might depend on the domain used to do the calculation, especially for desert dust. We observed an annual cycle on natural aerosols budget that is due to the influence of meteorological conditions, modulating the emissions of desert dust and sea salt. The annual cycle can also be affected by the differences in primary anthropogenic aerosol emissions or

25 variations on the importation of aerosols from outside (especially biomass burning events). We also show that natural aerosols (desert dust and sea salt) are predominant over this region all over the year, such as found in Rea et al. (2015) and Menut et al. (2015) for the summer 2012 and 2013.

Then, we made a sensitivity test to assess the importance of the marine and coastal regions of the Mediterranean basin. To do this, we removed the anthropogenic emissions over the sea and over a 50km wide band along the coast. We showed that around

30 30% of the emissions or chemical production, and 50% of the export of anthropogenic aerosols are due to the emissions within this area. There is also, for ammonium, the effect of transport and mixing of its precursor (NH_3) together with the influence of the decrease of nitrate and sulphate aerosol concentrations, as explained in section 5.

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The focus of this study is on primary aerosols and secondary inorganic aerosols. Once the SOA development validated in MOCAGE, it would be interesting to do the budget for this type of aerosol too. Also this would be the opportunity to analyse the gaseous phase compounds and their budget over the Mediterranean basin. This study will also use the sensitivity test simulation to compare the differences in behaviour between aerosols and gaseous compounds.

5   We showed in section 4 differences in the average meteorology between 2012 and 2013, and a direct link between the weather conditions and the aerosol concentrations, such as the effect of the wind speed. To go a step further, we propose in a future paper to analyse the aerosol distribution using a more detailed meteorological analysis, based on the concept of weather regimes. Weather conditions can be classified into weather regimes that correspond to idealized meteorological situations. These weather regimes can be used to gather similar meteorological conditions and to analyse the "aerosol regime" associated

10   to each weather regime. This kind of methodology could also be used in climate simulation to assess the expected behaviour of aerosols in the future.

Appendix A: Metrics used for evaluation

Several statistical indicators can be used for model evaluation against in situ data. Seigneur et al. (2000) state that past model performance evaluations have generally used observations to normalize the error and the bias. This approach can be misleading

15   when the denominator is small compared to the numerator. Following Seigneur et al. (2000), we chose to use the fractional bias and the fractional gross error instead of the bias and the root-mean-square error (RMSE).

The fractional bias, also called modified normalized mean bias (MNMB) or mean fractional bias (MFB), used to quantify, for N observations, the mean between modeled (f) and observed (o) quantities is defined as follow:

$$\text{MNMB} = \frac{2}{N} \sum_{i=1}^{N} \frac{f_i - o_i}{f_i + o_i} \tag{A1}$$

20   The fractional bias ranges between -2 and 2 varying symmetrically with respect to under and overestimation.

The fractional gross error (FGE), also called mean fractional error (MFE) aims at quantifying the model error. It varies between 0 and 2 and is defined by:

$$\text{FGE} = \frac{2}{N} \sum_{i=1}^{N} \left| \frac{f_i - o_i}{f_i + o_i} \right| \tag{A2}$$

The correlation coefficient r indicates the extent to which patterns in the model match those in the observations and is defined

25   by:

$$r = \frac{\frac{1}{N} \sum_{i=1}^{N} \left(f_i - \overline{f} \right) \left(o_i - \overline{o} \right)}{\sigma_f \sigma_o} \tag{A3}$$

Where σ_f and σ_o are standard deviation, respectively from the modelled and the observed time series and $\overline{f}$ and $\overline{o}$ their mean values.

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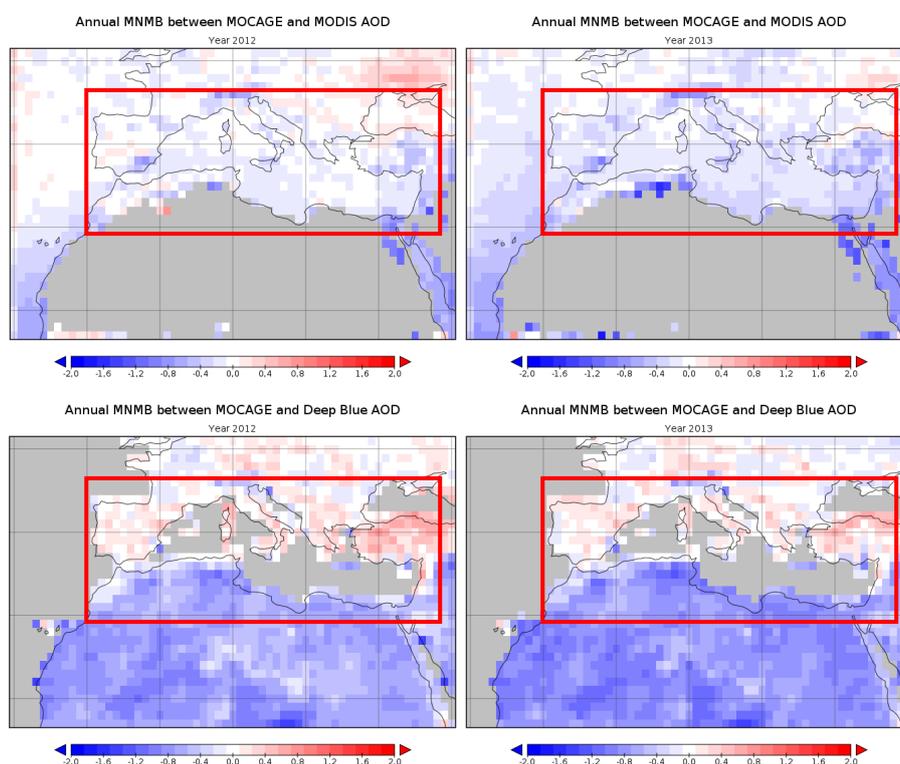
Figure 1. Map of the annual modified normalized mean bias (MNMB) of the aerosol optical depth against MODIS observations for the year 2012 (left) and 2013 (right) for MODIS (top) and Deep Blue (bottom).
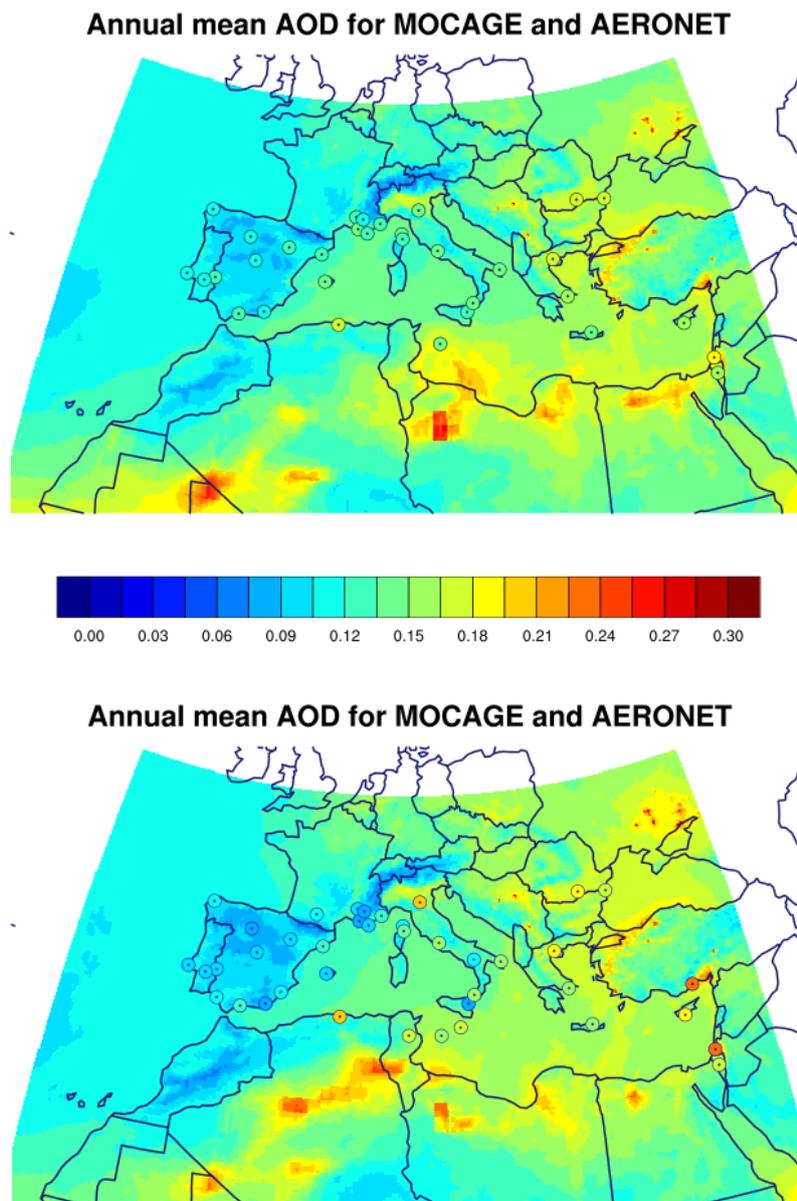
Figure 2. Map of the annual mean aerosol optical depth simulated with the model MOCAGE with superimposed AERONET observations (circles) for the years 2012 (top) and 2013 (bottom).
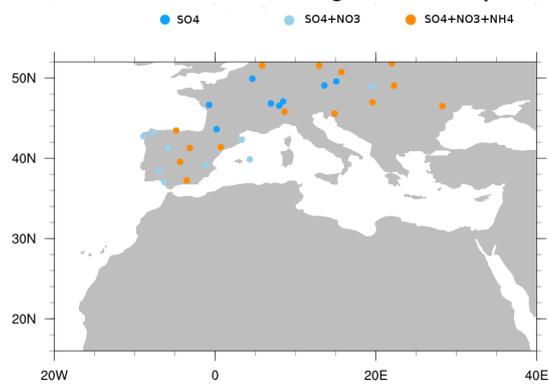
Figure 3. Location of the EMEP stations used in this study for the year 2013.

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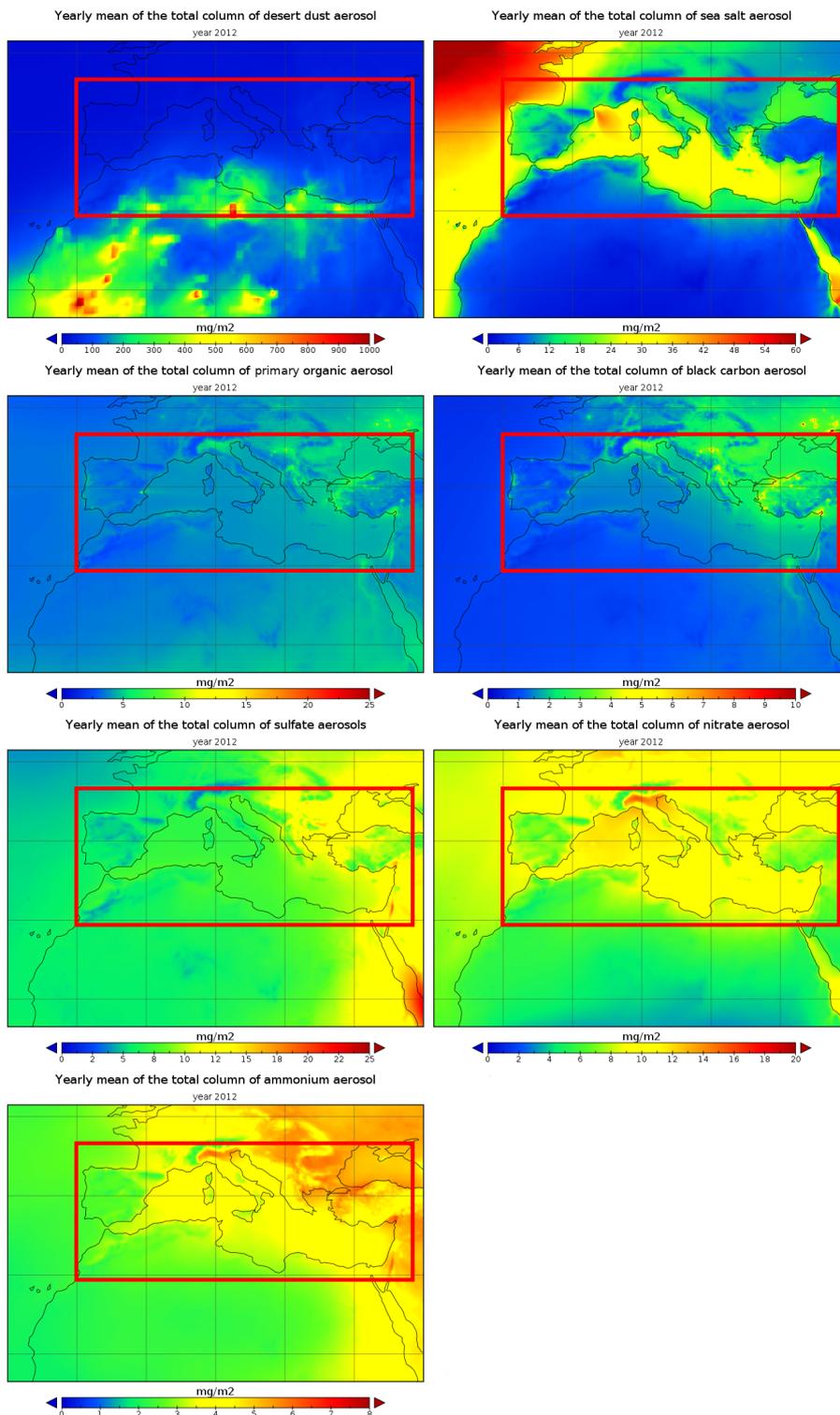
Figure 4. Yearly mean of the total column of aerosols for the year 2012. The red square on the figures represents the budget domain.
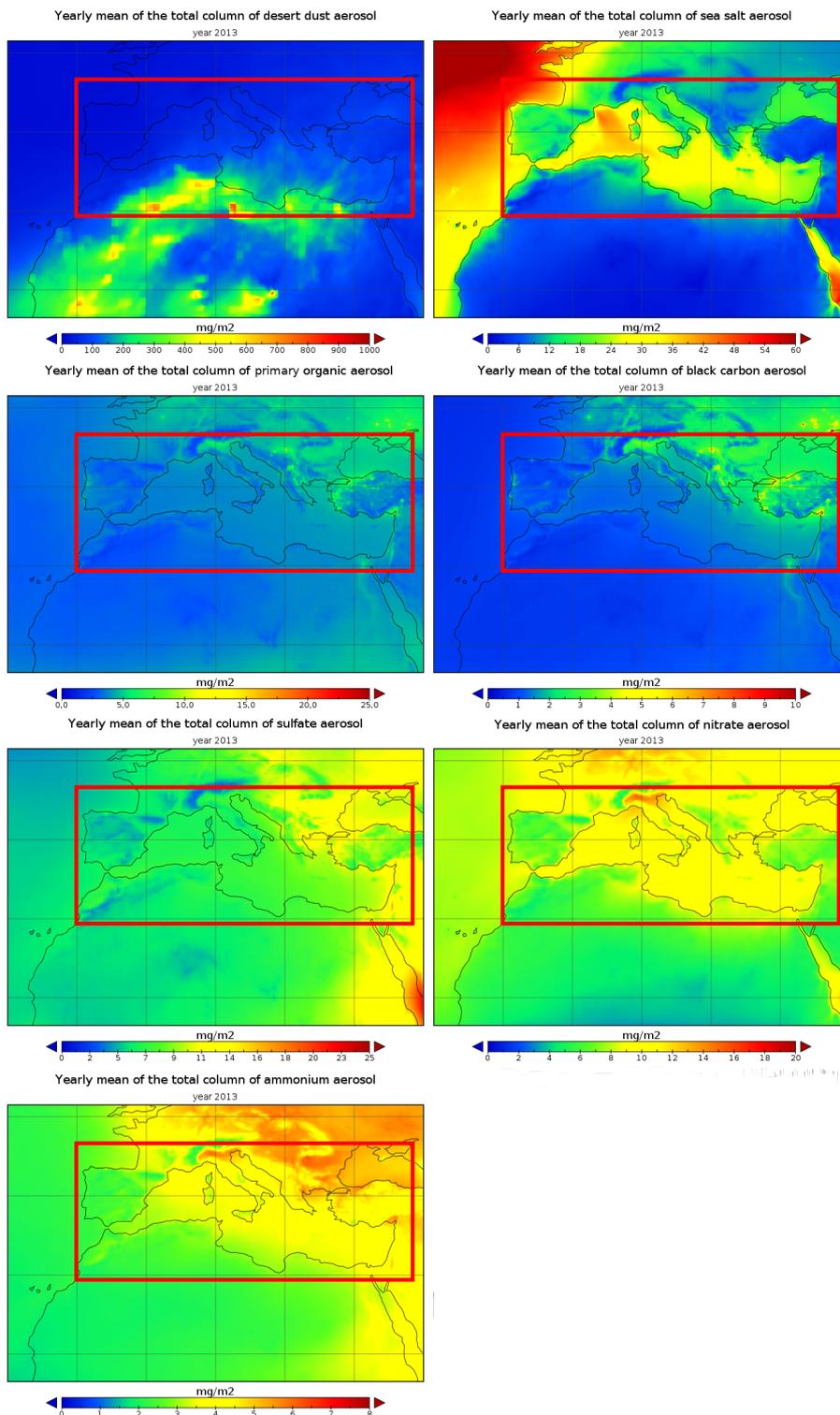
Figure 5. Yearly mean of the total column of aerosols for the year 2013. The red square on the figures represents the budget domain.
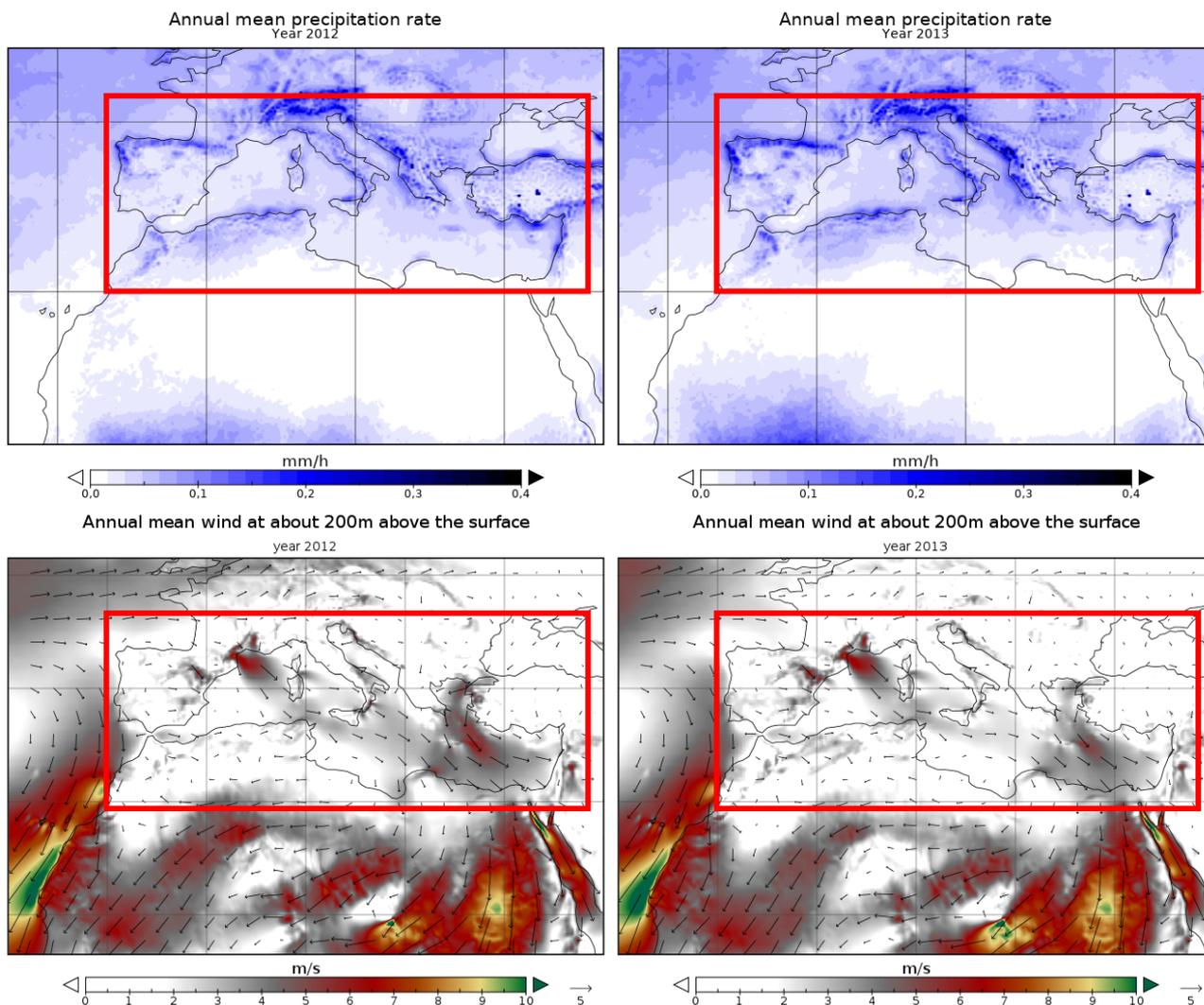
Figure 6. Yearly mean of precipitation rate (top panels) and wind vectors at 200m above the surface (bottom panels) for the year 2012 (left) and 2013 (right). The red square on the figures represents the budget domain.
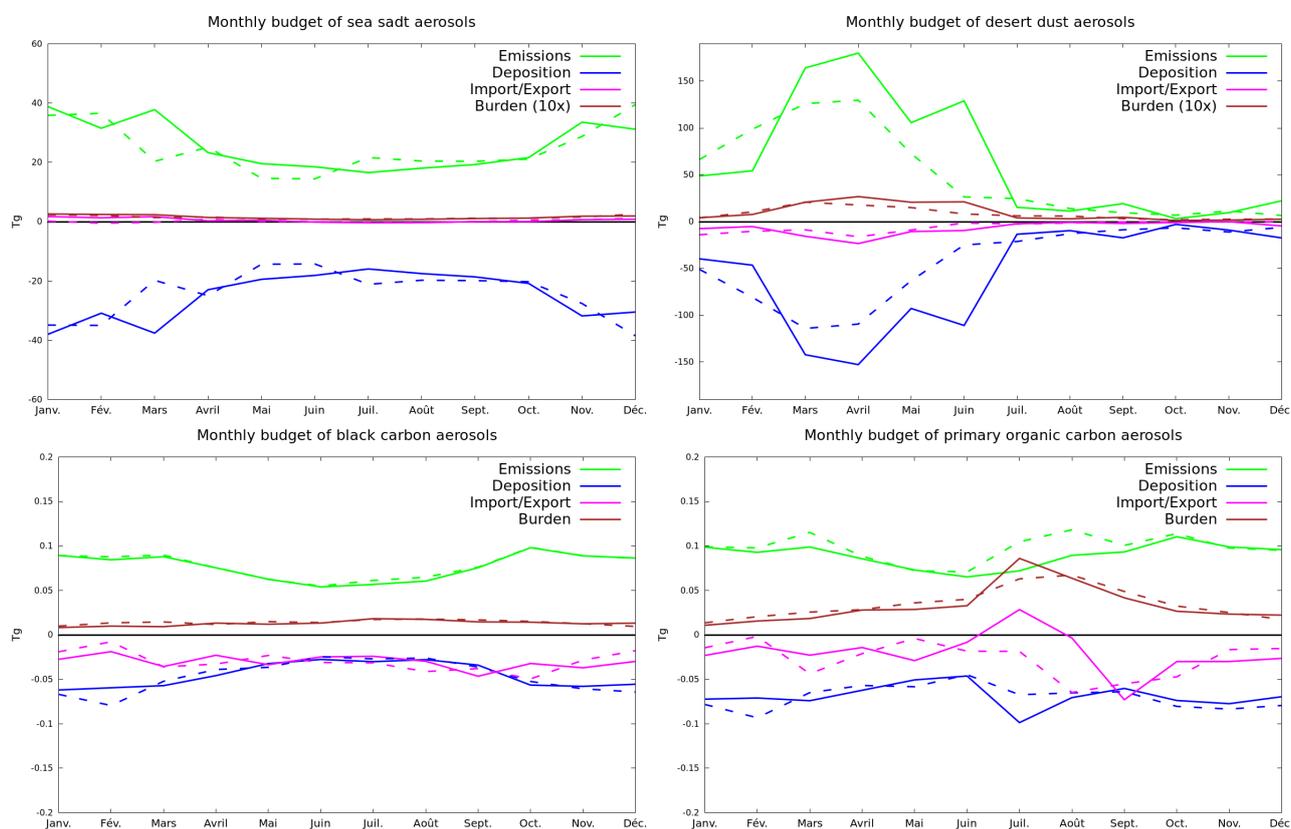
Figure 7. Monthly budget for the primary aerosols for the year 2012 (dashed lines) and 2013 (solid line). The green lines correspond to the emissions, the blue ones to deposition, the pink ones to the import/export part and the brown ones the burden.
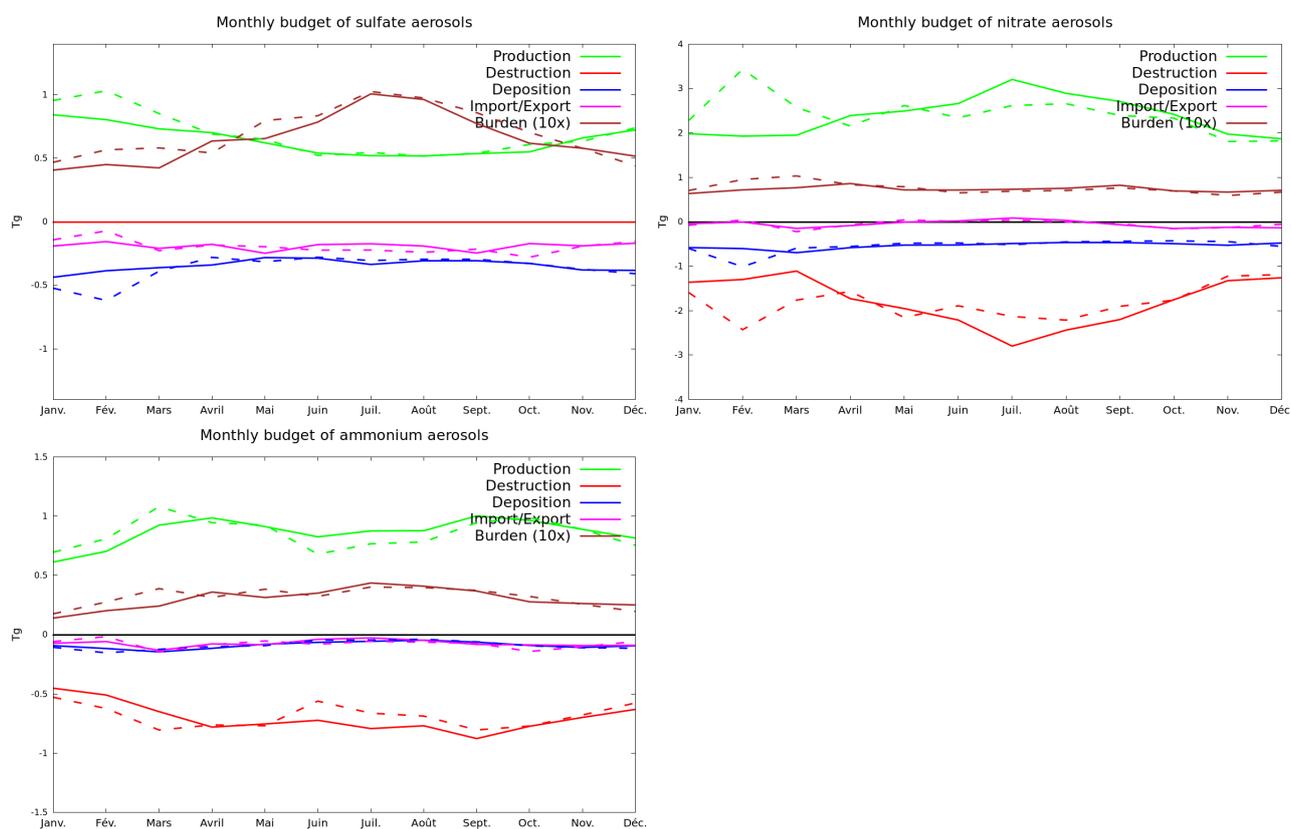
Figure 8. Monthly budget for the secondary aerosols for the year 2012 (dashed lines) and 2013 (solid line). The green lines correspond to the emissions, the red ones to the chemical loss, the blue ones to deposition, the pink ones to the import/export part and the brown ones the burden.
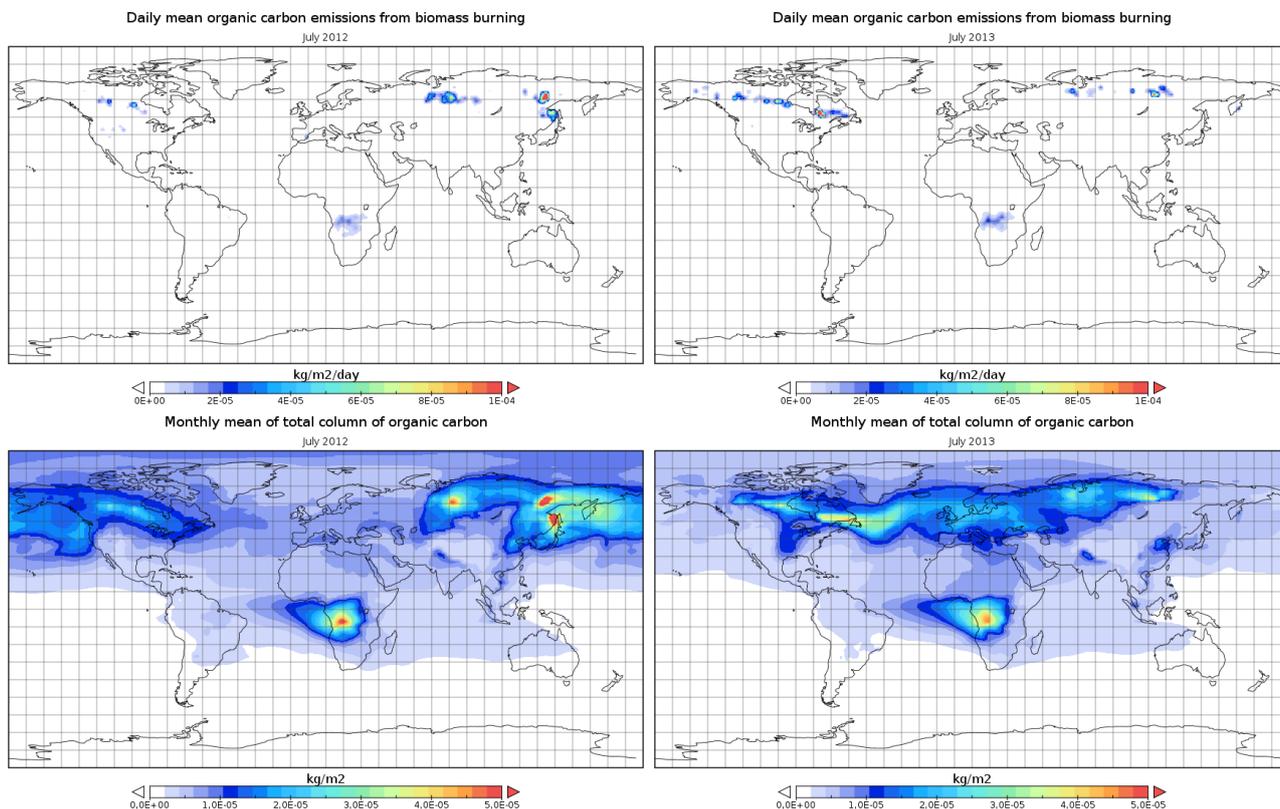
Figure 9. Maps of organic carbon emission from biomass burning (top) and total column of primary organic carbon aerosols (bottom) for July 2012 (left) and July 2013 (Right).
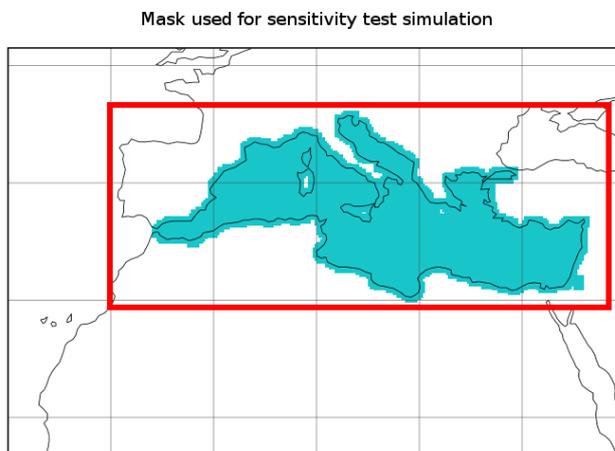
Figure 10. Map of the mask used to cancel the anthropogenic emission in the sensitivity test simulation in cyan and the budget domain in red.

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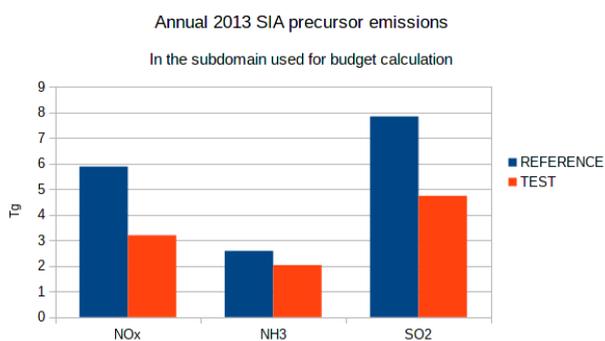
Figure 11. Annual emissions of SIA precursors, NO_x, NH_3 and SO_2 for the year 2013 computed over the budget domain in the reference simulation in blue and the sensitivity test in red.

Table 1. Mean statistics of the comparison between the MODIS AOD and the MOCAGE simulation for the years 2012 and 2013. See Appendix for information about statistical indicators.

Year	Bias	MNMB	FGE	Correlation
		MODIS		
2012	−0.04	−0.09	0.39	0.39
2013	−0.06	−0.23	0.43	0.57
		Deep Blue		
2012	−0.13	−0.37	0.61	0.39
2013	−0.15	−0.48	0.68	0.46

Table 2. Mean statistics of the comparison between the MODIS AOD and the MOCAGE simulation for the years 2012 and 2013 over the budget domain.

Year	Bias	MNMB	FGE	Correlation
		MODIS		
2012	−0.03	−0.09	0.37	0.39
2013	−0.05	−0.22	0.40	0.51
		Deep Blue		
2012	−0.08	−0.18	0.51	0.34
2013	−0.09	−0.28	0.58	0.40

Table 3. Mean statistics of the comparison between the AERONET AOD data and the MOCAGE simulation for the years 2012 and 2013. See Appendix for information about statistical indicators.

Year	Bias	MNMB	FGE	Correlation
2012	−0.01	0.10	0.41	0.69
2013	−0.02	0.02	0.40	0.67

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Table 4. Statistics of the comparison between the MOCAGE simulation and the AQeR database measurements, corresponding to classes 1 to 5 from the classification of Joly and Peuch (2012) for the years 2012 and 2013. The table presents results for PM_{10} and $PM_{2.5}$.

Year	stations	Bias (μgm^{-3})	MNMB	FGE	Correlation
		PM_{10}			
2012	334	−9.34	−0.64	0.68	0.62
2013	311	−8.94	−0.58	0.64	0.59
		$PM_{2.5}$			
2012	95	−3.49	−0.19	0.54	0.71
2013	111	−4.13	−0.27	0.54	0.68

Table 5. Statistics of the comparison between the MOCAGE simulation and the AQeR database measurements, corresponding to classes 1 to 5 from the classification of Joly and Peuch (2012) for the years 2012 and 2013 on the budget domain. The table presents results for PM_{10} and $PM_{2.5}$.

Year	stations	Bias (μgm^{-3})	MNMB	FGE	Correlation
		PM_{10}			
2012	75	−10.5	−0.75	0.77	0.49
2013	82	−10.0	−0.73	0.76	0.37
		$PM_{2.5}$			
2012	24	−3.91	−0.54	0.71	0.45
2013	29	−3.51	−0.45	0.65	0.48

Table 6. Statistics of the comparison between the MOCAGE simulation and the HTAP measurement database for the year 2013.

stations	Bias (μgm^{-3})	MNMB	FGE	Correlation
	Sulphate total			
31	−0.11	−0.34	0.71	0.58
	Nitrate			
23	−0.17	−0.19	0.85	0.49
	Ammonium			
14	−0.19	−0.21	0.72	0.53

Table 7. Statistics of the comparison between the MOCAGE simulation and the HTAP measurement database for the year 2013 over the budget domain.

stations	Bias (μgm^{-3})	MNMB	FGE	Correlation
		Sulphate total		
22	−0.24	−0.55	0.73	0.62
		Nitrate		
18	−0.05	−0.19	0.80	0.47
		Ammonium		
10	−0.33	−0.46	0.89	0.47

Table 8. Annual budget of the aerosols for the year 2012. The residual mass term corresponds to the values obtained when closing the budget. The different components are in Tg except the mean burden which is in Gg.

Year 2012	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	Chemical Loss	Import (> 0) Export (< 0)	Mean Burden
Primary Org. C	1.17	0.39	0.45	0.00	−0.32	34.79
Black carbon	0.93	0.27	0.29	0.00	−0.36	13.94
Desert dust	593.6	469.7	39.9	0.00	−64.1	828.9
Sea salt	298.9	273.0	17.4	0.00	2.11	146.2
Ammonium	10.26	0.35	0.73	8.23	−0.93	31.76
Nitrate	29.04	4.89	1.66	21.8	−0.62	75.65
Sulphate	7.56	3.65	1.50	0.00	−2.34	69.85

Table 9. Same as Table 8 but for 2013.

Year 2013	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	chemical Loss	Import (> 0) Export (< 0)	Mean Burden
Primary Org. C	1.07	0.39	0.44	0.00	−0.24	33.10
Black carbon	0.92	0.26	0.28	0.00	−0.36	12.98
Desert dust	763.5	625.3	28.9	0.00	−82.1	990.2
Sea salt	309.8	282.3	19.9	0.00	6.23	152.0
Ammonium	10.39	0.34	0.73	8.41	−0.89	30.10
Nitrate	28.48	4.76	1.66	21.4	−0.61	73.38
Sulphate	7.14	3.36	1.39	0.00	−2.30	65.20

Table 10. Annual budget of the aerosols for the year 2012 as a percentage of the emission or the production.

Year 2012	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	Chemical Loss	Import (> 0) Export (< 0)
Primary Org. C	100%	33.3%	38.0%	0.0%	-27.4%
Black carbon	100%	29.0%	31.5%	0.0%	-38.1%
Desert dust	100%	79.1%	6.7%	0.0%	-10.8%
Sea salt	100%	91.4%	5.8%	0.0%	0.71%
Ammonium	100%	3.5%	7.1%	80.2%	-9.1%
Nitrate	100%	16.8%	5.7%	75.1%	-2.14%
Sulphate	100%	48.3%	19.8%	0.0%	-34.4%

Table 11. Same as Table 10 but for 2013.

Year 2013	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	Chemical Loss	Import (> 0) Export (< 0)
Primary Org. C	100%	36.2%	40.8%	0.0%	-22.8%
Black carbon	100%	28.6%	30.8%	0.0%	-39.5%
Desert dust	100%	81.9%	3.8%	0.0%	-10.8%
Sea salt	100%	91.1%	6.4%	0.0%	2.0%
Ammonium	100%	3.3%	7.1%	80.9%	-8.6%
Nitrate	100%	16.7%	5.8%	75.3%	-2.2%
Sulphate	100%	47.1%	19.4%	0.0%	-35.2%

Table 12. Annual budget for the year 2012 of the aerosols for the sensitivity test simulation. The differents components are in Tg except the mean burden which is in Gg.

Year 2012	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	Chemical Loss	Import (> 0) Export (< 0)	Mean Burden
Primary Org. C	0.86	0.31	0.38	0.0	-0.17	32.19
Black carbon	0.66	0.20	0.23	0.00	-0.22	11.55
Ammonium	7.88	0.25	0.58	6.63	-0.43	26.70
Nitrate	21.18	3.53	1.35	16.22	-0.03	66.35
Sulphate	4.28	2.67	1.14	0.00	-1.04	58.03

Table 13. Same as Table 12 but for 2013.

Year 2013	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	chemical Loss	Import (> 0) Export (< 0)	Mean Burden
Primary Org. C	0.76	0.31	0.37	0.00	-0.10	30.62
Black carbon	0.64	0.20	0.22	0.00	-0.24	10.69
Ammonium	7.68	0.24	0.58	6.76	-0.43	25.38
Nitrate	20.90	3.48	1.34	16.05	-0.04	64.45
Sulphate	4.54	2.42	1.05	0.00	-1.11	54.26

Table 14. Annual budget for the year 2012 of the aerosols. The terms corresponds to the relative difference between the reference simulation and the sensitivity test. A negative value means the value is lower in the test simulation.

Year 2012	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	Chemical Loss	Import Export	Mean Burden
Primary Org. C	-26.5%	-21.4%	-15.2	N/A	-47.2%	-7.5%
Black carbon	-29.9%	-24.6%	-21.4%	N/A	-39.6%	-17.2%
Ammonium	-23.3%	-29.0%	-21.0%	-19.4%	-54.2%	-15.9%
Nitrate	-27.1%	-27.9%	-18.6%	-25.6%	-95.7%	-12.3%
Sulphate	-35.8%	-26.9%	-23.8%	N/A	-55.2%	-17.0%

Table 15. Same as Table 14 but for 2013.

Year 2013	Emission or Chemical Production	Sedimentation and Dry Deposition	Wet Deposition	Chemical Loss	Import Export	Mean Burden
Primary Org. C	-28.9%	-21.5%	-15.0%	N/A	-60.0%	-7.5%
Black carbon	-30.3%	-25.4%	-21.6%	N/A	-34.9%	-17.6%
Ammonium	-23.2%	-28.6%	-21.2%	-19.6%	-51.9%	-15.7%
Nitrate	-26.7%	-26.8%	-19.3%	-25.1%	-94.2%	-12.2%
Sulphate	-36.4%	-27.9%	-24.0%	N/A	-51.8%	-16.8%