Aerosol and Air Quality Research, 15: 1300–1312, 2015

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2014.11.0278

Contribution of Natural Sources to PM Emissions over the Metropolitan Areas of Athens and Thessaloniki

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ABSTRACT

The objective of this study is to examine the seasonal and inter-annual variation of particulate matter ($PM_{2.5}$ and $PM_{2.5–10}$) primary and secondary emissions from natural sources and their contributions to total PM emissions over the Athens and Thessaloniki metropolitan areas (Greece; AMA and TMA respectively), during the period 2000–2010. Therefore spatiotemporally disaggregated emission inventories for $PM_{2.5}$, $PM_{2.5–10}$ and BVOCs (Biogenic Volatile Organic Compounds), precursor to PM, from natural sources (vegetation, sea surface and wind erosion of soil) were created and compared to anthropogenic emissions in the areas. The results showed that the contribution of natural sources to PM_{10} emissions was significant (~79% for AMA; ~46% for TMA). Sea surface was the most abundant source of $PM_{2.5–10}$ emissions in both areas whereas windblown dust accounted for a relatively small fraction of total natural PM_{10} emissions in AMA and TMA (~8%; ~12.5%). In addition, BVOCs emissions accounted for approximately 0.3% and 1.6% of total primary and secondary PM_{10} emitted from the AMA and TMA, respectively. It was found that the relative contribution of natural sources to total PM_{10} emissions has increased in both areas (0.9% in AMA and 27.6% in TMA) from the beginning to the end of the studied period. There was no significant seasonal variation observed in the natural PM_{10} emissions or to their contribution to total PM_{10} emissions while BVOCs emissions were increased during the warm period due to the enhanced solar radiation and temperature. The period averaged share of primary PM_{10} and gaseous precursors to secondary aerosol formation from natural sources to total equivalent PM_{10} mass in the areas was approximately 32% in AMA and 12% in TMA.

Keywords: Anthropogenic emissions; Biogenic VOC; Marine aerosols; Mineral dust; Secondary aerosol.

INTRODUCTION

An important step in improving air quality in an area is to assess the impact of specific human activities and natural sources responsible for air quality deterioration through the quantification of pollutants emissions (Winiwarter *et al.*, 2009). The construction of an emission inventory is an important tool in air quality management and can be also used for the development and assessment of the results of specific mitigation strategies (Placet *et al.*, 2000; Karl *et al.*, 2009). Spatiotemporal emission data are important inputs for air quality models. The spatial and temporal evolution of emissions determines their atmospheric dispersion and their impact area.

Particles are emitted in the atmosphere by natural and anthropogenic sources. Most of primary anthropogenic emissions derive from combustion and industrial activities (e.g., biomass burning, vehicular exhaust, shipping, domestic heating, brake and tire abrasion, smelters, steel mills) and the emitted particles are in the PM_1 and $PM_{2.5}$ size range (particles with aerodynamic diameter < 1 μm and < 2.5 μm, respectively) (Kumar *et al.*, 2010; Kim *et al.*, 2015 and references therein). Coarse particles also arise from anthropogenic activities such as farming, mining and construction activities and resuspension of road dust (Kim *et al.*, 2015 and references therein). On the other hand, natural primary PM emissions which can result from a number of sources including the sea surface, soil, flora and biota, are mainly classified with respect to size as PM_{10} and can occur in the forms of e.g., windblown dust, sea-salt particles, fungal spores and plant debris (Kim *et al.*, 2015 and references therein). In addition, natural primary fine particles are also episodically emitted from wildfires, dust storms and volcanic eruptions (Kumar *et al.*, 2010 and references therein). Fine particles in the atmosphere originate also from gas-to-particle conversion processes of gaseous precursors emissions from both anthropogenic and natural sources (Liu and Harrison, 2011). Emissions from natural

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sources can be a significant contributor to air quality deterioration. Viana *et al.* (2014) showed that in Europe the major natural sources of atmospheric aerosols are African dust, sea spray and wildfires. Particularly for urban areas the natural sources with significant impact on air quality were sea spray, biogenic emissions and mineral dust and their share in emissions (in terms of PM mass) was found 20% in a typical urban environment in Southern Europe (Barcelona). In addition, Kassomenos *et al.* (2014) found that the share of non-combustion sources (natural and secondary particles) to PM_{10} in London, Athens and Madrid ranged between 38–67%, 26–50% and 31–58%, respectively, depending on site and season. The contribution of natural PM sources (African dust, sea salt and windblown dust) to PM_{10} concentrations has been evaluated to 17 μg/m^3 during the period 2001–2002 on a European scale (approximately 19.3 μg/m^3 particularly for Mediterranean sites; Moussiopoulos *et al.*, 2009 and references therein) whereas for the period 2008–2009 to 1–13 μg/m^3 (Viana *et al.*, 2014). The above values correspond to a large fraction of the EU air quality standard (AQS) value for annual PM_{10} concentrations and reflect the difficulty in reducing PM concentrations in the urban areas and to achieve compliance with the EU limit values (Directive 2008/50/EC).

In this study the contribution from natural sources to primary and secondary PM emissions over Athens and Thessaloniki metropolitan areas (AMA and TMA, respectively) is examined for the period 2000–2010 (Fig. 1). Athens and Thessaloniki Metropolitan Areas suffer air quality problems particularly in relation to particulate matter pollution due to the accumulation of population and major economic activities in the areas (Chaloulakou *et al.*, 2003; Grivas *et al.*, 2004, 2008; Aleksandropoulou *et al.*, 2011; Vlachokostas *et al.*, 2012; Aleksandropoulou *et al.*, 2013a). In addition, the topographical features/meteorological conditions of the areas exacerbate the problem of air pollution while they can hinder the dispersion of air pollutants, bring air masses loaded with Saharan dust aerosols and/or favor the production of photochemical pollutants (Melas *et al.*, 2005; H.M.E.P.P.P.W. 2007; Grivas *et al.*, 2008; Aleksandropoulou *et al.*, 2011). The cities of Athens and Thessaloniki show similar shares among emission sources with the difference

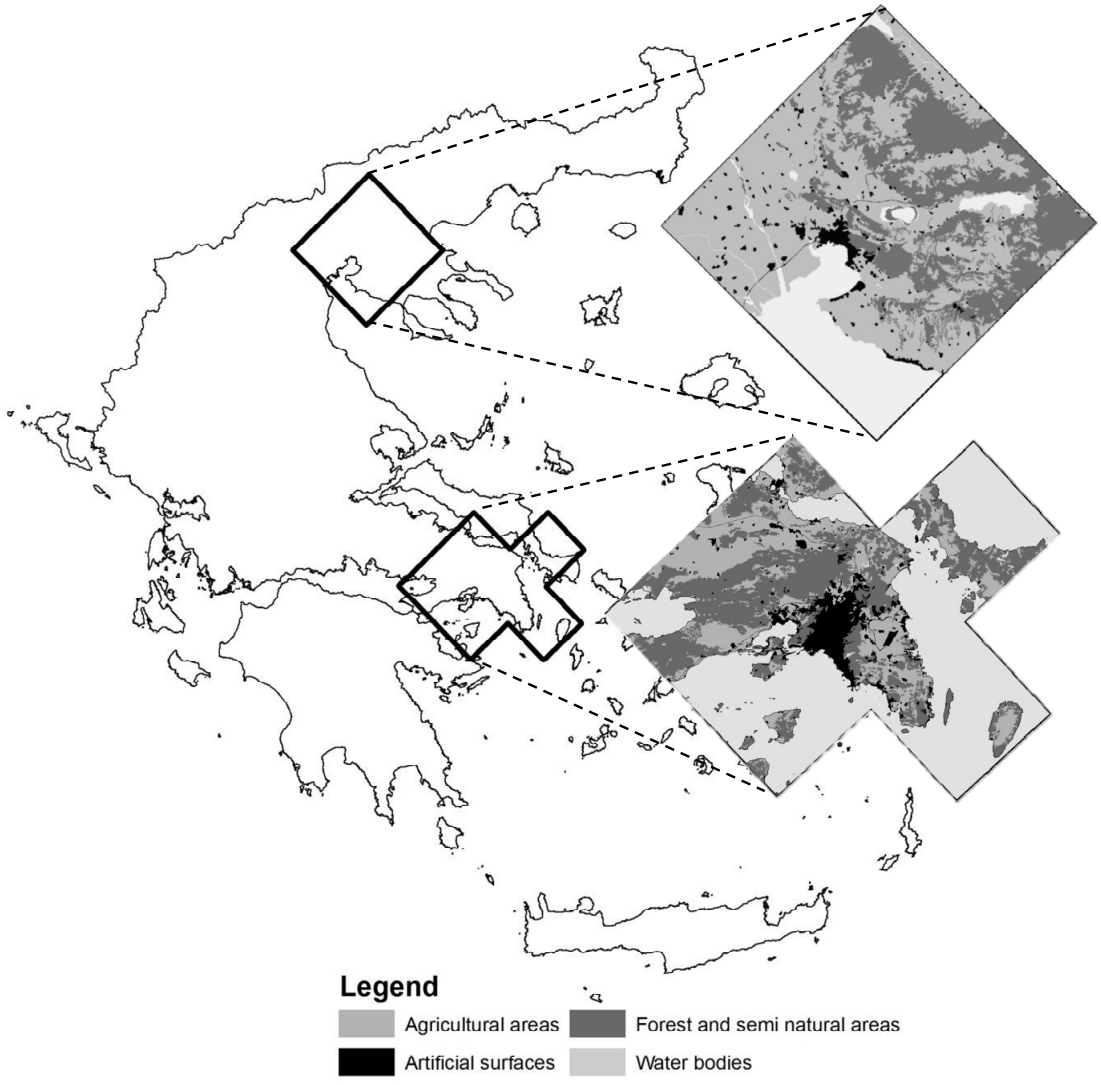

Fig. 1. Location and classification of study areas by Corine Land Cover (2000).

that industrial emissions in Thessaloniki are closer to the city centre compared to Athens (Markakis *et al.*, 2010). However, AMA is characterized by much higher source activity levels and therefore much higher emissions than TMA (a comparative description of emission sources is given in Table S1). The contribution from natural sources to PM_{10} concentrations over the urban areas of Athens and Thessaloniki is significant. In particular, Papanastasiou *et al.* (2010) report the results of two studies performed by Vardoulakis *et al.* (2008) in AMA and by Assael *et al.* (2008) in TMA, where the non-combustion related PM_{10} concentrations were estimated in the range 20–40 μg/m^3. Moreover, Karanasiou *et al.* (2009) showed, using source apportionment techniques, that during the March-December period 2002, at 3 sites located at the periphery of Athens city center, 18% of the PM_{10} mass collected was associated with marine aerosols, whereas 13% was resuspended soil particles and 8% was attributed to particles emitted from biomass burning (with peaks during winter due to residential wood burning). Also, Theodosi *et al.* (2011) have shown that 1/3 of coarse particles collected during the period September 2005–August 2006 at two monitoring stations in Athens (one traffic urban and one background suburban) was of natural origin. In addition, Salameh *et al.* (2014) showed that of the $PM_{2.5}$ mass collected in Thessaloniki over the period June 2011 to May 2012, 32 % was mineral dust (mostly linked to local sources; 12 μg/m^3), approximately 2% was sea-salt, while the majority was associated to anthropogenic sources (shipping activities, biomass burning, vehicle emissions).

Several emission inventories have been developed for Greece and/or its major metropolitan areas (e.g., Hayman *et al.*, 2001; Aleksandropoulou and Lazaridis, 2004; Sotiropoulou *et al.*, 2004; Symeonidis *et al.*, 2004; Poupkou *et al.*, 2007; Symeonidis *et al.*, 2008; Markakis *et al.*, 2010) but only a few regard or include spatiotemporally allocated emissions from natural sources. In particular, Aleksandropoulou and Lazaridis (2004) created an emission inventory of natural sources in Greece with a spatial distribution of 5 × 5 km^2 for a summer and a winter period in 2000–2001. Also, Symeonidis *et al.* (2008) estimated biogenic NMVOCs emissions in the Southern Balkan region with a spatial resolution of 1 × 1 km^2 using mean monthly climatic data for the period 1961–1990. The emissions of sea salt particles were presented by Athanasopoulou *et al.* (2008) in two domains with resolutions of 6 km and 2 km over Greece and Athens for the period 21–24 June 2008 whereas the emissions of windblown dust in the same domains for some days during May and April 2005–2007 were presented in Athanasopoulou *et al.* (2010). Moreover, Aleksandropoulou *et al.* (2011) presented natural emissions over Athens for 14 January 2008 with 1 km spatial resolution. In addition, studies on natural emissions on a European scale include also emissions from Greece (for BVOCs Steinbrecher *et al.*, 2008; Karl *et al.*, 2009; Oderbolz *et al.*, 2013, for windblown dust Korcz *et al.*, 2009).

In this study a spatially and temporally resolved emission inventory of particulate matter ($PM_{2.5}$ and $PM_{2.5–10}$) and gaseous pollutants (BVOCs) from natural sources was created for the AMA and TMA for the period 2000–2010 (Fig. 1). In particular, the inventory includes the emissions of primary particles from natural sources i.e., emissions of windblown dust (WB) from agricultural and vacant lands and sea salt particles emissions from the breaking of waves at the Sea Shore-surf zone (SS_SS) and the bursting of bubbles from oceanic whitecaps - Open Ocean (SS_OO). In addition, the inventory comprises potential secondary organic particle emissions from natural sources, in particular biogenic gaseous pollutants (BVOCs) emissions from vegetation during photosynthesis, plant respiration and vaporization from stores within the plant tissue and the emissions of NO_x, SO_x, NMVOCs, NH_3, $PM_{2.5}$ and $PM_{2.5–10}$ from anthropogenic sources (industrial, non-industrial, commercial and residential combustion; industrial production; transportation; agriculture; waste treatment; solvent use). The methodology for the creation and the spatial and temporal disaggregation of the emission inventory is described and the analysis is then focused on the temporal (inter-annual and seasonal/monthly) and spatial evolution of PM and their precursor gases emissions from natural sources in the metropolitan areas of Athens and Thessaloniki for the period 2000–2010. Also, the temporal and seasonal variation of their contribution to total primary and secondary PM emissions in the areas of interest is examined.

METHODS

Emissions of Fugitive Windblown Dust (WB)

Dust emissions (g/cm^{2}s) from wind erosion of agricultural and vacant lands were estimated as a function of landcover, soil texture, wind friction velocity and threshold friction velocity at the study areas during the study period using the method presented in Aleksandropoulou *et al.* (2013) (methodology from Choi and Fernando (2008) adjusted for data available for AMA and TMA). Surface roughness length values were assigned to each land cover type based on the values presented by Mansell *et al.* (2004). In order to account for the effect of soil moisture on emissions of windblown dust, the emissions evaluated were downscaled by adopting the assumptions previously used by Korcz *et al.* (2009) in their calculations of windblown dust emissions over Europe (erosion potential, reservoir recharging time, inactive periods).

Emissions of Sea Salt Particles

Sea Shore Emissions (SS_SS)

The sea salt emissions (in g/m^{2}s μm) by the breaking of waves at sea shore were estimated using the source function provided by de Leeuw *et al.* (2000) modified according to Zhang *et al.* (2005) in order to account for the effect of relative humidity (80% in the calculations) on the size distribution of emissions (applicable for wind speeds lower than 9 m/s and for particle diameter at formation in the range 1.6 to 20 μm). The length of the coastline covering sea shore was calculated from relevant spatial data available from the Hellenic Ministry for the Environment, Energy and Climate Change (geodata.gov.gr) and the surf zone width was assumed equal to 50 m (mean surf-zone).

Open-Ocean Sea Emissions (SS_OO)

Hourly sea-salt particle emissions (particles/m^2s) from the sea surface (PM_{10} disaggregated in eight size bins) were computed as a function of the wind speed and the size of particle which depends on the relative humidity (RH) of the atmospheric layer above the sea surface, according to Grini *et al.* (2002). It was assumed that the RH at the thin atmospheric layer above the sea surface has a constant value equal to 80% (Aleksandropoulou *et al.*, 2004), therefore the radius for dry particles equals to half of their wet radius (Fitzgerald 1975). For each size bin the particles flux F was converted to mass (g/h) using a density of ~2200 kg/m^3 for dry seasalt particles (Hess 1998). More details on the methodology can be found in Aleksandropoulou *et al.* (2013).

Emissions of Biogenic Volatile Organic Compounds (BVOCs)

BVOCs emissions (in μg/month) were estimated using the modification of the methodology presented in the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (2007) previously described in Aleksandropoulou *et al.* (2013). In particular, BVOCs monthly emissions were calculated as a function of the foliar biomass densities and emission potentials of the species found in the areas of interest (adapted from the EMEP/CORINAIR Guidebook (2007), Yay *et al.* (2005), Steinbrecher *et al.* (2008) and Karl *et al.* (2009) and assigned to each land cover class in accordance with predominant species of flora in the areas of interest according to FILOTIS database for the natural environment of Greece and the Ministry of Rural Development and Food), the number of standard daily light hours per month, the season (growing and dormant), and environmental correction factors representing the effects of temperature and solar radiation changes on emissions.

Emission Inventory of Anthropogenic Sources

Annual anthropogenic emissions of gaseous pollutants (NO_x, SO_x, NMVOCs and NH_3) and particulate matter ($PM_{2.5}$ and $PM_{2.5–10}$) were derived from the UNECE/EMEP database (EMEP/CLRTAP 2014; CEIP, Emission from Greece during 2000–2010 as used in EMEP models; classified according to SNAP 97; tn/yr; 50 × 50 km^2). The anthropogenic emissions were spatially and temporally disaggregated according to the methodology presented in Aleksandropoulou *et al.* (2011). Particularly agricultural emissions of NMVOCs and NH_3 from fertilizer use, unfertilized crops and animals (manure management) were estimated as described in Aleksandropoulou *et al.* (2011). The location and emissions of Large Point Sources (LPS) were derived from the E-PRTR v5.1 database (European Pollutant Release and Transfer Register). Large point sources are defined as facilities whose combined emissions, within the limited identifiable area of the site premises, exceed the pollutant emission thresholds specified in annex II of the E-PRTR Regulation (EC No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC; ECE/EB.AIR/125). PM_{10} emissions from the E-PRTR dataset were split to $PM_{2.5}$ and PMcoarse using the emission ratio $PM_{2.5}/PM_{10}$ from the EMEP database (≈0.64 for Sector 1, ≈0.23 for Sector 3, ≈0.37 for Sector 4, and ≈0.65 for Sector 10) and the TNO dataset (≈0.63 for Sector 6; Berdowski *et al.*, 1998). Table S2 in the supplementary material of the manuscript summarizes the anthropogenic and natural emission sources included in the analysis together with relevant details on the data and methodology used.

Aerosol Formation

Emissions of each gaseous pollutant precursor to PM were weighted to account for potential secondary aerosol formation according to the methodology of de Leeuw (2002). The weighting factors have been derived on European level and account for the fraction of emissions of pollutant changing into aerosol and the molecular weight difference (values are 1 for primary PM, 0.54 for SO_2, 0.88 for NO_x, 0.64 for NH_3 and 0.02 for NMVOC). Emissions of each pollutant are multiplied by the aerosol formation potential and results are reported in PM_{10} equivalents.

Input Data and Assumptions

The landuse data used in this study were derived from the Land Cover 2000 database of the European Commission programme to COoRdinate INformation on the Environment across Europe (EEA CLC 2000, v2009) (Level 1 classification is depicted in Fig. 1). Due to the absence of relevant data, changes in landcover in the areas during the period 2000–2010 were not taken into account in the calculations. In addition, changes in landcover due to forest fires were not incorporated in the calculations since the results from Aleksandropoulou *et al.* (2013) have shown that their effect in PM_{10} windblown dust and BVOCs emissions from AMA was insignificant (more than 2230 ha of forests and 1841 ha of woodlands burnt during the period 2000–2008 changed WB and BVOCs emissions during 2008 by 1.7% and –3.5%, respectively).

Data on the soil texture were available by the European Soil Database (ESDB v2.0 2004) either in the form of the soil type as in FAO-UNESCO, 1974 classification (used in modified CEC 1985) texture classes (the dominant and secondary surface textural classes are provided) or as a textural profile containing the fractions of clay, silt and sand in the soil horizon.

Monthly averages of temperature and air velocity were calculated from meteorological data retrieved from the FOODSEC Meteodata distribution page (action developed in the framework of the EC Food Security Thematic Programme; European Centre for Medium-Range Weather Forecast (ECMWF) ERA INTERIM reanalysis model data; temporal analysis 10-days; spatial resolution 0.25 degree). In addition, data on the monthly averaged days with rainfall used in the calculations were retrieved from the HNMS (Hellenic National Meteorological Service) database on climatology for meteorological stations in and round the area of interest (the values therefore correspond to a period spanning over at least 40 years). The temporal resolution of meteorological data can affect the emission estimates

especially on local scales as it has been previously shown by Ashworth *et al.* (2010) for global isoprene emission estimates. The use of ambient temperature and light-intensity provides a reasonable approximation to leaflevel light and temperature (moderate uncertainty for European conditions, EMEP/CORINAIR 2007). On the other hand, the use of monthly averaged daytime temperature leads to large errors in the calculations, but only of order 20%, which is much less than the uncertainties in the emission potentials (EMEP/CORINAIR 2007). Uncertainties in emission potentials can occur from species misidentification, inaccurate determination of VOC emission, unrealised discrepancy between assigned versus actual emission potential (Wang *et al.*, 2005). For example a uniform emission rate of 1.5 μg/g/h of OVOCs was used for all tree species (and consequently landcover classes) according to Guenther *et al.* (1994) although it is recognised that values can range from 0.5–5 μg/g/h (EMEP/EEA 2013). In addition the use of a constant emission factor at standard conditions for each plant is a simplification because they are influenced by many factors such as genetic disposition, flowering, herbivory, past environmental conditions, age of leaves, soil moisture stress (Guenther *et al.*, 2006; Müller *et al.*, 2008; Oderbolz *et al.*, 2013 and References therein). In particular, Smiatek and Bogacki (2005) assessed the uncertainty of a VOC emission inventory caused by each driving parameter (land cover, temperature, light intensity, foliar biomass, leaf area index and plant specific emission factors) using Monte Carlo analysis. Their findings indicated that the largest uncertainty results from errors of the emission factors (of up to 134% for monoterpene emissions) followed by errors in temperature (–25% to 31% for monoterpene and –34% to 45% for isoprene emissions, respectively) and foliar biomass (± 22%).

The uncertainty in BVOCs emissions inventories has been reported in previous studies to be in the range of factor 3 to 5 for isoprene and monoterpene and larger than 5 for other VOC (Simpson *et al.*, 1999). Also Hanna *et al.* (2005) estimated uncertainties caused by errors in BEIS3 model parameters with a Monte Carlo study in order of 3 for monoterpene emissions and of ± 20% for OVOCs, whereas Wang *et al.* (2005) estimated the uncertainty of the BVOCs emission inventory for Yunnan Province to be over 100% and Guenther (2000) to 300% for North America (ranging from 50% in summer regional values to over 1000% for OVOCs).

It has also been assumed that monthly averaged wind speed values can be used in predicting the emissions of WB and of sea salt particles. Although windblown dust emission rates calculated using monthly averaged wind speed values can differ substantially from the actual ones, the error introduced in predicted monthly emissions is not so significant and can be considered the same to that introduced by uncertainty in other parameters (i.e., the soil moisture content and texture, the surface roughness length, and constraining factors like the vegetation coverage and the presence of non-erodible elements) (Aleksandropoulou *et al.*, 2013). As regards the SS_OO and SS_SS emissions, the same methodology applied in Aleksandropoulou *et al.* (2013) was used to justify the assumption. In particular, the emissions from the sea surface were calculated using both monthly averaged values of meteorological parameters and 3 h instantaneous values (assumed to occur throughout the 3 h period) derived from the EMEP UNIFIED model input files (EMEP/MSC-W 2011) for one month (August 2008). It was found that 446 Mg of sea salt $PM_{2.5}$ and 2050 Mg of sea salt $PM_{2.5–10}$ were emitted from the open ocean whereas at sea shore were emitted 501 Mg $PM_{2.5}$ and 3903 Mg $PM_{2.5–10}$ of sea salt during August 2008. Based on the 3 h instantaneous wind speed values during August 2008 approximately 22% and 8% more sea salt particles were emitted from open ocean and at sea-shore, respectively. It must be also noted that changes due to snow cover and rain on daily PM and BVOCs emissions could not be taken into account in the calculations due to the spatial and temporal resolution of the meteorological data. However, their effects on monthly emissions were incorporated in the calculations by downscaling the results by considering periods with rain and snow as inactive for WB emissions.

The annual emissions were spatially disaggregated and allocated to grids covering each area of interest. The domain for each area of interest was created based on the availability and spatial resolution of the officially reported emission data in the UNECE/EMEP database (EMEP/CLRTAP 2009; for comparison with anthropogenic emissions). Each domain was covered with a high resolution grid (1×1 km^2) for the spatial distribution of emissions (European Terrestrial Reference System (ETRS) 1989 Lambert Azimuthal Equal Area (LAEA) projection, Central Meridian: Greenwich, false easting: 4321000 m, false northing: 3210000 m, central meridian: 10.0, latitude of origin: 52.0, D_ETRS_1989). The emission estimation methodology used in this study resulted in the calculation of emissions either in the form of emissions per cm^2 of area with specific landcover and soil characteristics (SS, WB) or as emissions over areas (in m^2) of specific vegetation type which were then combined to produce emissions per grid cell (1 km^2). The spatial resolution of meteorological data can also affect the emission estimates and their spatial distribution especially on local scales as it has been previously shown by Pugh et al (2013) for global isoprene emission estimates. In this study we used meteorological data averaged over the domains therefore the spatial distribution of emissions depends only on the landuse, the soil characteristics and the vegetation type. Finally, based on the above assumptions any observed variation in natural emissions arises solely from changes in meteorological conditions.

RESULTS AND DISCUSSION

Annual PM Emissions

The annual anthropogenic and natural emissions of $PM_{2.5}$, and $PM_{2.5\text{-}10}$ from the AMA during the period 2000–2010 are presented in Fig. 2(a). A decreasing trend in natural PM_{10} emissions (8.6%) was observed as while on the other side anthropogenic PM_{10} emissions were enhanced (51%), particularly during the last four years compared to the rest of the period (increase of emissions from commercial and residential heating and industrial combustion). It was found

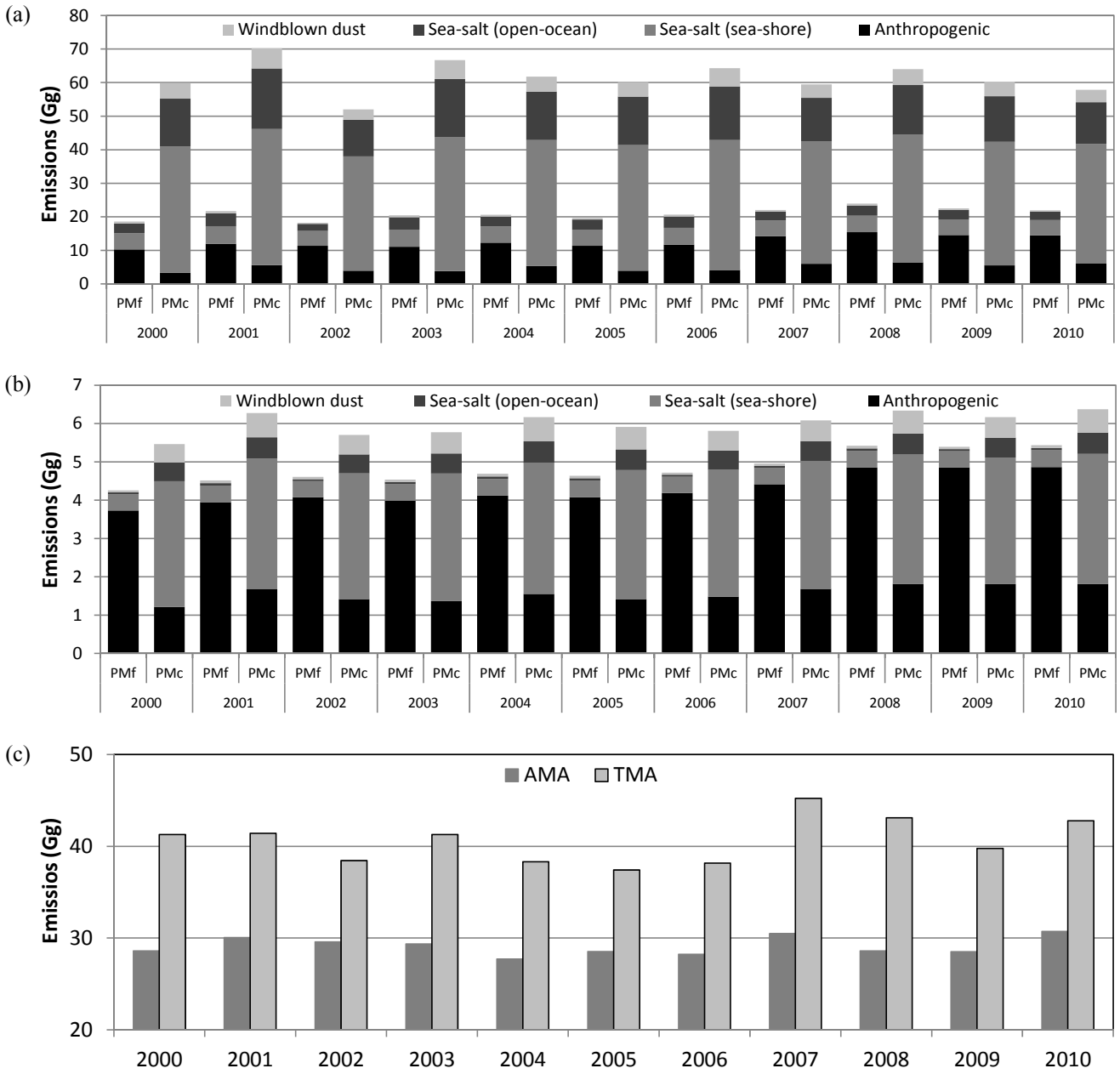

Fig. 2. Annual emissions of $PM_{2.5}$ (PMf) and $PM_{2.5–10}$ (PMc) from natural and anthropogenic sources in (a) AMA and (b) TMA and (c) annual emissions of BVOCs from AMA and TMA, for the period 2000–2010.

that the annual amount of $PM_{2.5}$ emitted from the sea surface was in the range 6.5 to 9.1 Gg, in particular 3.0 ± 0.5 Gg of SS_OO and 4.8 ± 0.2 Gg of SS_SS were emitted. Emissions of WB ranged from 0.35 to 0.67 Gg per year whereas anthropogenic emissions were 12.6 ± 1.6 Gg. As regards $PM_{2.5–10}$, the annual averages of emissions were in the range 10.9–18.1 Gg and 34.1–40.6 Gg for SS_OO and SS_SS emissions, 3.1–6 Gg for WB and 3.4–6.4 Gg for anthropogenic emissions. $PM_{2.5}$ emissions from natural sources in AMA in 2010 were decreased by approximately 9.6% compared to their 2000 values, while $PM_{2.5–10}$ emissions dropped by 8.5%. Specifically, $PM_{2.5}$ and $PM_{2.5–10}$ emissions of WB have decreased 22% while for sea salt particles the decrease was approximately 9% for the fine fractions of particles and 7.3% for the coarse. Natural SS emissions were decreased due to lower wind speeds in 2010 (4.2 ± 0.65 m/s) compared to 2000 (4.4 ± 0.6 m/s) while the decrease in WB emissions is also attributed to the lower seasonal wind speeds during the dryer warmer period of the year (average of values used in emission calculations; 2010: 3.7 ± 0.5 m/s; 2000: 4.3 ± 0.7 m/s).

Overall, the contribution from natural sources to total primary PM_{10} emissions was 78.7 ± 3.04%, specifically 39.9 ± 4.2% and 92 ± 1.7% for $PM_{2.5}$ and $PM_{2.5–10}$ emissions, respectively. In particular, the contribution from the sea surface to the primary particulate pollution over the AMA was in the range of 32.3–42.8% for $PM_{2.5}$ while it was 84.5 ± 1.4% for $PM_{2.5–10}$. Likewise, WB emissions from agricultural

and vacant lands accounted for approximately 2.5 ± 0.4% and 7.4 ± 0.8% of $PM_{2.5}$ and $PM_{2.5–10}$ emissions in AMA, respectively. The annual variability in the relative contribution from natural sources to primary PM emissions depends on the meteorological conditions as well as on the variation of anthropogenic emissions. Specifically, the major anthropogenic sources for $PM_{2.5}$ in AMA during the studied period have been the combustion in the non-industrial sector (mainly emissions from heating) and other mobile sources and machinery. Emissions from the above two sectors have increased by 31% and 3.5% since 2000, respectively (see Table S1 for relative activity statistics).

Likewise, particulate matter emissions during the period 2000–2010 from TMA are depicted in Fig. 2(b). It was found that natural PM_{10} emissions have increased by approximately 7.4%. In particular, $PM_{2.5}$ emissions from TMA, the majority of which were anthropogenic (4.3 ± 0.4 Gg; ~88.6%), were increased by 28%, whereas $PM_{2.5–10}$ emissions were increased by 17% and were mainly produced by natural sources. Natural $PM_{2.5}$ emissions from the sea surface and agricultural and vacant lands increased approximately 8% during the period 2000–2010. The annual amount of $PM_{2.5}$ SS_OO emissions ranged from 0.05 to 0.07 Gg, SS_SS from 0.42–0.44 Gg whereas $PM_{2.5}$ WB emissions ranged from 0.05 to 0.07 Gg. $PM_{2.5–10}$ emissions from natural sources were also increased from 2000 (4.2 Gg) to 2010 (4.6 Gg), approximately 7%. Their main source was sea salt particles with approximately 3.9 ± 0.1 Gg of $PM_{2.5-10}$ emitted annually during the period 2000–2010 (87.3 ± 0.8%), whereas WB emissions ranged from 0.48 to 0.63 Gg. The emissions of $PM_{2.5}$ and $PM_{2.5–10}$ WB have increased 27% while for sea salt particles the increase was approximately 6% for the fine fraction of particles and 4.8% for the coarse fraction. The observed increase in natural PM_{10} emissions is attributed to the higher wind speeds in 2010 compared to 2000 (average of values used in emission calculations; 2010: 2.3 ± 0.3 m/s; 2000: 2.2 ± 0.2 m/s). The contribution from natural sources to PM_{10} emissions was 46.1 ± 2.2% for TMA, specifically 11.4 ± 0.9% and 74 ± 2.2% to $PM_{2.5}$ and $PM_{2.5–10}$ emissions, respectively. In particular, the contribution from the sea surface to the total particulate pollution over the TMA was 10.1 ± 0.8% for $PM_{2.5}$ and 64.6 ± 2.2% for $PM_{2.5–10}$ while WB accounted for approximately 1.3 ± 0.1% and 9.4 ± 0.6% of $PM_{2.5}$ and $PM_{2.5–10}$ emissions, respectively, during the period 2000–2010.

Seasonal Variation of Natural PM Emissions

The monthly variation of natural PM emissions depends on the meteorological conditions. It was found that SS_SS emissions did not exhibit significant seasonal variation while on the other hand SS_OO emissions were more enhanced during the cold period of the year (October–March). In AMA enhanced emissions of sea salt particles occurred also during the warm period due to the Etesian winds. Most of the emissions of natural PM occurred during the cold period of the year in both areas due to the higher wind speeds in the cold season of the year. In particular, the Warm/Cold period emission ratios in AMA equal to 0.9 for $PM_{2.5}$ and $PM_{2.5–10}$ SS_SS emissions, 0.88 for $PM_{2.5}$ and $PM_{2.5–10}$ WB emissions, 0.69 for $PM_{2.5}$ and 0.73 for $PM_{2.5–10}$ SS_OO emissions. Likewise, in TMA the Warm/Cold period emission ratios equal to 0.94 for $PM_{2.5}$ and $PM_{2.5–10}$ SS_SS emissions, 0.74 for $PM_{2.5}$ and $PM_{2.5–10}$ WB emissions, 0.64 for $PM_{2.5}$ and 0.8 for $PM_{2.5–10}$ SS_OO emissions. Higher values were found during the period December to February/March and lower for May to June.

The seasonal variability in contributions from natural sources to total $PM_{2.5}$ and $PM_{2.5–10}$ emissions in AMA and TMA was also examined. It was found that in AMA SS_SS particles had the largest contribution to PM emissions with monthly average values ranging from 17.3 ± 2% to 27.5 ± 1.7% for $PM_{2.5}$ and from 57.8 ± 5.2% to 67.7 ± 2.2% for $PM_{2.5–10}$ and relatively the smaller variation during the studied period (Fig. S1). The minimum contribution values were observed in February whereas the maximum in September for $PM_{2.5}$ and in May for $PM_{2.5–10}$ due to the increase in anthropogenic PM emissions in AMA during the winter months (the contribution to $PM_{2.5}$ emissions from non-industrial combustion increased from 19% to 28%). On the other hand, in AMA the monthly contribution to $PM_{2.5}$ and $PM_{2.5–10}$ emissions from SS_OO particles ($PM_{2.5}$: 4.7%–31.7%; $PM_{2.5–10}$: 11.9%–36.4%) and WB ($PM_{2.5}$: 0.7%–7.7%; $PM_{2.5–10}$: 2.3%–15.7%) showed large variation during the period 2000–2010. In TMA the monthly variation in contributions was similar to AMA, however with smaller values (due to land cover differences in the two areas; Fig. S2). Particles emitted at the sea shore (SS_SS) had the largest contribution to primary $PM_{2.5}$ emissions, compared to other natural sources, with monthly values in the range from 6.1 ± 0.7% to 12.1 ± 0.7%. Additionally, the mean monthly contributions to total primary $PM_{2.5}$ emissions from SS_OO and WB particles during the period 2000–2010 in TMA were 1.2 ± 0.1% and 1.3 ± 0.1%, respectively, in agreement with the results from Terzi *et al.* (2010) on the seasonal variation of crustal elements in PM_{10} in Thessaloniki. The monthly variation was mainly associated with seasonal changes in anthropogenic emissions rather than changes in meteorological conditions. With regard to $PM_{2.5–10}$ emissions, the monthly contribution from natural sources was ranged from 7.8 ± 0.7% to 10 ± 0.6% for SS_OO, from 6.9 ± 2.2% to 12 ± 2% for WB while for SS_SS were large compared to the other sources, approximately 55.8 ± 2.1%.

Overall, there was no significant difference in the relative contribution of natural $PM_{2.5–10}$ emissions to primary $PM_{2.5–10}$ emissions in AMA during the cold and warm period of the year (up to 1.96% for 2010; yearly average value of 91.97 ± 1.69%) since they are mainly of natural origin. On the other hand the contribution of $PM_{2.5}$ emissions from natural sources to the total emissions over the area was generally enhanced during the warm period of the year (difference up to 9.53% for 2009; warm period average value of 43 ± 3.9% compared to 37.6 ± 4.4% during cold periods) due to the decrease of emissions for heating. In TMA no significant difference in the relative contribution of natural emissions to primary $PM_{2.5}$ and $PM_{2.5–10}$ emissions during the cold and warm period of the year (average values for: $PM_{2.5}$ warm period 13.8 ± 1.0%, cold period 10.3 ± 0.8%; $PM_{2.5–10}$ warm period 73.8 ± 2.6%, cold period 73.8 ± 2.1%).

BVOCs Emissions

In Fig. 2(c) are shown the average emissions of BVOCs for the areas of interest. It is observed that emissions of BVOCs are enhanced in 2010 compared to 2000. In particular, BVOCs emissions have increased since 2000 by 7.4% in AMA and by 3.6% in TMA. The average emissions of BVOcs during the period 2000–2010 from AMA and TMA were 29.1 ± 0.94 Gg, 40.7 ± 2.35 Gg and 9.8 ± 0.4 Gg, respectively. The annual variability in the emissions of BVOCs depends on the meteorological conditions. Although the average temperature has increased slightly from 2000 to 2010, there was a clear increasing trend observed in the minimum temperatures which is important to emissions. Specifically, the minimum temperature was almost doubled in 2010 compared to 2000 in AMA (4°C increase, both values above 0°C) and was more than 6°C enhanced in 2010 (above 0°C) compared to the 2000 value (below 0°C) in TMA. In addition, BVOCs emissions were found increased from April to September (warm season) due to the enhanced solar radiation and temperature, while the maximum monthly emissions were observed in July and the minimum during January at both areas (Fig. S3). During the warm period are emitted 86.9 ± 0.6% and 91.3 ± 0.4% of annual BVOCs emissions in AMA and TMA, respectively.

Contribution from Natural Sources to Total Primary and Secondary PM Emissions

The contributions from sea-salt, windblown dust, secondary PM formed by BVOCs and anthropogenic emissions to total annual primary and secondary PM emissions for the areas of interest were also examined. Sea-shore was the most abundant source of natural PM emissions in all areas. In particular, SS_SS particles accounted for approximately 64.8 ± 2.3% of natural primary and secondary PM emissions and 20.4 ± 1.8% of total primary and secondary PM emissions in AMA during the period 2000–2010. The corresponding values are 65.1 ± 0.9% and 7.8 ± 1.1% for TMA. Overall the contribution from natural sources to total primary and secondary PM_{10} emissions were 31.5 ± 2.8% for AMA and 11.97 ± 1.63% for TMA. Natural PM_{10} emissions remained relatively unchanged throughout the period 2000–2010 however the contribution from natural emissions to total primary and secondary PM emissions have increased from the beginning to the end of the studied period because of the decrease observed in gaseous PM precursors emissions from anthropogenic sources (e.g., by the increase of the share of clean technology passenger cars in the vehicles fleet; decline in agricultural land and livestock numbers because of the boost in construction activities; replacement of oil boilers with electrical heaters and natural gas boilers; increase in the use of natural gas and renewable sources for electricity production; Progiou *et al.*, 2011; Aleksandropoulou *et al.*, 2012).

The monthly variation of natural sources contribution to total primary and secondary PM_{10} emissions in AMA and TMA are depicted in Figs. 3(a) and 3(b). Each box depicts the lower, the median and the upper quartile (bottom: 25^{th}, band: 50^{th} and top: 75^{th} percentile) of emission contributions for each month, whereas the point and the whiskers show the average, minimum and maximum values. Particles emitted at the sea shore have the largest, compared to other natural sources of emissions, contribution to PM_{10} equivalent emissions in both areas with monthly values in the range from 19 ± 1.8% to 21.9 ± 1.7% in AMA and 7.2 ± 1% to 8.6 ± 1.2% in TMA. SS_OO were the second significant natural contributor to PM_{10} equivalent emissions in AMA with monthly average contribution values in the range of 5.2 ± 1.1 to 10.9 ± 3.2%. Moreover, the monthly averages of contribution values for WB dust ranged from 1.3 ± 0.4% to 3.4 ± 1.5% in AMA and 0.9 ± 0.3% to 1.9 ± 0.5% in TMA. The average contribution of BVOCs to total PM_{10} equivalent emissions (anthropogenic and natural) ranged from 0.05 ± 0.01%–0.7 ± 0.1% in AMA and 0.2 ± 0.03%–4.4 ± 0.9% in TMA and was increased during the warm period due to the enhanced solar radiation and temperature. Overall the contribution from natural sources to total primary and secondary PM_{10} equivalent emissions was 33.1 ± 3.2% and 29.8 ± 2.9% during the cold and warm periods in AMA, respectively, whereas in TMA the corresponding seasonal contributions were 11.3 ± 1.5% and 12.7 ± 1.8%.

Spatial Distribution of PM Emissions

Based on the assumptions (no landcover changes and meteorological conditions averaged over each domain) the spatial distribution of natural PM emissions was the same for every year throughout the period 2000–2010 and the same for $PM_{2.5}$ and $PM_{2.5–10}$ emissions. Inter-annual changes were found only in the cells including coastal areas which were considered insignificant. It was found that natural PM emissions are scattered over arable land, areas with sclerophyllus vegetation and the sea. In particular, emissions of sea salt particles are equally distributed over the open sea whereas observed variations at coastal cells correspond to differences in the length and complexity of the shoreline. The spatial variation of WB emissions is attributed to differences in the soil texture and landcover. With regards to landcover, the PM emission rates from natural sources increase in the order of partly built-up areas to dense forest with higher values over agricultural land (see Fig. 1). On the other hand, the spatial distribution of BVOC emissions varies seasonally (due to changes in seasonal emission factors and foliar biomass densities) and from year to year. BVOCs emissions in AMA concentrated over the Northern part of the area, the Eastern part of the Attica peninsula, Evoia at the NE and the Gerania mountains at the W part of the domain where areas with significant natural vegetation occur (forests and semi-natural areas) whereas in TMA were enhanced over the eastern part of the domain during both the warm and cold periods. OVOCs emissions, which are emitted from every non-artificial surface, were scattered over the whole domains.

In Fig. 3(c) is presented the spatial distribution of the average contribution from natural sources to total anthropogenic and natural primary and secondary PM_{10} equivalent emissions in the AMA and TMA during the period 2000–2010. It is observed that anthropogenic and natural emissions are concentrated over different areas. In particular, the average contribution from natural sources in

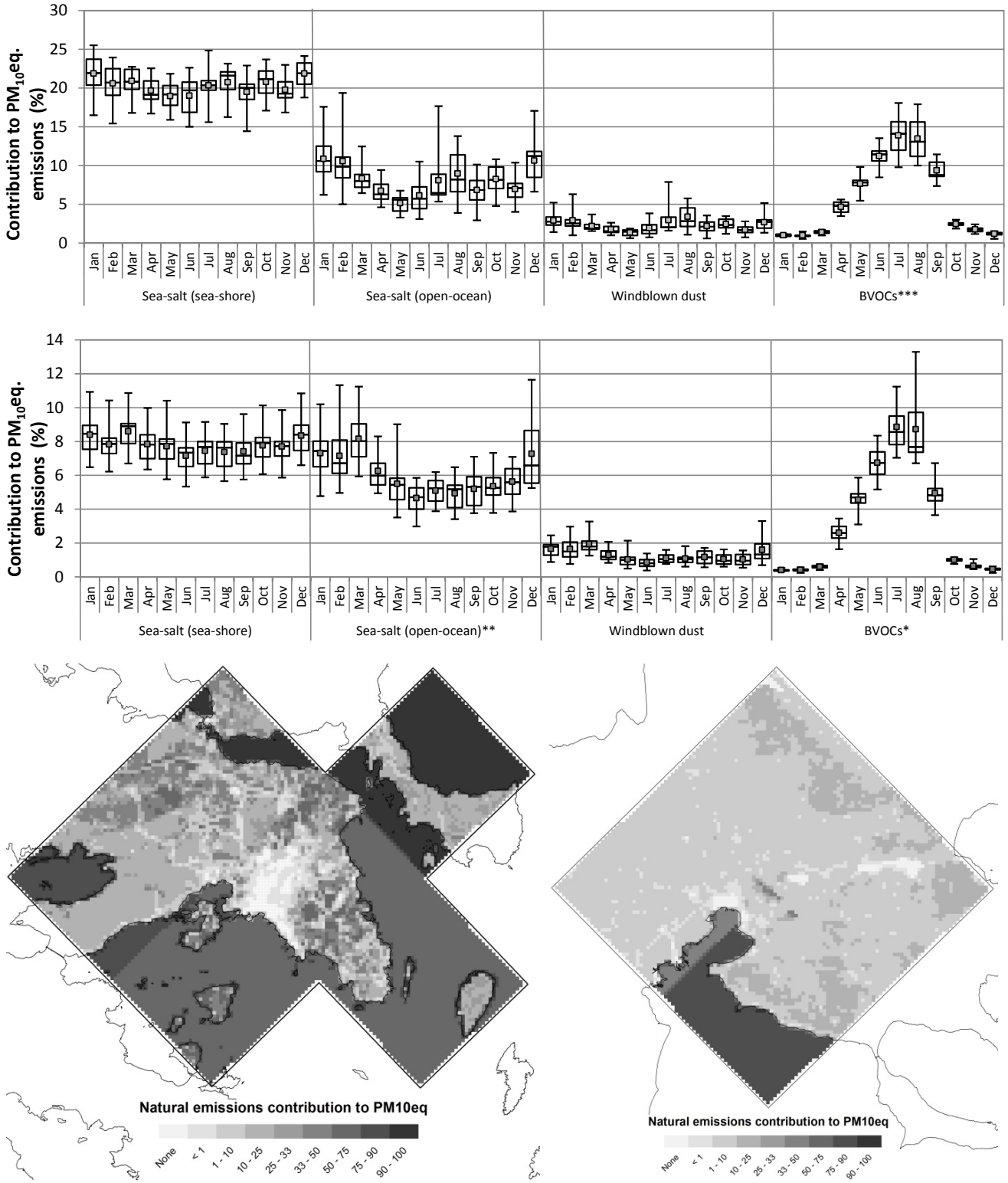

Fig. 3. Variation of monthly natural emissions contribution to total primary and secondary PM_{10} emissions (PM_{10} equivalents) in (a) AMA and (b) TMA (*Values are multiplied by 2; **Values are multiplied by 5; ***Values are multiplied by 20) and (c) the spatial distribution of the average contribution of natural sources to total anthropogenic and natural primary and secondary PM_{10} equivalent emissions in the AMA and TMA, for the period 2000–2010.

AMA was enhanced over marine waters (75.5 ± 23.5%; sea-salt particles), agricultural areas (31.2 ± 24.7%) and forests (34.7 ± 29.6%). Over artificial surfaces the contribution was 15.5 ± 23.9% (average of not null values). For TMA the contribution from natural sources was low compared to anthropogenic sources except for marine areas (38.4 ±

34.7%), agricultural areas (5.7 ± 6.9%) and in forests and seminatural areas (7.3 ± 5.2%). The contribution from natural sources to PM_{10} equivalent emissions over artificial surfaces in TMA, where it was not null, was 4.1 ± 10.3%.

CONCLUSIONS

The emissions from natural sources can be a significant contributor to air quality deterioration in urban areas resulting in PM_{10} background concentrations significant compared to the EU AQS. In this study the temporal and spatial distribution of the contribution from natural sources to primary and secondary emissions of PM in two large urban agglomerations in Greece over a period of 11 years (2000–2010) was investigated. The contribution from natural sources to primary PM emissions during the studied period was approximately 79% in the AMA and 46% in the TMA, with windblown dust emissions accounting for only a small fraction of total PM emissions (approximately 6% in both areas). Emissions of BVOCs were increased during the summer period whereas during the winter period anthropogenic emissions, especially from non-industrial combustion plants, were enhanced. Anthropogenic and natural emissions were concentrated over different areas in each domain. Natural PM_{10} emissions remained relatively unchanged throughout the period 2000–2010. However, the anthropogenic emissions of primary PM have been slightly increased and gaseous PM precursors were significantly decreased therefore the contribution from natural emissions to total primary and secondary PM emissions have increased from 2000 to 2010. The share of primary PM_{10} and gaseous precursors to secondary aerosol formation from natural sources to total equivalent PM_{10} mass in the areas was approximately 32% in AMA and 12% in TMA. Although primary emissions from natural sources cannot be reduced because they are subject to meteorological conditions, the production of secondary aerosols from pollutants emitted from natural sources can be suppressed by reducing the emissions from anthropogenic sources.

ACKNOWLEDGMENTS

This work was supported by the European Community (LIFE + Environment Policy and Governance) in the framework of the ACEPT-AIR LIFE+ 09 ENV/GR/000289 project.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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Received for review, November 10, 2014
Revised, March 21, 2015
Accepted, April 1, 2015

Contribution of natural sources to PM emissions over the metropolitan areas of Athens and Thessaloniki

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Supplementary material

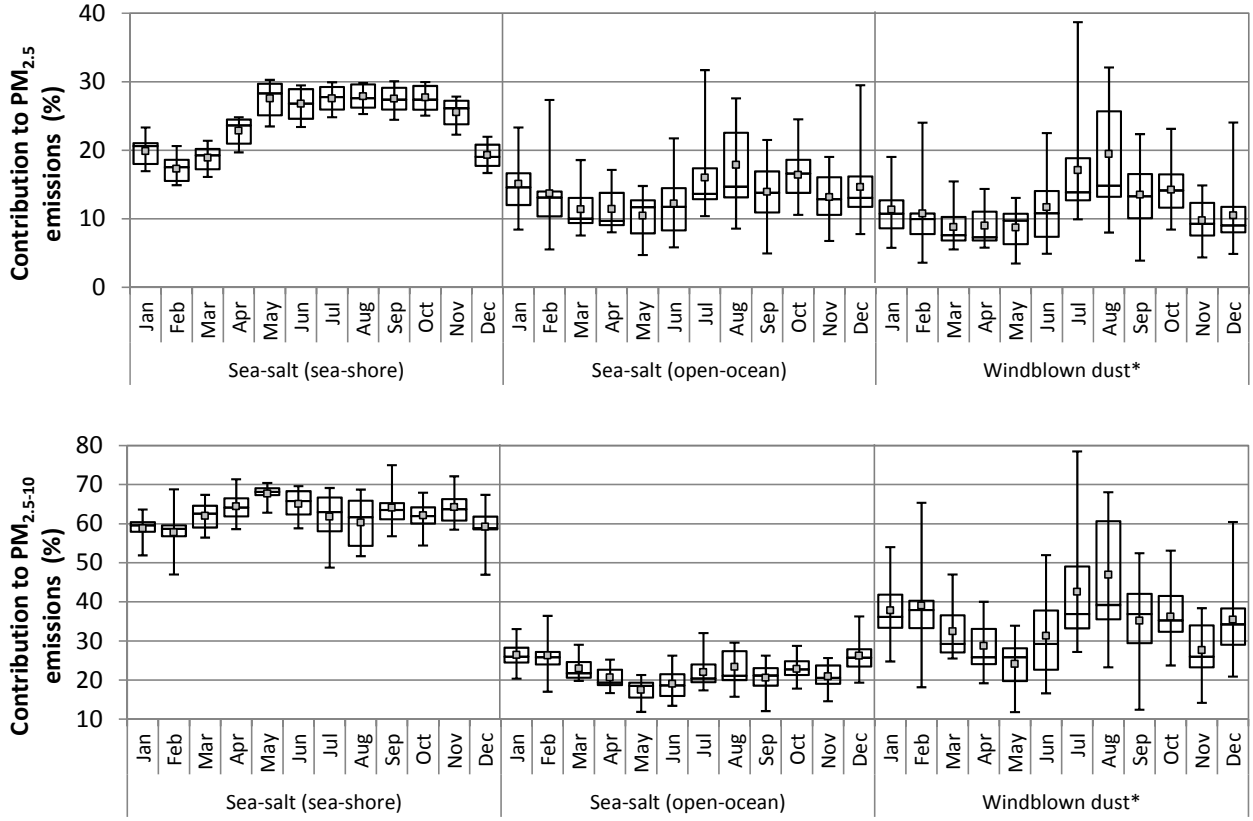

Fig. S1. Variation of monthly natural emissions contribution to (a) total primary $PM_{2.5}$ emissions and (b) total primary $PM_{2.5\text{-}10}$ emissions in AMA during the period 2000-2010 (*Values multiplied by 5).

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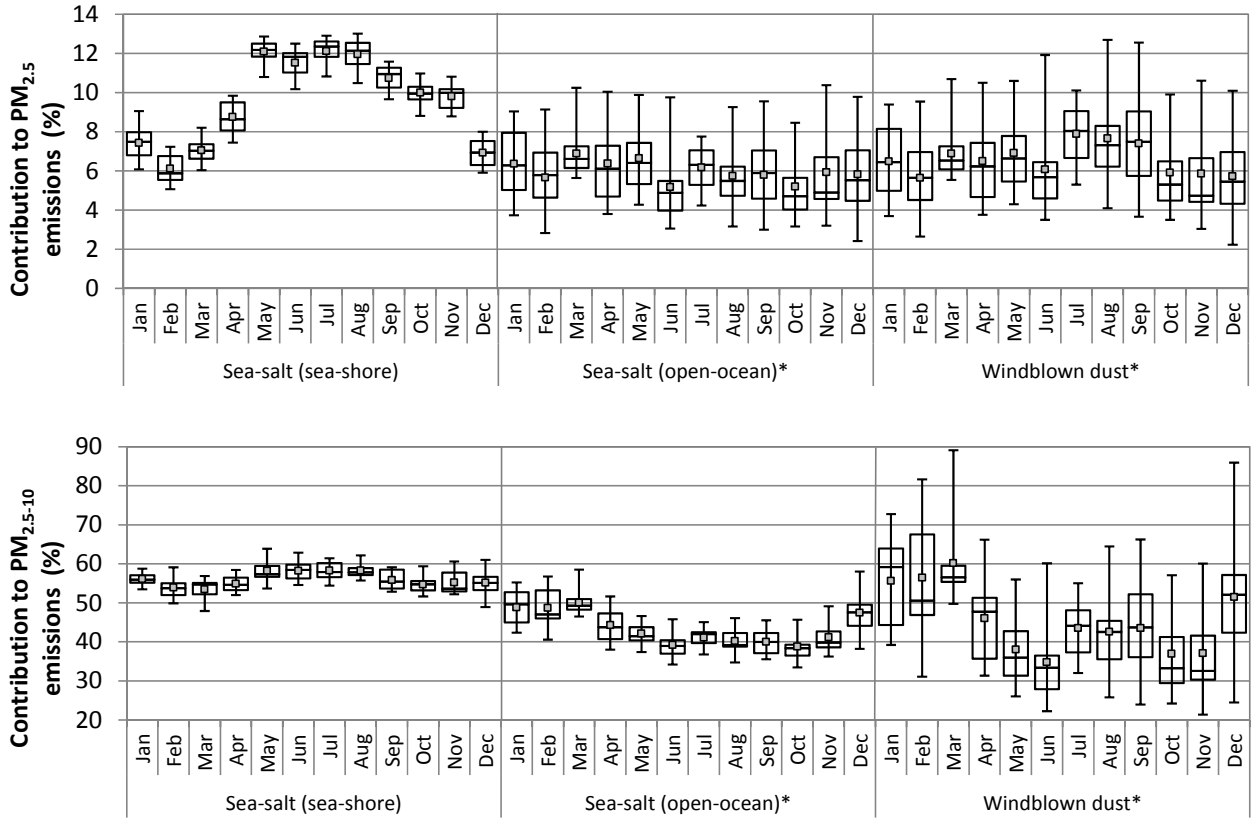

Fig. S2. Variation of monthly natural emissions contribution to (a) total primary $PM_{2.5}$ emissions and (b) total primary $PM_{2.5-10}$ emissions in TMA during the period 2000-2010 (*Values multiplied by 5).

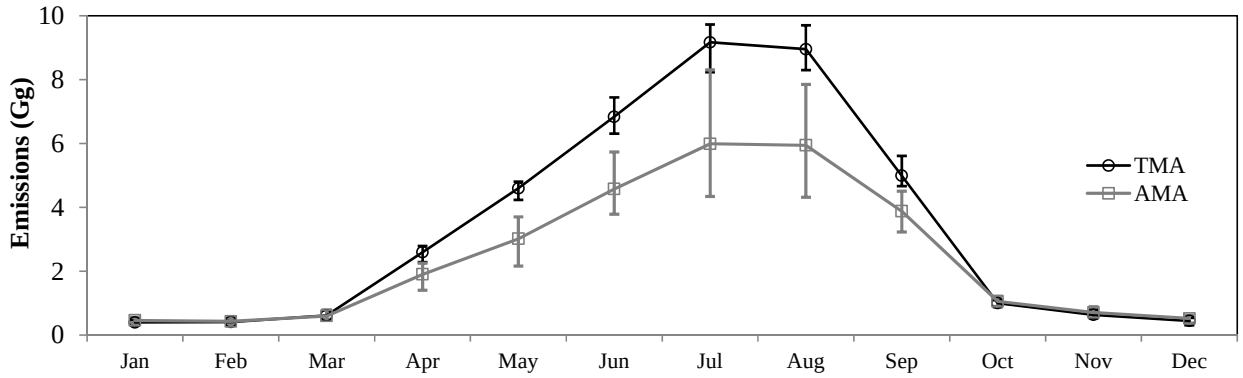

Fig. S3. Inter-annual monthly variation of BVOCs emissions in AMA and TMA for the period 2000-2010. Average, minimum and maximum monthly emission values are depicted.

Table S1 Comparison of emission sources and activity data in AMA and TMA for the year 2010 and % change compared to 2000 values (values retrieved from the EL.STAT.).

Parameter	AMA [a]		TMA [b]	
	2010	**% change**	**2010**	**% change**
Population (millions of inhabitants) [c]	3.83	-0.03	1.11	2
Electric energy consumption (thousand kwh)				
Domestic [d]	7349680	23	1864003	17
Commercial	5499426	37	150145	-86
Industrial	2617166	13	1325325	-23
Agricultural	72039	13	92860	-22
Public and Municipal	668163	26	167136	51
Street lighting	248596	26	69615	49
Number of Vehicles [e]				
Passenger	2756052	63	550844	61
Trucks	285817	19	101523	22
Busses	12733	1.2	2535	4.2
Motorcycles	669614	86	125852	87
Aircraft traffic				
Departures - Arrivals	181859		44938	
Freight and mail (tons)	96676		8902	
Coastal traffic (millions of passengers) [f]				
Embarked	5.00	31.6	0.06	-26
Disembarked	5.00	31.6	0.06	-19
Industry [g]	West Attica and Piraeus		Close to city centre	
Heating degree days (base temperature of 18°C) [h]	1253		1756	
Agriculture (thousands acres) [i]				
Annual crops	98	-27.4	1178	-5
Vineyards	50	-15.3	12	0
Areas under trees	249	-10.8	26	13
Other areas	73	9.0	190	850
Livestock (heads) [i]				
Cattle	4290	-31	67006	-5.9
Sheep	80156	-30	165286	-5.1
Goats	39517	-34	135130	-26
Pigs	6499	-64	11229	-28
Horses, Mules, Asses	239	-55	1016	232
Rabbits	18064	19	4860	32
Poultry	5140938	109	4959510	22
Construction (number) [j]				
New built properties	3740	-54	1343	-48
Extension of built properties	2307	-37	427	-27
Land distribution in each domain (km^2) [k]				
Artificial	640		243	
Agricultural	2103		4018	
Forest and semi-natural	2780		2294	

[a] Values refer to Attica region; [b] Values refer to Thessaloniki prefecture; [c] Population census 2001 and 2011; [d] of which approximately 64% are used for space heating according to the survey on energy consumption in households conducted during the period 01/10/2011 to 30/09/2012 by the Hellenic statistical authority; [e] In Thessaloniki the absence of a contemporary public transportation system forces people to overuse private cars and consequently leads to high emission regimes in the urban sites of the city (Kassomenos et al. 2011).; [f] values refer to Piraeus and Thessaloniki ports; [g] E-PRTR database; [h] Papakostas et al. 2005; [i] Results of Agricultural-Livestock Census 1999-2000 and 2009; [j] rapid expansion of road network and of Athens urban area occurred mainly before the Athens 2004 Olympics (Fameli et al. 2013); [k] EEA Corine LandCover 2000

Table S2 Summary of emission sources, methodology and data used for the construction of the emission inventory of the period 2000 – 2010.

	Emission Source sector	Input data and notes	Spatial analysis and allocation
Anthropogenic	2. Non industrial combustion plants	1; 2; 3	Area based on population density
	3. Industrial combustion	1; 2; 4	Area over artificial surfaces; Point at source location
	5. Extraction and distribution of fossil fuels and geothermal energy	1; 2; 3; 4	Area over artificial surfaces based on population density
	6. Solvent and other product use	1; 2; 3	Area based on population density; Point at source location
	7. Road transport	1; 2; 3; Road network	Line over road network, based on population density
	8a. Other mobile sources and machinery	1; 2; 4	Area based on landcover
	9. Waste treatment and disposal	1; 2; 3; 4	Area based on landcover and population density
	10. Agriculture	Livestock number and distribution of agricultural area from the Hellenic Statistical Authority, Emission factors as in Aleksandropoulou et al. 2011; 1; 2; 4	Area over agricultural land; Point at source location
	8b. International ship emissions	1; 2; 4	Distributed over sea areas
	Large Point Source emissions from sectors 1 (Combustion in energy production and transformation industries), 3, 4 (Combustion in manufacturing industries), 5, 6, 9 and 10	E-PRTR data at LPS coordinates in tn/yr gap filled based on the Industrial production indicator and the procedure described in the European Union emission inventory report 1990-2008; data handling as in Aleksandropoulou et al. 2011; 2 (for sector 1 modified as in Simpson et al. 2012)	Point at source location
Natural	Biogenic emissions	Meteorological data from FOODSEC Meteodata distribution page and the Hellenic national meteorological service; 4; Soil texture from the European soil database; Vegetation species from FILOTIS database; Emission factors as in Aleksandropoulou et al. 2013; Temporal profile based on monthly meteorological data	Area estimated for each cell
	Sea salt from open ocean		
	Sea salt at sea shore		
	Windblown dust		

[1] UNCLRTAP/EMEP database; 50 × 50 km^2; Mg/year

[2] temporal profile by GENEMIS

[3] Population density map

[4] Landcover map CLC 2000 v2009