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Total exposure to airborne particulate matter in cities: The effect of biomass combustion

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HIGHLIGHTS

- Exposure to PM increases significantly in wintertime due to biomass combustion for space heating
- Biomass burning significantly increases the levels of indoor PM of lower diameter
- Meteorological parameters explain about 80% of the ambient PM concentrations variability
- Peaks of intra-day PM intake rate do not correspond to intra-day ambient air concentrations
- Exposure assessment is greatly facilitated by coupling in silico tools to in situ measurements

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ABSTRACT

The study deals with the seasonal variability of PM exposure and the effect that biomass combustion has upon it in the urban environment. The study is based on measurements, chemical analyses and modeling results performed in Thessaloniki (Greece). The measurements campaign included the assessment of outdoor and indoor air quality and the evaluation of biomass use for domestic heating. The outdoor measurements highlighted a significant increase of PM10 (from 30.1 to 73.1 μg/m^3) and PM2.5 (from 19.4 to 62.7 μg/m^3) concentrations during the transition from the warm to the cold period of the year 2012 compared to 2011. The increase in ambient air PM during the winter was attributed to the use of biomass burning for space heating. The latter was verified by the presence of levoglucosan in the PM (concentrations up to 8 μg/m^3), especially for samples taken from the urban background site. Outdoor PM concentrations were also modeled using an artificial neural network model taking into account major meteorological parameters; the latter explained more than 90% of PM10 and PM2.5 day-to-day variability. Indoor concentrations followed a similar pattern, while in the case of fireplace use, average daily concentrations rise to 10 μg/m^3 and 14 μg/m^3 for PM2.5 and PM10 respectively. Indoor air concentrations were affected the most by the ambient air particle infiltration. Indoor air quality went down after 3 h of open fire biomass combustion for space heating. Personal exposure was significantly determined by overall indoor air quality. Yet, dynamic exposure analysis revealed that peaks of intake do not correspond to peaks of ambient air PM concentrations altering thus total exposure patterns. Thus, cost-effective public health protection has to aim at reducing the exposure profile of susceptible population sub-groups combining awareness raising, emission reduction measures and financial incentives to influence the choice of space heating systems.

1. Introduction

Particulate matter (PM) is currently one of the most serious urban environmental pressures on public health. PM can be directly emitted from a variety of sources, both natural and anthropogenic, or generated by atmospheric reactions, leading to a complex mixture of solid particles and liquid droplets with different size and chemical composition (Galindo et al., 2011), met in both outdoor and indoor environments (He et al., 2004; Lai et al., 2006).

Macro and micro environmental concentrations of PM are affected by seasonality, reflecting both changes in the prevalent meteorological conditions as well as PM emission patterns, traffic emissions and domestic heating being dominant among them. In fact PM levels in cities tend to be higher in the winter with respect to summertime especially when intensive emissions from human activities (e.g. traffic and spatial heating)

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are coupled with adverse weather, e.g. prevalence of anticyclonic conditions that limit long-distance transport of polluted air masses (Viana et al., 2008). Meteorology is a significant determinant of PM concentrations in ambient air since dispersion processes, removal mechanisms, and chemical formation of atmospheric particles depend on common meteorological descriptors such as wind speed, rainfall rate, and solar radiation. Increased levels of ambient air PM are generally associated with colder air temperature, especially when in tandem with lowering of the atmospheric mixing layer and atmospheric stability (Katsouyanni et al., 2001).

However, changes in prevalent meteorological conditions accompanying seasonality changes are also correlated to changes in emission patterns, although the latter are difficult to be dissociated from the direct effects of meteorology. Kinney et al. (2002) identified that negative correlation between PM10 and temperature was attributed to increased traffic density and domestic heating during winter. In fact, increased PM concentrations due to biomass combustion for space heating are a problem that mars different European regions (Puxbaum et al., 2007). Over the last five years this phenomenon has spread beyond the Scandinavian and alpine regions of Europe where wood biomass is used regularly for domestic heating (Fuller et al., 2014). A combination of two distinct drivers may be behind the observed trend. Biomass as heating fuel has been heralded as a valid CO_2 reduction alternative (Wagner et al., 2010) across Europe. Furthermore, the financial crisis in southern Europe over the last two to three years has brought about a significant increase in the market price of alternative fuels primarily due to exorbitant taxation—the increase on the non-solid fuel price was ca. 40–60%; the ultra-high market price together with the limited financial capacity of many households has resulted in an excessive use of biomass for space heating.

Indoor air PM concentrations are affected by the penetration of outdoor air as well as the presence of indoor sources (Karakitsios et al., 2014). Smoking and biomass use are the dominant among them (He et al., 2004; Lai et al., 2006). Irregular pollution peaks attributable to vacuuming, candle, or incense burning may also be observed. However, they are likely to contribute only a little to 24-h mean PM levels (He et al., 2004; Semple et al., 2012). Biomass-using households have two to four times higher PM10 and PM2.5 concentrations as measured from Banerjee et al. (2012) by a real-time laser photometer.

Exposure to PM is the result of aggregation of several components. It mainly reflects the outdoor and indoor concentrations, as well as the interaction between ambient and indoor air and the time spent by the exposed individuals in specific macro- and micro-environments. Refined aggregate exposure assessment reduces the uncertainties incorporated in exposure assessment with regard to specific exposure scenarios such as the contribution of individual indoor emission sources related to either different consumer behavioral patterns (Sarigiannis et al., 2012a) or accidental events that may take place indoors (Sarigiannis et al., 2012b). Computational tools supporting aggregate exposure assessment enable us to forecast population exposure to PM. However, due to the complexity of the processes that control formation, transportation and removal of particulate matter in the atmosphere, modeling and prediction of aerosol concentrations are considered to be more difficult and complex than forecasting of common gaseous pollutants. Thus, statistical techniques based on existing time-series are expected to be more reliable forecasting tools than deterministic approaches (Karakitsios et al., 2006). Among the several statistical techniques, artificial neural networks (ANN) are expected to show better aerosol forecasting performance when compared to the traditional ones such as regression models (Paschalidou et al., 2011; Vlachogianni et al., 2011). This is because they adapt better to fitting data describing highly non-linear physico-chemical processes (Grivas and Chaloulakou, 2006; Kassomenos et al., 2011a) or to assimilating different environmental data classes (Sarigiannis et al., 2009).

The study presented herein aimed at assessing in detail the population exposure to PM during wintertime in a large Greek metropolitan area (Thessaloniki) and how this exposure is affected by the use of biomass for domestic heating (use of open fireplaces). Exposure assessment was based on the computation of the total exposure of population sub-groups taking into account both ambient and indoor air quality, as well as the time-activity patterns of the respective individuals to account for physiological changes in the intake rate. Measurements and model results were fused to complete data gaps and to derive total exposure estimates.

2. Methodology

2.1. Study design

The study assesses overall personal exposure and actual population intake of PMx, taking into account both outdoor and indoor exposure patterns, the multiple interactions between outdoor and indoor particulate matter and interseasonal variability. The results are geared to support integrated health risk assessment for the urban population. Our methodology couples an extensive network of ambient air measurements across the urban canopy for a period of 6 months (from October 2012 to April 2013) to targeted indoor air PMx measurements in dwellings and exposure modeling. Field measurements are supported by laboratory analyses of the PM chemical composition focusing on the quantification of chemical markers revealing the effect of biomass combustion to the PM mass concentrations. PMx levels in the ambient air provide the input needed for the INTERA computational platform (INTERA, 2011), for the calculation of indoor concentrations, exposure and intake. The INTERA platform is linked to a database that provides the necessary data for estimating indoor PMx concentrations (emissions from various sources, indoor/outdoor air exchange rates, infiltration and deposition rates), as well as data related to exposure (time activity patterns, types of locations encountered) and intake (inhalation rates based on activities, gender and age group). The detailed time dynamics incorporated in the INTERA platform allow capturing in detail intra-day exposure variability related to changes in outdoor concentrations, selection of activities, and change in the indoor emission sources. This is very important, since different types of complex interactions (e.g. simultaneous changes in indoor emissions and outdoor concentrations) are translated into actual terms of human exposure and intake, thus transforming qualitative hypotheses into quantitative estimates. In order to support exposure scenario analysis an exposure forecasting model was built based on an artificial neural network (ANN) that uses the ambient air PMx measurement data from previous days and meteorological information to predict next day PMx levels in different types of urban environments and for different days in the week. Coupling the ANN to the INTERA platform allows us to predict actual total population intake of PMx and eventually assess intervention scenarios and risk management measures.

2.2. Field measurements

With regard to the outdoor measurements, PM10 and PM2.5 samplers were installed at 3.5 m above ground, located at two traffic and two background sites. Several streets with typical city heavy-traffic levels surrounded the traffic sites; in contrast the background sites were not exposed to direct traffic emissions. The measurements lasted for 6 months, covering the transition from the warm to the cold period (average daily temperatures 23 and 4 °C respectively) and vice versa.

Parallel measurements of indoor air quality (for PM10 and PM2.5) were carried out in 30 houses close to the traffic and the urban background station respectively, so as to validate the INTERA platform estimates. In order to identify the contribution of biomass burning in indoor air quality, targeted measurements for the effect of the open fireplaces operation on PM concentrations were carried out in a selected indoor location and under controlled conditions of air exchange rate (AER). More specifically, within a third floor apartment of 140 m^2, extensive measurements of PMx were carried out, while a Particle Number Count sizer was used for measuring temporal variation of PMx number and mass concentration.

Meteorological data needed for the study were provided by the local meteorological station from the traffic site.

2.3. Sampling, laboratory analyses and quality assurance

PM2.5 and PM10 samples were collected using 6 low-flow air samplers (ENCO PM, TCR TECORA, Italy). The samplers used sampling heads meeting the EN 12341 (PM10) and EN 14907 (PM2.5), and operated at a flow-rate of 38 L/min, with a collection time of 24 h per sample. Samples were collected on PTFE membrane filters with PMP supporting ring (PALL Life Sciences, Ø 47 mm, pore size 2 μm, USA). Teflon filters were analyzed gravimetrically for particle mass concentrations using an electronic microbalance with a sensitivity of ±1 μg after 24-h equilibration at a temperature between 20 °C and 23 °C and a relative humidity (RH) between 30 and 40%. Each filter was weighed at least three times before and after sampling, and the net mass was obtained by subtracting the average of the pre-sampling weights from the average of the post-sampling weights. Differences among replicate weightings were <5 μg for the blanks and the samples. Prior to the start of the sampling campaign, the flow rate of the PM2.5 and PM10 samplers was calibrated. Field blank filters were also collected and used to correct for background concentrations or influences from handling and transport.

The same PM samplers were used for 24 h sampling of PM10 and PM2.5 in 30 dwellings with and without the operation of fireplace or other open biomass combustion source. In addition, particulate matter was also monitored by a handheld Particulate Counter (Lasair II, Model. 525, Particle Measuring System). According to the operating principle of Lasair II, a built-in pump draws aerosol sample through the instrument with a flow rate of 0.01425 m^3/min. The resulting droplets are counted by a diode laser, 780 nm. The counter enables particle number concentration measurements in the size classes 0.5–0.7 μm, 0.7–1.0 μm, 1.0–5.0 μm, 5.0–10.0 μm, and 10–25 μm and pm above 25.0 μm. Lasair II has been used during indoor measurements with and without the operation of fireplace. Particles number concentrations were transformed into mass concentration using the following formula:

$$C_{\mu g/m^3} = \frac{PNC \cdot d \cdot (D_{median})^3 \cdot \pi}{6}$$

where *PNC* is the particle number concentration for the given range of particles diameter, *p* is the particle density, taken equal to 1 g/cm^3 and *D-median* is the median diameter for the selected class of particles.

The collected filters were analyzed for specific markers allowing us to estimate the relative contribution of biomass combustion to the generation of PMx in the air of Thessaloniki. Black carbon content of the sampled PMx was measured using a Magee Scientific SootScan™ Model OT21 Optical Transmissometer. The instrument measures the optical absorption of the deposited particles on the sampled filter using a wavelength light source operating at 880 nm (IR).

Levoglucosan content was determined according to the following procedure (Fabbri et al., 2008): a quarter of each 47 mm filter was cut and spiked with a known quantity of surrogate standard. The spiked filter parts were extracted twice for 20 min with 15 mL ethyl acetate (EtOAc) under ultrasonic agitation in sealed flasks. Each extract was filtered by means of a 5 mL syringe through a 0.2 mm teflon filter into a conical flak vial. The combined extracts were dried by rotary evaporation, and the residue was re-dissolved with EtOAc and transferred into 4 mL glass vials. The EtOAc solution (0.5 mL) was filled with 20 mL pyridine and 100 mL bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (Supelco). The vials were sealed and the reaction was conducted at 60 °C for 2 h by a heater. After the reaction, the solution was allowed to cool down and a known quantity of the internal standard solution (2-fluorobiphenyl in EtOAc) was added prior to gas chromatography-mass spectrometry (GC-MS) analysis.

Aliquots of 1 μL were analyzed with a GC 7890A/5975C-Innert MSD SYSTEM. Separation was performed with an Agilent HP-5 ms (30 × 0.25 mm, i.d. 0.25 μm) with a temperature program from 100 °C to 300 °C at 18 °C min^{-1} with helium as carrier gas. The injector was maintained at 260 °C and operated under splitless conditions for 0.75 min. Data acquisition was performed in the full scan mode under electron ionization at 70 eV in the 45–450 *m/z* range. Peak integrations of 2-fluorobiphenyl were performed from the mass chromatograms at *m/z* 172, the LG, at *m/z* 204. The efficiency of the silylation procedure was checked prior to integration by the known GC-MS characteristics of the partially silylated LG.

2.4. Modeling tools

2.4.1. Indoor concentrations

Indoor concentrations were estimated by the INTERA computational platform. The estimation was based on a mass balance model, which takes into account the major processes governing particle concentration i.e. emissions, deposition, indoor/outdoor exchange rate, and outdoor infiltration. The mass balance is described by the following formula:

$$V \cdot \frac{dc}{dt} = Q \cdot (inf \cdot C_{out} - C_{ind}) + E - K_{dep} \cdot C_{ind} \cdot V$$

where:

E	*the strength of the emission sources (mass/time)*
V	*the volumes of the indoor location*
C_{out}	*the outdoor concentration*
C_{ind}	*the indoor concentration of the indoor location*
Q	*the indoor–outdoor air exchange rate*
inf	*the infiltration rate*
k_{dep}	*the deposition rate*

Particle penetration into buildings from the ambient air depends on pollutant species, geometry, surface materials and pressure drop across the leakage path. It is usually expressed by means of a dimensionless penetration factor; typical values of the latter for domestic environments were taken from the PTEAM study (Özkaynak et al., 1996). These values are normally distributed with a mean of 1 and standard deviation of 0.06. Background emission rates for PM10 and PM2.5 were taken equal to 5600 and 1400 μg/h respectively (not including indoor smoking or long-term burning activities). These values are considered to be representative for Greece (Hänninen et al., 2004). Biomass burning emissions into the indoor environment from open fireplaces and other biomass combustion sources (e.g. stoves) were estimated experimentally in our study, found to be equal to 2300 μg/h. Deposition of atmospheric aerosol particles on indoor surfaces (the floor, walls, ceiling and furniture) takes place via electrostatic and thermostatic processes, and it is significantly affected by the type of air mixing (turbulent vs. laminar flow). The distribution for this variable was taken from the PTEAM study (Özkaynak et al., 1996) and the respective values for PM10 and PM2.5 were 0.67 and 0.39 h^{-1} respectively. Finally, a typical residence volume equal to 245 m^3 was considered as representative (UNECE, 2006).

2.4.2. Personal exposure

Exposure to PM was estimated based on the indoor/outdoor concentration data for two clusters of exposed individuals, based on whether they lived in a house using a fireplace or not. Personal exposure is the average concentration of a pollutant to which an individual is exposed to over a given period of time. If over the given period of time, ***T***, the person goes through *n* locations, spending a fraction f_n of the time in location ***n*** where the concentration of the pollutant under consideration is C_n, then the personal exposure for this period ***T***, represented by the concentration E_T, is given by (Ott, 1982):

$$E_T = \sum_n f_n \cdot C_n$$

Micro-environments were differentiated in terms of time spent within them. Time-weighted factors were used, based on the time–activity data from the EXPOLIS study enriched with data from the

Table 1
Prior distributions of the indoor air and personal exposure determinants.

Parameter	Distribution	Mean	Max	Min	S.D.
PM10 2011-warm period (μg/m^3)	Lognormal	41.4	59.2	20.4	10.3
PM2.5 2011-warm period (μg/m^3)	Lognormal	31.1	56.4	11.3	12.1
PM10 2011-cold period (μg/m^3)	Lognormal	53.1	111.9	12.7	31.2
PM2.5 2011-cold period (μg/m^3)	Lognormal	43.5	91.9	9.4	25.8
PM10 2012-warm period (μg/m^3)	Lognormal	30.6	52.8	14.2	8.7
PM2.5 2012-warm period (μg/m^3)	Lognormal	19.4	34.2	9.8	6.3
PM10 2012-cold period (μg/m^3)	Lognormal	73.1	228.1	16.6	59.2
PM2.5 2012-cold period (μg/m^3)	Lognormal	62.7	210.6	15.5	52.3
Air exchange rate (warm period) (h^{-1})	Lognormal	1.3	2.5	0.6	0.3
Air exchange rate (cold period) (h^{-1})	Lognormal	0.8	1.2	0.1	0.2
Penetration factor	Normal	1.0	1.2	0.8	0.06
PM10 deposition rate (h^{-1})	Lognormal	0.67	2.1	0.2	0.28
PM2.5 deposition rate (h^{-1})	Lognormal	0.34	1.2	0.1	0.16
Residential volume (m^3)	Lognormal	245	440	80	70
PM10 background emissions (μg/h)	Lognormal	3600	20,000	235	1300
PM2.5 background emissions (μg/h)	Lognormal	1100	7200	32	1300
PM10 biomass burning emissions (μg/h)	Lognormal	2300	10,200	270	1500
PM10 biomass burning emissions (μg/h)	Lognormal	2300	10,200	270	1500

MTUS[1] database. Exposure factors used were cross-checked against the European Commission's EXPOFACTS database.[2] Thus, to estimate exposure, we used information on actual detailed time activity patterns, linking the several types of activities and the respective duration, to specific indoor micro-environments. For reasons of parsimony and considering the limitations of concentrations of data regarding the types of dwellings, we divided indoor locations in four major groups, namely residential, workplace (for adults), schools (for kids and adolescents) and other indoor locations. The latter included all indoor locations related to leisure, entertainment, services or several unclassified activities.

By using detailed activity patterns and linking them to specific microenvironments an additional factor influencing the actual human intake of PMx, i.e. is inhalation rate, was accounted for. Different types of activities demand different levels of effort that correspond to different inhalation rates. Detailed description of the activity based inhalation rates is given elsewhere (Sarigiannis et al., 2012b). For this purpose, based on the time–weight contribution of the activities, the level of intensity and the corresponding inhalation rate, we derived adjustment factors for each location type. As a result, PMx intake was given by the following formula:

$$E = \sum_{n} f_{loc} \cdot C_{loc} \cdot inh_{act}$$

where ***inh*** is the inhalation adjustment factor for each type of microenvironment encountered in the calculations.

2.4.3. Model simulations

All modeling calculations were carried out through the INTERA computational platform (INTERA, 2011), which is specialized for addressing aggregate and cumulative exposure from indoor sources. The platform allows for dynamic calculations in time and incorporates probabilistic analysis using Monte-Carlo sampling. The probabilistic framework allows the incorporation of uncertainty and variability across the source-to-intake dose continuum. The Monte Carlo method involves a large number of samples (50,000 iterations were executed for each calculation) from the distributions of the input parameters. Literature-derived prior distributions (Table 1) with regard to ambient air concentrations, air exchange rate, penetration coefficient, deposition and emission rates were used and allowed to converge through a Markov chain Monte Carlo procedure, so as to derive the actual distributions of indoor concentrations and personal exposure.

2.4.4. Exposure forecasting tool

A key requirement for the effective operational management of air pollution in order to protect efficiently public health is being able to forecast the pollution levels to which the local population is exposed. Such a forecasting tool would ideally be not very sensitive to changes in emissions inventories for it to be operationally useful. Thus, we have opted to couple the INTERA computational platform with an artificial neural network that would allow exposure predictions based on inference rather than explicit and deterministic calculation. In Fig. 1 the structure of the exposure forecasting platform is described in detail. A multi-layer perceptron (MLP) was utilized. This is a feed-forward artificial neural network model that maps sets of input data onto a set of appropriate output. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm was used for training the network. The BFGS algorithm (Dennis and Schnabel, 1996) is a method widely used to solve unconstrained nonlinear optimization problems. The selection of the BFGS quasi-Newton algorithm was consistent with the findings of Schlink et al. (2003), who have reported the good performance of the quasi-Newton algorithm, in the case of neural networks that use the early stopping technique for the improvement of their generalization ability. The input layer of each ANN consisted of 8 neurons, corresponding to the following predictors: PM10 and PM2.5 concentrations of the previous day, wind speed and direction, temperature, humidity, precipitation and one categorical variable identifying the day of the week (weekday or weekend).

The output layer consisted of two nodes, corresponding to the output parameters, namely the average daily PM10 and PM2.5 concentrations for each station. The hidden layer consisted of 14 neurons, experimentally found to yield the best results (Fig. 2).

3. Results

3.1. Ambient air PMx concentrations

The inter-day variability among the sampling sites is illustrated in Fig. 3a–b. Both PM2.5 and PM10 concentrations tend to rise significantly during the transition from the warm to the cold period. The latter was marked by lower temperatures starting in mid-November. PMx concentrations at the traffic station (53.1 and 29.5 μg/m^3 for PM10 and PM2.5 respectively) were constantly higher than the concentrations at the background station (30.6 and 19.4 μg/m^3) during the warm sampling period because of the high traffic load, which is the dominant emission source in the urban area under study. This is the combined result from direct tailpipe emissions and re-suspension processes (movement of vehicles, loading and unloading operations). However, during the cold period, PM concentrations increase rapidly at the urban background sites, becoming eventually higher than the ones at the traffic sites. PM10 and PM2.5 concentrations in ambient air exceed the thresholds (for both PM10 and PM2.5) proposed by the 2008/50/EC guide values most of the days.

[1] MTUS: Multinational Time Use Study (http://www.timeuse.org/mtus/).
[2] EXPOFACTS: Exposure Factors database maintained by the European Commission's Joint Research Centre (http://expofacts.jrc.ec.europa.eu/).

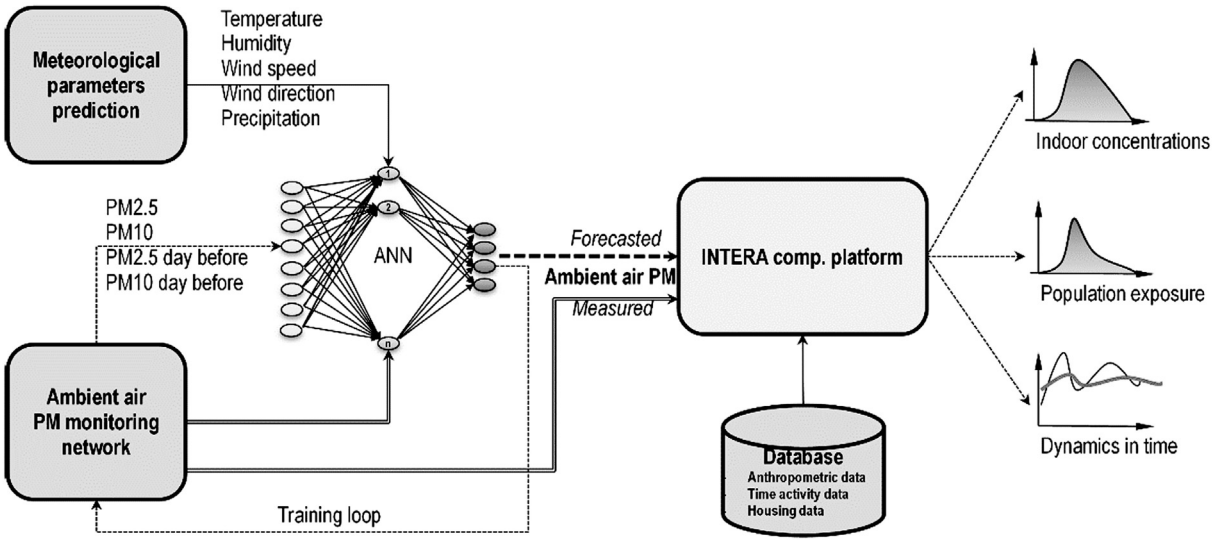

Fig. 1. Information flowchart of the total exposure forecasting tool developed.

3.2. Contribution of biomass combustion to ambient PMx levels

A key process that changed the usual PMx profile in Thessaloniki as soon as the mean ambient air temperature fell below 10 °C was the apparently widespread use of biomass as fuel for domestic heating. In order to determine how much biomass combustion contributed to the mass concentration of PMx in the ambient air black carbon (BC) and levoglucosan were quantified analytically. Results for different size fractions of PM are shown in Fig. 4.

The BC content in PMx sampled at the urban background sites was 25–30% higher than the corresponding value at the traffic sites, revealing that combustion processes other than traffic-related internal engine combustion contribute to the observed PMx values.

The contribution of biomass burning to PM air pollution was verified by levoglucosan analysis of PM; levoglucosan is considered the most specific tracer of biomass burning (Belis et al., 2013; Perrone et al., 2012; Zhang et al., 2008). The amount of PMx mass that was due to biomass burning was determined using the empirical function proposed by Caseiro et al. (2009), according to which:

$$\text{wood smoke PM}\left(\text{in } \mu g/m^3\right) = \text{Levoglucosan}\left(\text{in } \mu g/m^3\right) \cdot 10.7$$

Levoglucosan found in PMx at the urban background sites was between 90 and 120% more than the corresponding values near intense traffic. The contribution of biomass combustion to PM mass concentration varied significantly with an average value of 34% and maximum values up to 70% (Fig. 5) especially when extreme pollution incidents occurred (mean daily concentration of PM10 close to 150 $\mu g/m^3$). Biomass contribution to PM mass concentration was much higher at the urban background sites than close to intense traffic.

3.3. Indoor air concentrations—measurements and modeling results

Indoor PM concentrations are close to the ones of the outdoor air if no strong emission source (e.g. smoking indoors or combustion) is present (see Fig. 6). When biomass combustion is the method of choice for domestic heating (i.e. through the use of fireplace and/or wood stoves), indoor PMx concentrations tend to rise significantly. Similar results were obtained during the cold period, when household fireplaces burned for 3–5 h daily on the average. In this case, average daily indoor concentrations tended to be similar or higher than the ones in the ambient air, with an average daily increase of about 10 $\mu g/m^3$ and 14 $\mu g/m^3$ for PM2.5 and PM10 respectively (see Fig. 6) compared to

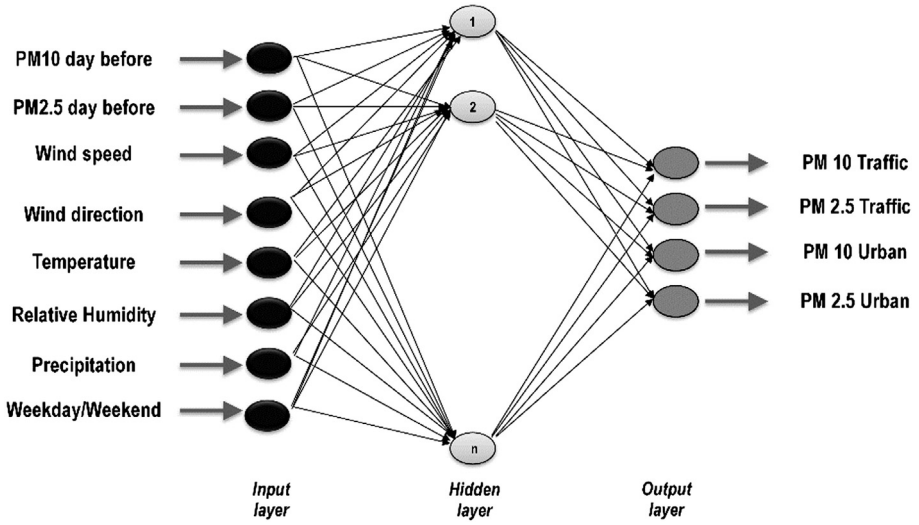

Fig. 2. ANN conceptual representation.

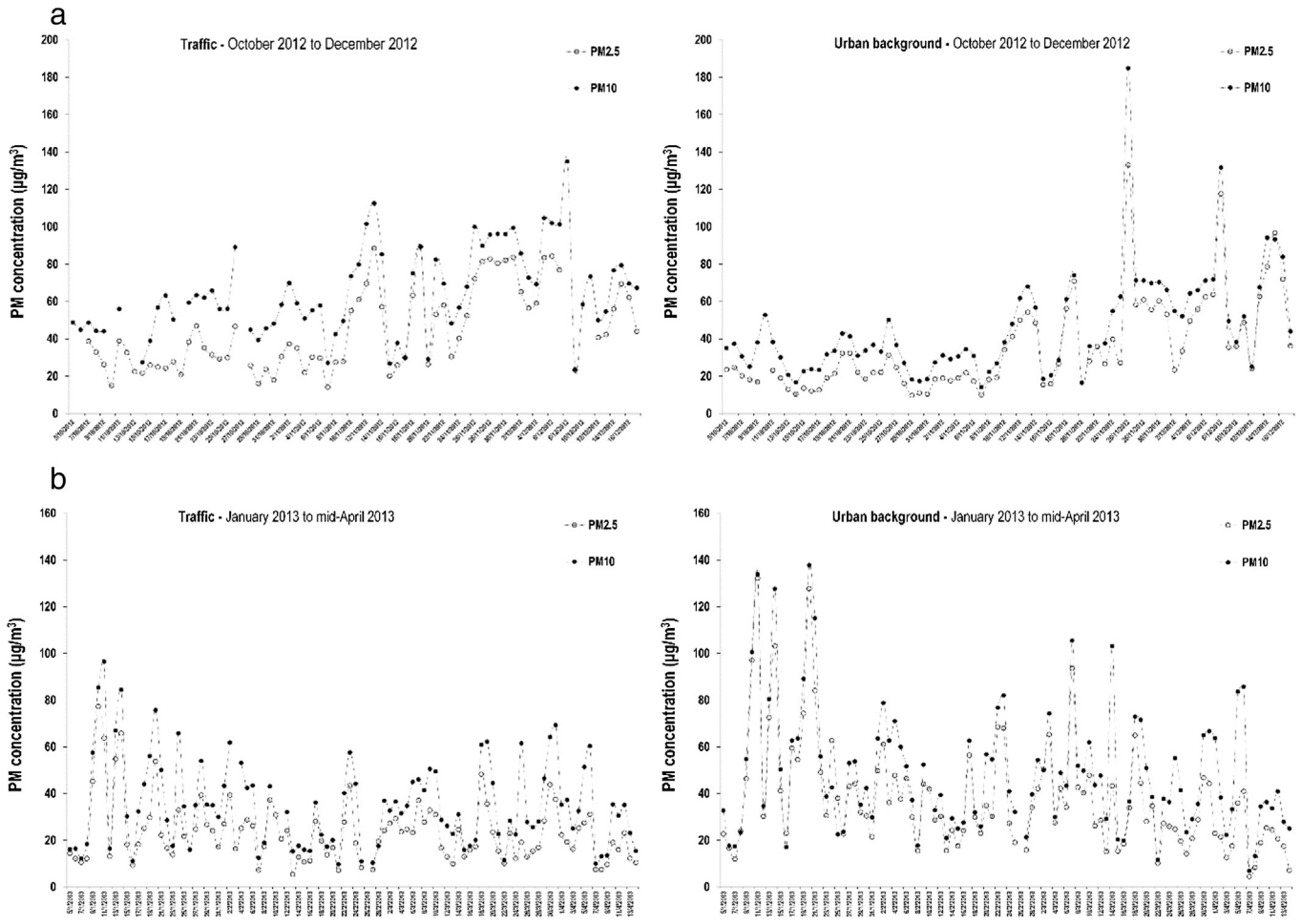

Fig. 3. Ambient air PM10 and PM2.5 concentrations at the traffic and the urban background measurement sites.

the houses where the fireplace was not in use. However, this variability depends on many parameters, such as the daily duration of fireplace usage, the type of wood used and to a smaller degree the intensity of burning. It is noteworthy that a very close agreement was noticed between the measured and the modeled concentrations. Very interesting results were obtained by the PNC measurements during the time when fireplaces were used. During fireplace operation, PM concentrations increased significantly, with an average rise of 6 and 3 μg/m^3 for the fractions PM1–5 and PM5–10 respectively. Depending on the fireplace combustion conditions (type and humidity of woods, placement of woods within the fireplace, intensity of burning) the PM concentrations might become as high as 30–40 μg/m^3. However, the rapid increase in

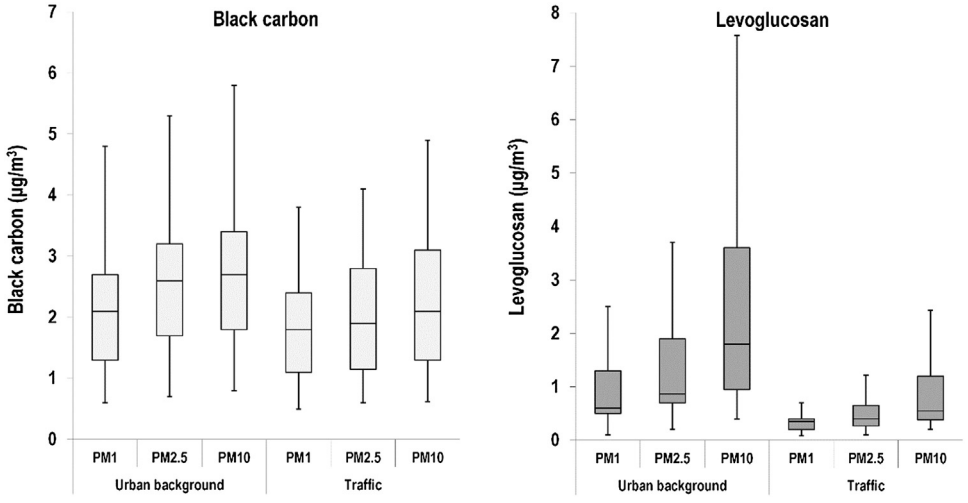

Fig. 4. Content of black carbon and levoglucosan in PMx in different urban settings.

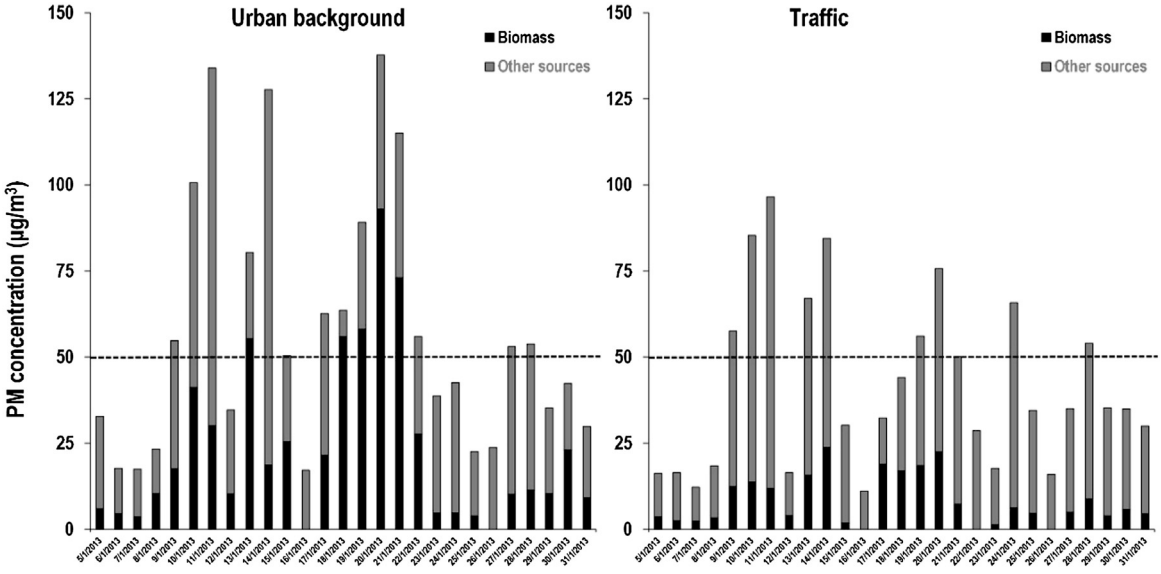

Fig. 5. Relative contribution of biomass combustion to PM mass concentration in January 2013.

the particle number is characteristic for particles of smaller aerodynamic diameter; namely, the concentration of PM0.5–0.7 particles undergoes a 5-fold increase (Fig. 7). The PM was rapidly dispersed uniformly within the indoor location, and spatial differences in PM concentrations within the room were negligible, even very close to the fireplace.

3.4. Forecasting model performance

The model performed very well considering that the explanatory variables accounted for more than 90% of the observed values; R^2 scores of the training set for the traffic sites were equal to 0.90 and 0.97 for

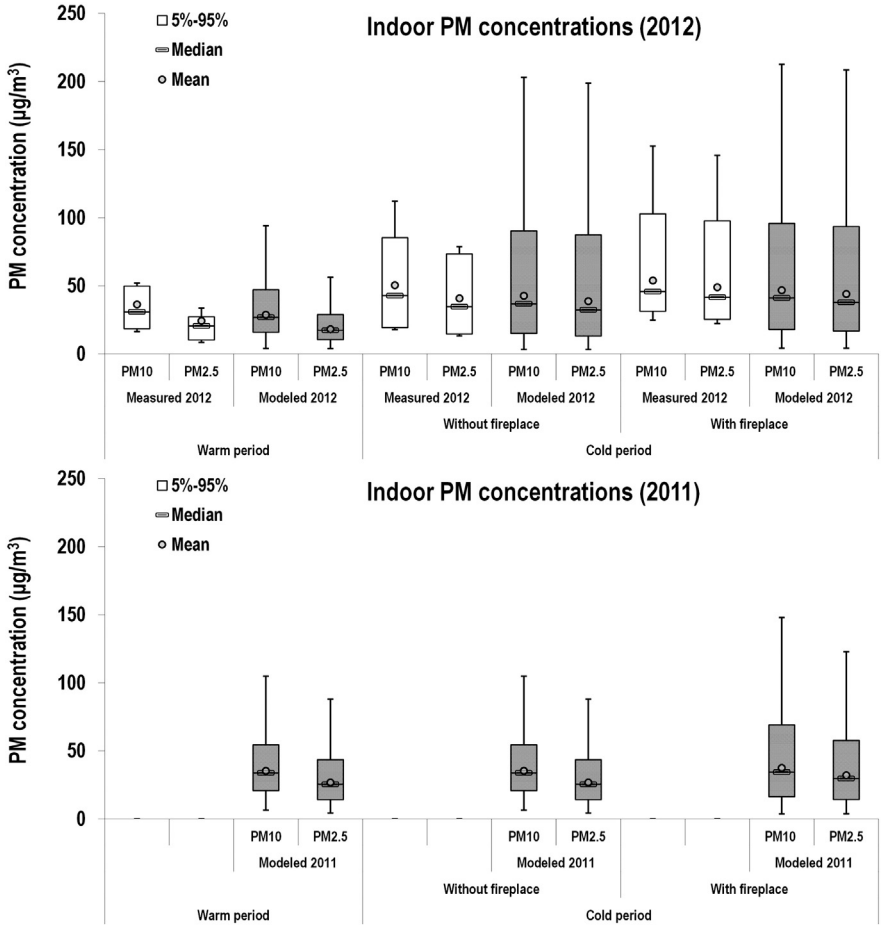

Fig. 6. Indoor PM10 and PM2.5 concentrations for the years 2012 and 2011, during the warm and the cold period respectively. Dwellings with and without fireplaces are considered. Measurements are presented in white and modeled values are plotted as grey-shaded box plots.

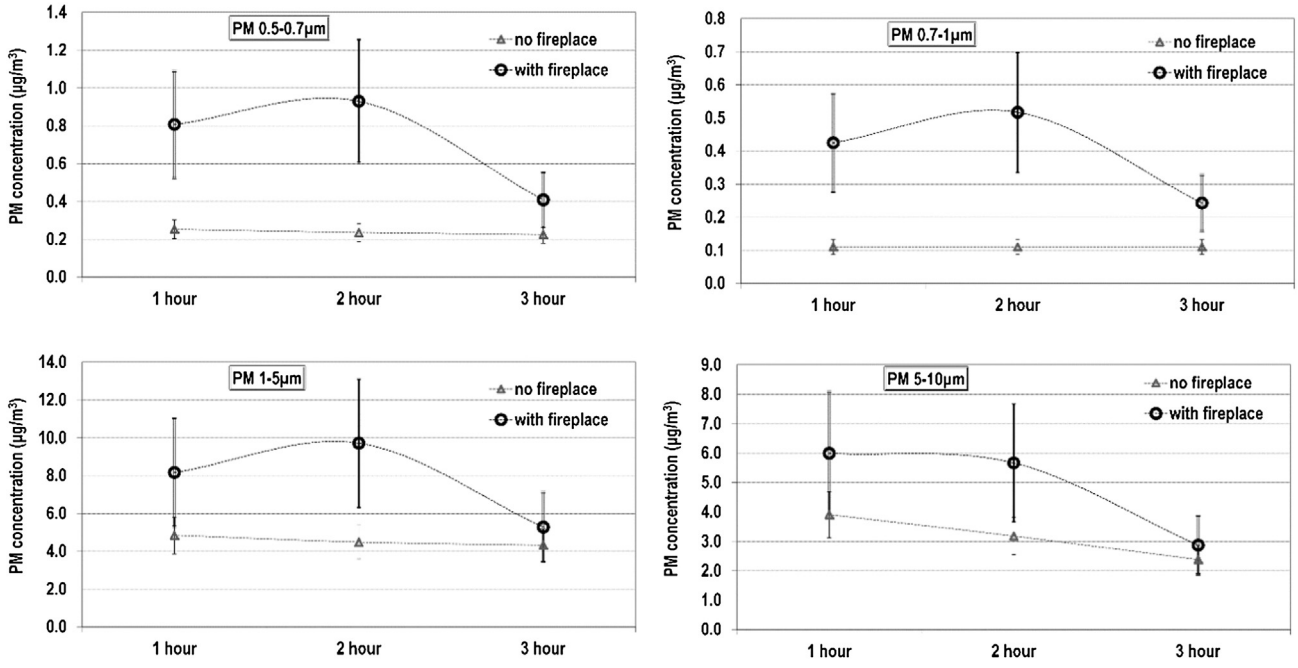

Fig. 7. Effect of biomass burn for domestic heating on different fractions of indoor air PM.

PM10 and PM2.5 respectively and for the urban background sites equal to 0.97 and 0.93.

The overall performance of the developed ANN was also validated against an independent validation set, including measurements at different traffic and background sites within the city. The results of the validation of the ANN model are illustrated in Fig. 8. Considering the limited number of data used for training, the performance of the ANN (R^2 ranging between 0.68 and 0.78) is considered more than adequate.

3.5. Personal exposure

Personal exposure variability follows a similar pattern to indoor concentrations. This was expected considering that almost 85% of the exposed individual activities are performed indoors. A very interesting result is that for 2012, exposure to PM (mean of 47 and 42.7 μg/m^3 for PM10 and PM2.5 respectively) of population living in houses not equipped with fireplaces, is higher than the exposure of people living in a house equipped with fireplace for year 2011 (mean of 39.6 and 34.6 μg/m^3 for PM10 and PM2.5 respectively) during the cold season.

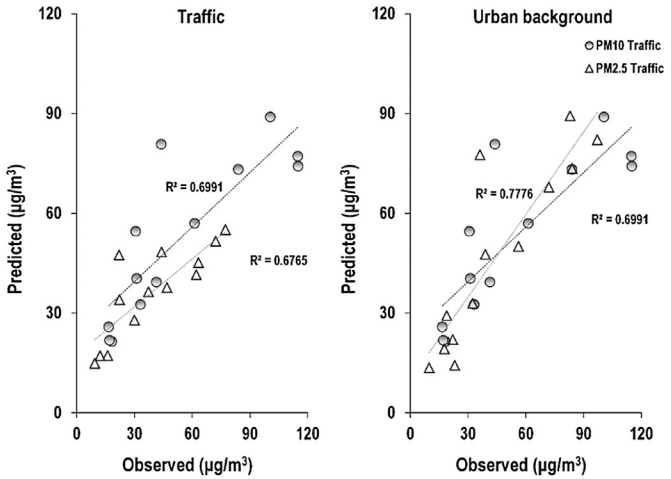

Fig. 8. Observed vs. predicted values of PMx concentrations using the forecasting model.

This highlights the heavy exposure burden to the population that is attributable to the significant increase of ambient air PMx concentrations in Thessaloniki during the cold period of 2012–2013 (Fig. 9).

For individuals exposed to indoor biomass burning in 2012, average daily exposure rises up to 50.1 and 46.8 μg/m^3 for PM10 and PM2.5 respectively. During the warm period, exposure is clearly higher in year 2011, due to the higher ambient air concentrations. The difference is even more profound for PM 2.5 (32.1 μg/m^3 for 2011 instead of 20.9 μg/m^3 for 2012). This trend was due to the higher traffic load in the warm period of 2011 compared to the crisis-stricken traffic sector in 2012.

Beyond average exposure we investigated the intra-day variability of exposure. In Fig. 10, we present a typical daily winter time profile of an individual living in a house with fireplace.

During most of the day exposure follows the indoor concentration profile; the latter depends strongly on the outdoor concentration, which in turn is affected by the intensity of outdoor emission sources, namely mainly traffic during the day time and domestic heating during the evening and night hours. Fig. 10, however, shows that the most intense PM intake (as expressed by the grey line that represents exposure concentration modified by the activity relevant inhalation coefficient) occurs mostly during daytime. During sleep inhalation rate is lower; thus, despite the elevated outdoor concentrations, the actual intake is lower than the one estimated by the monitoring ambient and indoor air concentrations.

4. Discussion

Interesting conclusions can be drawn by the comparative study of daily values for the same period between the winters of 2011–2012 and 2012–2013. During the warm period of early October–early November the year 2011 at the traffic station, PM10 concentrations were 59.8 and PM2.5 47.0 μg/m^3, while during the cold period, they amounted to 82.9 and 68.3 μg/m^3 respectively, i.e. they were similar to the levels described by Kassomenos et al. (2011b), for the years 2006–2007. During the warm period of year 2012, the respective concentrations remain lower, being 53.1 and 29.5 mg/m^3 for PM10 and PM2.5 during the warm period, while a more significant elevation occurs during the cold period (76.5 and 59.7 μg/m^3 for PM10 and PM2.5

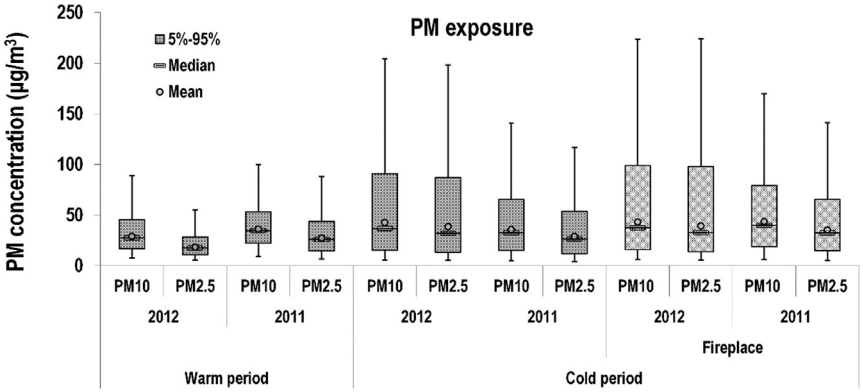

Fig. 9. Population exposure to PM10 and PM2.5 in different periods of the year and for different methods of domestic heating.

respectively). Since average wind speed was similar in both seasons, reduced concentrations of year 2012 at the traffic station are attributed to reduced traffic emissions, which in turn are due to the reduced traffic load by 30% in 2012, as evidenced by in situ traffic measurements carried out by our team and corroborated by official statistics. Moreover, while in 2011 the ratio of PM2.5/PM10 remains almost constant (~0.8) between the two periods (warm–cold), in 2012 it increases significantly during the cold period in 2012 (from ~0.55 up to 0.78); the latter indicates that additional emission sources beyond traffic become important.

At the background sites concentrations of PM10 and PM2.5 were higher during the warm period of 2011, namely 41.4 and 31.1 μg/m^3 versus 30.6 and 19.4 μg/m3 for 2012 respectively. On the contrary, during the coldest period of 2012, PM concentrations are significantly higher, i.e. 73.1 and 62.7 μg/m^3 for PM10 and PM2.5 respectively versus 53.1 and 43.5 in 2011. The increase of concentrations in 2012 is accompanied by a sharp increase in the ratio PM2.5/PM10 (from 0.63 to 0.86), in contrast to 2011, where the corresponding change was smaller (from 0.75 to 0.82). Between the two years there is a significant variation in emission patterns: the traffic component appears to be reduced in 2012, while during the colder period the component associated with biomass heating dramatically increased. Given that temperatures during the cold season of 2012–2013 are close to the ones of 2011–2012 (daily average 11.1 °C for both years), these differences cannot be attributed to increased need for domestic heating, but rather to the different means of space heating (biomass burning). This fact was verified by measurements of biomass markers such as levoglucosan (concentrations of levoglucosan in the PM samples collected during the cold period were as high as 9 μg/m^3, and biomass contributed to 34% of the PM10 mass concentration on average).

Indoor concentrations of PM present also an interesting behavior when considering the complex interaction of indoor/outdoor air exchange and the relative strength of indoor sources. The higher air exchange rate in the summer (an average of 1.3 h^{-1}) makes outdoor concentrations the dominant parameter. On the contrary, in the cold season, air exchange rate is lower (average value of 0.8 h^{-1}), and indoor sources become more significant. However, since outdoor background concentrations are very high during the cold season of year 2012–2013, average indoor concentrations are even higher than the ones in 2011–2012 for indoor locations where biomass was used for domestic heating. The latter is very important, showing that the massive use of biomass in Greek cities resulted in a commensurate increase of indoor concentrations overall.

Combustion of biomass contributes to elevated ambient air background concentrations as well. This contribution is not only associated to open fireplaces, but rather to all combustion apparatus using wood and wood products. The latter comprise a very important PM source both in- and outdoors. Although their contribution depends on many parameters, PM concentrations during the time of operation have been found to rise up to 70–80 μg/m^3. These results are comparable albeit lower to the ones presented by Guo et al. (2008). In that study peak levels of PM10 (167 μg/m^3) and PM2.5 (155 μg/m^3) coincide with the open fireplace usage time. PM10 and PM2.5 levels in this case were ca. four and nine times higher than during normal occupancy conditions respectively. What is more important is the increase in the number of fine and ultrafine particles, which are the most hazardous to man,

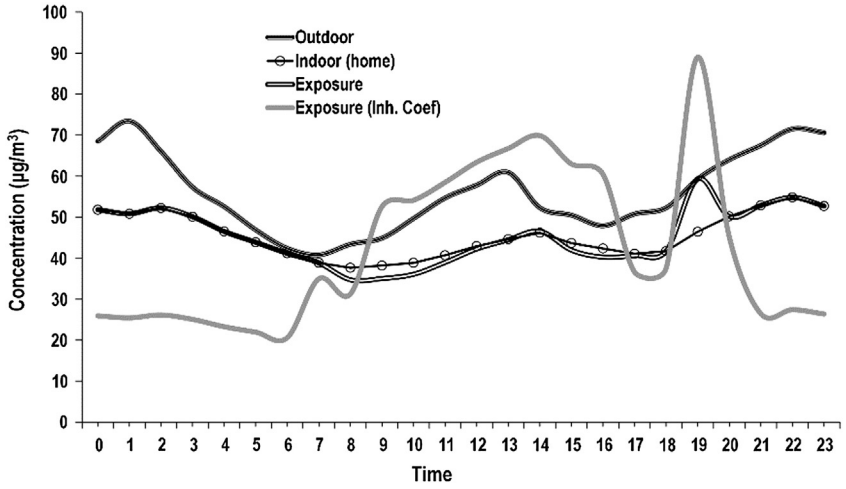

Fig. 10. Intra-day variability of ambient and indoor air, personal exposure and intake.

since they can reach the lower part of the respiratory tract (bronchioles) and translocate in the body via systemic circulation (Brook, 2008). This is also linked to the actual human exposure and intake.

A key finding of this study is the fact that intra-day variability shows that peaks of ambient PM concentrations do not necessarily reflect peaks of exposure, since the timing and the location where people are performing their activities affect significantly the actual PMx intake rate. Late night peaks of ambient PM concentrations (related to domestic heating emissions) do not correspond to peaks of actual intake (especially for people not operating a fireplace), since people stay indoors, most of the time sleeping (thus inhalation rate is low) in an environment with minimized indoor/outdoor interaction. Peaks of exposure (and potential intake) are related to specific activities performed outdoors (e.g. commuting by any transportation means) or indoors (use of open fireplace). Thus, policy interventions to protect public health from extreme values of particulate air pollution need to be targeted to curbing human exposure rather than simply ambient air concentrations to be cost-effective. Time differences between peaks of ambient air PM and the actual PM intake during the day have to be accounted for when assessing the actual public health impact of PM exposure. Health risk and impact would be overestimated if epidemiologically established concentration response functions were simply applied to ambient air PM levels, while risks of families using open fireplaces as a space heating source might be underestimated. Thus, a comprehensive risk assessment/health impact evaluation should take into account the complex outdoor/indoor air interactions, as well as exposure and intake dynamics taking stock of time–activity and intensity of activity patterns of the population. The latter are important modifiers when it comes to assessing population exposure to airborne pollutants.

The good performance in the results of the exposure forecasting tool confirms the fact that ambient air concentrations are strongly influenced by meteorological conditions both directly and indirectly. A major advantage of the ANN model is its capability to capture the effect of parameters with complex influence on the PM concentration levels, such as temperature. Emission patterns tend to rise significantly when average daily temperature falls below 6–7 °C, especially emissions related with domestic heating. The fact that the model performs better in predicting PM2.5 levels confirms the correlation of temperature change with the change in residential heating emissions, especially those associated with biomass burning (Perrone et al., 2012; Reisen et al., 2013). In addition, temperature affects traffic emissions, by increasing the fraction of cold emissions (Ntziachristos and Samaras, 2001) for typical vehicle routes. Wind speed and direction affect dispersion, diffusion and re-suspension of particles. Humidity affects the hydroscopic growth of particles (Sarigiannis et al., 2002, 2004), while rainfall (wet deposition) is a dominant mechanism of atmospheric clearance (Lohse et al., 2008). The performance of the ANN was enhanced by distinguishing between weekends and weekdays in the overall model, incorporating in this way inter-day differences in emissions intensity and PMx composition. Using as input the ambient air concentrations of the previous day enhances the performance of the ANN, by providing an indication of the background concentrations.

5. Conclusions

PM exposure of urban population during the cold period of the year is significantly higher, due to the increased traffic emissions and mostly due to emissions from domestic heating. In Greece this difference was further amplified in the winter of 2012–13; although overall traffic emissions were reduced compared to previous years (due to lower traffic volumes associated to the economic crisis), residential heating emissions were increased due to the introduction of biomass as a fuel widely used in Greek cities for space heating. The latter was verified by the determination and quantification of a biomass-specific tracer (levoglucosan) obtained by chemical analysis of PMx. Overall exposure to PM was also increased due to the direct indoor emissions of open fireplaces or wood stoves, especially for particles of small diameter, which are considered the most harmful in term of health effects. The actual exposure of the population to different PMx size fractions was estimated by coupling outdoor as well indoor measurements to validated exposure modeling tools. This allowed us to identify that intra-day peaks of ambient PM concentrations do not always correspond to peaks of actual intake. In fact, overall exposure of the population can be significantly modulated by acting upon the time–activity patterns of susceptible individuals and the intensity of the respective activities during daytime. This has to be taken into account when calculating the expected health impact on the exposed population.

Two significant conclusions can be drawn for policy interventions aiming to protect the population health from extreme levels of airborne particulate pollution in cities:

1. We need to control ambient air PMx levels, paying attention to the size distribution of airborne particles and not only to the mass concentration of PMx in contrast to the currently predominant policy in the European Union. This means that among policy interventions possibly available to curb PMx emissions, priority should be given to the ones that not only reduce the mass concentration of PMx, but also curb emissions of fine and ultra-fine particle fractions in particulate matter.
2. Policy measures need to be focused towards reducing the total exposure of the population as opposed to simply controlling ambient air concentrations. These comprise various aspects:
   a. Delivery of timely, precise and reliable information to the local population with specific guidance on how to limit individual exposure to hazardous PM. This can be achieved by both modulating daily time–activity patterns and showing extra caution when selecting space heating technologies and fuel in dwellings. Enhanced awareness of consumers of the importance that both wood quality and burning conditions have for maintaining a healthy indoor environment is a sine qua non for effective environmental health policy-making.
   b. Adoption of incentives to limit the use of open fire biomass combustion as a space heating option in large cities.
   c. Limitation of PMx emissions from other sectors such as traffic and industrial activities in order to put a cap on the increasing PMx levels in ambient air when local meteorology creates conditions that favor atmospheric inversions.

Overall, our composite methodology that combines measurements and modeling data provides the appropriate framework for refined exposure assessment at the individual and population levels. This could serve as the basis for health impact assessment and analysis of different intervention scenarios. In addition, our combined measurement–modeling scheme can be the basis of an early warning system for days when meteorological conditions favor the occurrence of extreme PM air pollution episodes.

Acknowledgments

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