Characteristics and application of receptor models to the atmospheric aerosols research

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1. Introduction

Atmospheric aerosols can be defined as solid and liquid particles suspended in air. Due to their confirmed role in climate change (IPCC, 2001), impact on human health (Dockery and Pope, 1994; Schwartz et al., 1996; Schwartz et al., 2001; WHO, 2002, 2003; Dockery and Pope, 2006), role on the radiative budget (IPCC, 2007), effects on ecosystems (Niyogi et al., 2004; Bytnerowicz et al., 2007), and local visibility they are of major scientific interest. The human activities in various aspects cause a change in the natural air quality. This change is more marked in very inhabited areas with high industrialization. Epidemiological research over the past 15 years has revealed a consistent statistical correlation between levels of airborne particulate matter (PM) and adverse human health effects (Pope et al., 2004; Dockery and Stone, 2007). Airborne particulate matter contains a wide range of substances, such as heavy metals, organic compounds, acidic gases, etc. Chemical reactions occurring on aerosols in the atmosphere can transform hazardous components and increase or decrease their potential for adverse health effects. Especially organic compounds react readily with atmospheric oxidants, and since small particles have a high surface-to-volume ratio, their chemical composition can be efficiently changed by interaction with trace gases such as ozone and nitrogen oxides. The impact of atmospheric aerosols on the radiative balance of the Earth is of comparable magnitude to greenhouse gases effect (Anderson et al., 2003). Atmospheric aerosol in the troposphere influences climate in two ways: directly, through the reflection and absorption of solar radiation, and indirectly through the modification of the optical properties and lifetime of clouds. Estimation of the radiative forcing induced by atmospheric aerosols is much more complex and uncertain compared with the well-mixed greenhouse gases because of the complex physical and chemical processes involved with aerosols and because of their short lifetimes which make their distributions inherently more inhomogeneous.

In order to protect public health and the environment i.e. to control and reduce particulate matter levels, air quality standards (AQS) were issued and target values for annual and daily mean PM_{10} (particles with aerodynamic diameter less than 10 μm) and $PM_{2.5}$ (particles with aerodynamic diameter less than 2.5 μm) mass concentrations were established. For the first stage, the EU Directive (EC, 1999) required an annual limit of 40 μg m^{-3} and a 24h limit

of 50 µg m^{-3} (not to be exceeded more than 35 times in a calendar year) for PM$_{10}$ to be met by 2005. In the spring 2008 EU decided on the future PM$_{10}$ regulations and the conclusions are that PM$_{10}$ regulations have been somewhat relaxed despite the fact that the numerical values of the limits have not changed (EC, 2008). The annual PM$_{2.5}$ limit value was set on 25 µg m^{-3}, to be met in 2015 (WHO, 2006). The discussion of these limit values, regulations and relations of new EU standards to US EPA standards can be found elsewhere (Brunekreef and Maynard, 2008). Many epidemiology studies related to the adequacy of the new cut off values were published (Pope et al., 2002; Laden et al., 2006). Although current regulations only target total mass concentrations, future regulations could be focused on to the specific components that are related to inducing the adverse health effects.

One of the main difficulties in air pollution management is to determine the quantitative relationship between ambient air quality and pollutant sources. Source apportionment is the process of identification of aerosols emission sources and quantification of the contribution of these sources to the aerosol mass and composition. The term "source" should be considered short for "source type" because this more general term accounts for the potential that there could be a cluster of sources within short distances of each other and/or there could be multiple sources along the wind flow pattern reaching the receptor thereby creating source types. Identification of pollutant sources is the first step in the process of devising effective strategies to control pollutants. After sources are identified, characterization of the source's emission rate and emission inventory can be followed by the development of a control strategy including the possibility of revised or new regulations.

Although significant improvements have been made over the past decades in the mathematical modelling of the dispersion of pollutants in the atmosphere, there are still many instances where the models are insufficient to permit the full development of effective and efficient air quality management strategies (Hopke, 1991). These difficulties often arise due to incomplete or inaccurate source inventories for many pollutants. Therefore it is necessary to have alternative methods available to assist in the identification of sources and the source apportionment of the observed pollutant concentrations. These methods are called receptor-oriented or receptor models since they are focused on the behaviour of the ambient environment at the point of impact as opposed to the source-oriented dispersion models that focus on the transport, dilution, and transformations that begins at the source and continue until the pollutants reach the sampling or receptor site. The problem is, using the data measured at the receptor site alone, to estimate the number of sources, to identify source composition and most importantly, from a regulatory point of view, to asses the source contributions to the total mass of each sample.

This paper will briefly review the most popular receptor models that have been applied to solve the general mixture problem and link ambient air pollutants with their sources. Some of these models will be applied on originally PM data set from Belgrade and the results will be discussed. Atmospheric monthly deposition fluxes for Belgrade urban area already determined were also used to demonstrate the applicability of receptor modelling for pollution source apportionment. Deposition fluxes were calculated from monthly sampled bulk deposits composed from dry and wet atmospheric deposition.

2. Receptor Modelling

The fundamental principle of receptor modelling is that the mass conversation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne particulate matter. In order to obtain data set for receptor modelling individual chemical measurements can be performed at the receptor site what is usually done by collecting particulate matter on a filter and analyzing it for the elements and other constituents. Electron microscopy can be used to characterize the composition, size and shape of particles as well. If we assume that N samples are analyzed for n species which come from m sources a mass balance equation can be written as

$$C_{ij} = \sum_{k=1}^{m} a_{jk} S_{ik} + e_{ij} \quad i = 1,...N; j = 1,...n \tag{1}$$

where C_{ij} is the concentration of the j-th species in the i-th sample. The mass fraction of species j in source k is a_{jk} (e.g. source composition) and S_{ik} is the total mass of material from source k in the i sample (e.g. source contribution). Obviously, equation above represents the general mixture problem and includes errors e_{ij} which may be the result of analytical uncertainty and variations in the source composition. It is well known that there are insufficient numbers of constraints to define a unique solution, therefore this problem is related to the class of so called ill-posed problems. There is variety of ways to solve equation (1) depending on some physical constraints (like non negativity of source composition and contribution) and a priori knowledge about sources (Henry et. al., 1984; Kim and Henry, 2000).

From a receptor point of view, pollutants can be roughly categorized into three source types: source known, known source tracers (i.e. pollutant is emitted with another well characterized pollutant) and source unknown. One of the main differences between models is the degree of knowledge required about the pollution sources prior to the application of receptor models. The two main extremes of receptor models are chemical mass balance (CMB) and multivariate models.

The chemical mass balance method requires knowledge of both the concentrations of various chemical components of the ambient aerosol and their fractions in source emissions. A complete knowledge of the composition of emissions from all contributing sources is needed and if changes of the source profiles between the emitter and the receptor may be considered as minimal, CMB can be regarded as the ideal receptor model. This method assumes a priori that certain classes of sources are responsible for ambient concentrations of elements measured at the receptor. Furthermore it is assumed that each source under consideration emits a characteristic and conservative set of elements. However, these requirements are almost never completely fulfilled, and thus, pure CMB approaches are often problematic. For sources that have known tracers but do not have complete emission profiles, factor analysis tools such as Principal Component Analysis (PCA), UNMIX, Positive Matrix Factorization (PMF) can be used to identify source tracers. These are commonly used tools, because software to perform this type of analysis is widely available and detailed prior knowledge of the sources and source profiles is not required. There are many related published papers (Poirot et al., 2001; Song et al., 2001; Azimi et al., 2005; Elbir et al., 2007; Olson et al., 2007; Brown et al., 2007; Song et al., 2008; Duan et al., 2008; Nicolas et al., 2008; Marković et al., 2008; Aničić et al., 2009). Principal component and factor

analyses attempt to simplify the description of a system by determining a minimum set of basis vectors that span the data space to be interpreted. PCA derives a limited set of components that explain as much of the total variance of all the observable variables (e.g., trace element concentrations) as possible. An alternative approach called Absolute Principal Components Analysis (APCA) (Thurston and Spengler, 1985) has also been used to produce quantitative apportionments.

For pollutant sources that are unknown, hybrid models that incorporate wind trajectories (Residence Time Analysis, Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT) can be used to resolve source locations. Hybrid models combine the advantages and reduce the disadvantages of CMB and factor analysis. The multilinear engine (ME) can solve multilinear problems with the possibility of implementing many kinds of constraints using a script language. Receptor models offer a powerful advantage to the source attribution process as their results are based on the interpretation of actual measured ambient data, what is especially important when ubiquitous area sources exist (e.g., windblown dust). Dispersion models can estimate point source contributions reliably if the source and atmospheric conditions are well characterized. From a mathematical point of view none of these models can give a unique solution but only solutions physically acceptable with different probability levels. These models therefore must be integrated by an at least indicative knowledge of the source profiles and/or by specific analyses such as the determination of the dimensional and morphological characterizations of the particulate matter. The comparison of source apportionment results from different European regions is very complex and many recent publications focus on this issue (Viana et.al, 2008). The combined application of different types of receptor models could possibly solve the limitations of the individual models, by constructing a more robust solution based on their strengths. Each modelling approach was found to have some advantages compared to the others. Thus, when used together, they provide better information on source areas and contribution than it could be obtained by using only one of them.

When evaluating the European publications (Vianna et. al. 2008) PCA was the most frequently used model up to 2005, followed by back-trajectory analysis. Other models commonly used were PMF, CMB and mass balance analysis. Data from 2006–2007 show a continued use of PCA (50% of the new publications) and an increase in the use of PMF and Unmix. Investigation of uncertainty estimates for source apportionment studies as well as quantification of natural emission sources and specific anthropogenic sources is of growing interest, therefore the US Environmental Protection Agency supported development user friendly software for some receptor models which is widely available.

The capabilities of some of the most commonly used models (PMF, Unmix, PSCF and CWT) will be demonstrated using original data set obtained in Belgrade and the fundamentals of these models are described below.

2.1 Unmix

The latest version of Unmix is available from the US Environmental Protection Agency (U.S. EPA, 2007). The concepts underlying Unmix have already been presented in geometrical and intuitive manner (Henry, 1997) and mathematical details are presented elsewhere (Henry, 2003). If the data consist of many observations of n species, then the data can be plotted in an n-dimensional data space where the coordinates of a data point are the observed concentrations of the species during a sampling period. The problem is to find the

vectors (or points) that represent the source composition. In the case of two sources the data are distributed in a plane through the origin. If one source is missing from some of the data points, then these points will lie along a ray defined by the composition of the single, remaining source. Points that have one source missing are the key for solving the mixture problem. The appropriate number of these vectors (also called factors) is determined using computationally intensive method known as the NUMFACT algorithm (Henry et. al., 1999). If there are N sources, the data space can be reduced to an N-1-dimensional space. Fig. 1 illustrates the essential geometry of multivariate receptor models for three sources of three species, the most complex case that can be easily graphed. It is assumed that for each source there are some data points where the contribution of the source is not present or small compared to the other sources. These are called edge points and Unmix works by finding these points and fitting a hyperplane through them; this hyperplane is called an edge (if N = 3, the hyperplane is a line). For any number of sources and species, the relative source composition can be identified if there are sufficient edge points for each source to define identified edges in the data space. The source vectors are plotted in the direction of the source compositions and the open circles are observed data. The non-negativity constraints on the data and the source compositions require that the vectors and data lie in the first quadrant. Furthermore, the non-negativity of the source contributions requires that all the open circles lie inside the region bounded by the source vectors. This is made easier to see by projecting the data and source vectors from the origin into a plane. The source vectors are the vertices of a triangle in this plot and the projected data points are the filled circles. The solution to the multivariate receptor modelling problem can now be seen as finding three points that represent the source compositions that form a triangle that encloses the data points and lie in the first quadrant, thus guaranteeing the nonnegativity constraints are satisfied. The edge-finding algorithm developed for Unmix is completely general and can be applied to any set of points in a space of arbitrary dimension. Unmix itself can be applied to any problem in which the data are a convex combination of underlying factors. The only restriction is that the data must be strictly positive.

Some special features of Unmix are the capability to replace missing data and the ability to estimate large numbers of sources (the current limit is 15) using duality concepts applied to receptor modelling (Henry, 2005). Unmix also estimates uncertainties in the source compositions using a blocked bootstrap approach that takes into account serial correlation in the data.
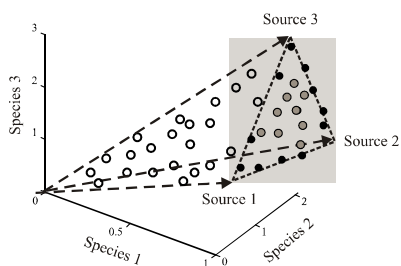

Fig. 1. Plot of three sources and three species case: the grey dots are the raw data projected to a plane, and the solid black dots are the projected points that have one source missing (edge points)

2.2 Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) has been shown to be a powerful receptor modelling tool and has been commonly applied to particulate matter data (Song et al., 2001; Pollisar et al., 2001; Chuenita et. al., 2000) and recently to VOC (volatile organic compounds) data (Elbir et al., 2007; Song et al., 2008). To ensure that receptor modelling tools are available for use in the development and implementation of air quality standards, the United States Environmental Protection Agency's Office of Research and Development has developed a version of PMF with the name of EPA PMF1.1 that is freely available (Eberly, 2005).

PMF solves the general receptor modelling equation using a constrained, weighted, least-squares approach (Paatero, 1993; Paatero and Tapper, 1993; Paatero and Tapper, 1994, Paatero, 1997; Paatero, 1999; Paatero, et. al., 2005; Paatero and Hopke, 2003). The general model assumes there are p sources, source types or source regions (termed factors) impacting a receptor, and linear combinations of the impacts from the p factors give rise to the observed concentrations of the various species.

The model can be written as

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{2}$$

where x_{ij} is the concentration at the receptor for the j-th species on the i-th sample, g_{ik} is the contribution of the k-th factor to the receptor on the i-th sample, f_{kj} is the fraction of k factor that is species j or chemical composition profile of factor k and e_{ij} is the residual for the j-th species on the i-th sample. The objective of PMF is to minimize the sum of the squares of the residuals weighted inversely with error estimates of the data points. Furthermore, PMF constrains all of the elements of G and F to be non-negative. The task of PMF analysis can thus be described as to minimize Q, which is defined as

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{p} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{s_{ij}} \right)^2 \tag{3}$$

where s_{ij} is uncertainty of the j-th species measured in i-th sample.

In this study the robust mode has been used for analyzing element concentrations in bulk atmospheric deposition data set. The robust mode was selected to handle outlier values (that is any data that significantly deviates from the distribution of the other data in the data matrix) meaning that outliers are not allowed to overly influence the fitting of the contributions and profiles. This can be achieved by a technique of iterative reweighing of the individual data values, thus, the least-squares formulation becomes to

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{h_{ij} s_{ij}} \right)^2 \tag{4}$$

where

$$h_{ij}^2 = \begin{cases} 1 & \text{if } \left| e_{ij}/s_{ij} \right| \leq \alpha, \\ \left| e_{ij}/s_{ij} \right|/\alpha & \text{otherwise} \end{cases}$$

The parameter α is called the outlier threshold distance and the value $\alpha = 4$ was used in this analysis. One of the most important advantages of PMF is the ability to handle missing and below detection limit data by adjusting the corresponding error estimates. In this analysis missing values were replaced with the geometrical mean of the measured concentrations for each chemical species, and large error estimates were used for them.

2.3. Potential Source Contribution Function (PSCF)

The potential source contribution function (PSCF) was originally presented by Ashbaugh et. al. (1985) and Malm et.al. (1986). It has been applied in a series of studies over a variety of geographical scales (Gao et. al., 1993; Cheng et.al., 1993). Air parcel back trajectories, ending at the receptor site, are represented by segment endpoints. Each endpoint has two coordinates (latitude, longitude) representing the central location of an air parcel at a particulate time. To calculate PSCF, the whole geographic region of interest is divided into an array of grid cells whose size is dependent on the geographical scale of the problem so that PSCF will be a function of locations as defined by the cell indices i and j. The construct of the potential source contribution function can be described as follows: if a trajectory end point lies at a cell of address (i, j), the trajectory is assumed to collect material emitted in the cell. Once aerosol is incorporated into the air parcel, it can be transported along the trajectory to the receptor site. The objective is to develop a probability field suggesting likely source locations of the material that results in high measured values at the receptor site.

Let N be the total number of trajectory segment endpoints during the whole study period. If segment trajectory endpoints fall into the ij-th cell (represented by n_{ij}) the probability of this event is given by

$$P[A_{ij}] = \frac{n_{ij}}{N} \tag{5}$$

where $P[A_{ij}]$ is a measure of the residence time of a randomly selected air parcel in the ij-th cell relative to the total time period. In the same ij cell there is a subset of m_{ij} segment endpoints for which the corresponding trajectories arrive at the receptor site at the time when the measured concentration are higher than a pre-specified criterion value. The choice of this criterion values has usually based on trial and error and in many applications, the mean value of the measured concentration was used. In some publications the use of the 60th and 75th percentile criterion produced results that appeared to correspond better with known emission source locations. Thus, the probability of this high concentration event is given by

$$P[B_{ij}] = \frac{m_{ij}}{N} \tag{6}$$

where $P[B_{ij}]$ is subset probability related to the residence time of air parcel in the ij-th cell for the contaminated air parcel. Finally, the potential source contribution function is defined as

$$PSCF_{ij} = P[B_{ij} \mid A_{ij}] = \frac{m_{ij}}{n_{ij}} \tag{7}$$

where $PSCF$ is the conditional probability that an air parcel which passed through the ij -th cell had a high concentration upon arrival at the receptor site. A sufficient number of endpoints should provide accurate estimates of the source location. Cells containing emission sources would be identified with conditional probability close to 1, if the trajectories that have crossed over the cells effectively transport the emitted contaminant to the receptor site. One can draw the conclusion that PSCF model provides a map of source potential of geographical areas, but it can not apportion the contribution of the identified source area to the measured concentration at the receptor site. Thus, the potential source contribution function can be interpreted as a conditional probability describing the spatial distribution of probable geographical source locations inferred by using trajectories arriving at the sampling site. Cells related to the high values of potential source contribution function are the potential source areas. However, the potential source contribution function maps do not provide an emission inventory of a pollutant but rather show those source areas whose emissions can be transported to the measurement site. To reduce the effect of small values of n_{ij}, an arbitrary weight function W(n_{ij}) is multiplied into the PSCF value to better reflect the uncertainty in the values for these cells.

2.4. Concentration Weighted Trajectory (CWT)

In the current PSCF method, grid cells having the same PSCF values can result from samples of slightly higher than the criterion concentrations or extremely high concentrations. As a result, larger sources can not be distinguished from moderate sources. According to this problem, a method of weighting trajectories with associated concentrations (CWT - concentration weighted trajectory) was developed (Hsu et. al, 2003). In this procedure, each grid cell gets a weighted concentration obtained by averaging sample concentrations that have associated trajectories that crossed that grid cell as follows:

$$C_{ij} = \frac{1}{\sum_{l=1}^{M} \tau_{ijl}} \sum_{l=1}^{M} C_l \tau_{ijl} \tag{8}$$

C_{ij} is the average weighted concentration in the grid cell (i,j), C_l is the measured PM concentration observed on arrival of trajectory l, τ_{ijl} is the number of trajectory endpoints in the grid cell (i,j) associated with the C_l sample, and M is the total number of trajectories. Similar to PSCF model, a point filter is applied as the final step of CWT to eliminate grid cells with few endpoints. Weighted concentration fields show concentration gradients across potential sources. This method helps determine the relative significance of potential sources.

3. Experimental Methods and Procedures

3.1 Studies Sites and Sampling

Sampling of particulate matter PM_{10} and $PM_{2.5}$ started in the very urban area of Belgrade in June 2002 and has continued afterwards. Belgrade, (Hs = 117 m, $\varphi = 44^0 44' N$ and $\lambda = 20^0 27' E$) the capital of Serbia, with about 2 million inhabitants, is situated at the confluence of the Sava and Danube rivers. The sampling site was the platform above the entrance steps to the Faculty of Veterinary Medicine (FVM) at a height of about 4 m from the ground, 5 m away from a street with heavy traffic and close to the big Autokomanda junction with the main state highway. This point can be considered as traffic-exposed. During the sampling, meteorological parameters including temperature, relative humidity, rainfall, wind direction and speed were provided by the Meteorological Station of the Hydro-Meteorological Institute of the Republic of Serbia located inside the central urban area, very close (≈ 200 m) to the Autokomanda sampling site.

Suspended particles were collected on preconditioned and pre-weighed Pure Teflon filters (Whatman, 47 mm diameter, 2 µm pore size) and Teflon-coated Quartz filters (Whatman, 47 mm diameter) using two MiniVol air samplers (Airmetrics Co. Inc., 5 l min^{-1} flow rate) provided with PM_{10} and $PM_{2.5}$ cutoff inlets. Particulate matter mass concentration was determined by weighting of the filters using a semi-micro balance (Sartorius, R 160P), with a minimum resolution of 0.01 mg. Loaded and unloaded filters (stored in Petri dishes) were weighed after 48 hours conditioning in a desiccator, in the clean room at a relative humidity of 45-55% and a temperature of 20 ± 2 ˚C. Quality assurance was provided by simultaneous measurements of a set of three ''weigh blank'' filters that were interspersed within the pre- and post- weighing sessions of each set of sample filters and the mean change in "weigh blank" filter mass between weighing sessions was used to correct the sample filter mass changes. After completion of gravimetric analysis, PM samples were digested in 0.1 N HNO3 on an ultrasonic bath. An extraction procedure with dilute acid was used for the evaluation of elements which can become labile depending on the acidity of the environment. This procedure gives valid information on the extractability of elements, since the soluble components in an aerosol are normally dissolved by contact with water or acidic solution in the actual environment. Details on sampling procedures and PM analysis are given in detail elsewhere (Rajšić et al., 2004; Tasić et al., 2005; Rajšić et al., 2008, Mijić et. al., 2009).

The bulk deposition (BD) collection was performed using an open polyethylene cylinder (29 cm inner diameter and 40 cm height) fitted on a stand at about 2 m above the ground. The devices collected both rainwater and the fallout of particles continuously for one month periods from June 2002 to December 2006 at FVM site. The collection bottles were filled before each sampling period with 20 ml of 10% acidified (HNO3 65% (Suprapure, Merck) ultra pure water. Precautions were taken to avoid contamination of samples in both the field and laboratory. Details on studied sites and sampling procedures are given by Tasić et al (2008; 2009).

The elemental composition (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb) of the aerosol samples and bulk deposition, was measured by the atomic absorption spectroscopy (AAS) method. Depending on concentration levels, samples were analyzed for a set of elements by flame (FAAS) (Perkin Elmer AA 200) and graphite furnace atomic absorption spectrometry (GFAAS) using the transversely-heated graphite atomizer (THGA; Perkin Elmer AA 600) with Zeeman-effect background correction.

3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) coupled with Energy-Dispersive X-ray analysis (EDX) was used for the characterization (size, size distribution, morphology and chemistry of particles) of suspended atmospheric particulate matter in order to improve source identification (US-EPA, 2002).

Approximately 0.5x0.5 cm^2 of the quartz filter was cut off and mounted onto an copper SEM stub using carbon conducting tap and then coated with a thin gold film (<10 nm) using JFC 1100 ion sputterer in order to get a higher quality secondary electron image. The measurements were carried out by the JEOL 840A instrument with INCAPentaFETx3 energy dispersive X-ray microanalyzer at the Faculty of Physics, Belgrade. The electron beam energy was 0-20 keV, probe current of the order of 100 μA and magnification up to 10 000. Analyzing SEM images we determined the particle size distribution in relation to heating and non-heating period. Further more, shape factor (SF) defined as

$$SF = 4\pi \frac{A}{P^2} \tag{9}$$

where, A is the particle area and P is the particle perimeter was determined. The perimeter refers to the circumference of the projected area and the area refers to the projected area of a particle. Both parameters are derived from SEM images. For a perfect circle SF equals one, and SF decreases as the circle is more and more distorted (for example SF equal to 0.785 for square like and 0.436 for oblong). The SF was determined for all particles analyzed and SF-size distributions were established based on these data. Shape factor distribution can reveal the dominant shape groups of the particles and thus contribute to identification of source emission.

3.3 Receptor Models Application

In the current study, the Unmix model and PMF have been used to analyze a 2-years $PM_{2.5}$ data set and 5-years element bulk depositions respectively for source apportionment purpose. The analysis generated source profiles and overall percentage source contribution estimates for source categories.

Demonstration of PSCF and CWT usage was presented on five years PM_{10} data set (2004-2008) continuously recorded by the Institute of Public Health of Belgrade and Trajstat software (Wang et al., 2008). The PSCF value can be interpreted as the conditional probability that the PM concentrations greater than the criterion level (in this case PM average value for the investigated period) are related to the passage of air parcels through the *ij*-th cell during transport to the receptor site. Cells with high PSCF values are associated with the arrival of air parcels at the receptor site that have concentrations of the PM higher than the criterion value. These cells are indicative of areas of high potential contributions for the PM. Air masses back trajectories were computed by HYSPLIT (HYbrid Single Particle Lagrangian Integrated Trajectory) model (Draxler, 2010; Rolph, 2010) throw interactive READY system. Backward trajectories started at different heights traverse different distances and pathways. For longer range transport (>24h), trajectories that started at different heights may vary significantly. If this occurs, PSCF modelling results might also be different. Daily back trajectories were evaluated for 2 days and different heights (m) above ground level (300, 500, 1000, 1500, 2000, 3000). The grid covers area of interest with cells 0.5^0x0.5^0 latitude and longitude.

4. Results and Discussion

4.1 Unmix Model – PM$_{2.5}$

Descriptive statistic for daily mass and trace element concentrations in PM$_{2.5}$ sampled in urban Belgrade, during the period from June 2003 through July 2005, is given in details by Rajšić et al (2008). Unmix receptor model was run with 50 observations of 10 input variables (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb). Three factors were chosen as the optimum number for the Unmix model, details of which are discussed as follows. The element profiles of the sources for PM $_{2.5}$ are given in Table 1.

The first profile extracted by Unmix is the **fossil fuel combustion** source having the high loadings of Ni and V, which are the fingerprint elements for fuel oil burning. It also includes high loadings of Cu and Cr which are also characteristics of emissions by vehicles using diesel fuel and local industry. This source most probably reflects urban region where residual oils are common fuels for utility and industrial sources and it has average contribution of 40%.

The second Unmix profile has high loadings of Cd that is typical for emission of high temperature combustion processes such as **metallurgical industry** and fossil fuel combustion. This factor having also low loadings of Fe accounts for 13% of the total and can be indicated as industry source.

The third Unmix profile is dominated by Al, Zn, Fe, Mn and Cr with average contribution of 47%. Its bulk matrix is soil, while correlations with other metals indicate some other sources, such as tire treat, brake-drum abrasion etc. This factor is interpreted as **resuspended road dust**, which includes soil dust mixed with traffic related particles.

Scatter-plots of measured and Unmix predicted PM$_{2.5}$ element (Zn, Mn, Al, Cd) concentrations are presented in Fig. 2. The correlation coefficients are in the range of 0.7-0.94. The results of Unmix modelling on PM$_{2.5}$ samples indicate that resuspended road dust and fossil fuel combustion play the most significant role.

	Fossil fuel combustion	Metallurgical industry	Resuspended road dust
Pb	5.36	1.53	16.70
Cu	30.10	0	0
Zn	60.40	0	1900
Mn	2.97	0	13.40
Fe	0	288	852
Cd	0	0.75	0.02
Ni	72.60	0	0
V	69.30	0	0
Al	0	0	1740
Cr	3.00	0	2.07

Table 1. The element profile of the sources for PM$_{2.5}$ resolved by Unmix
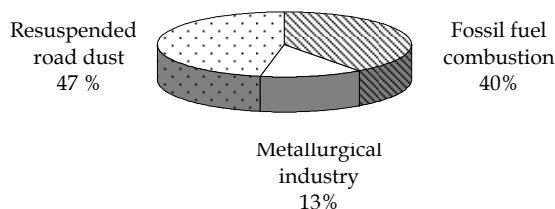
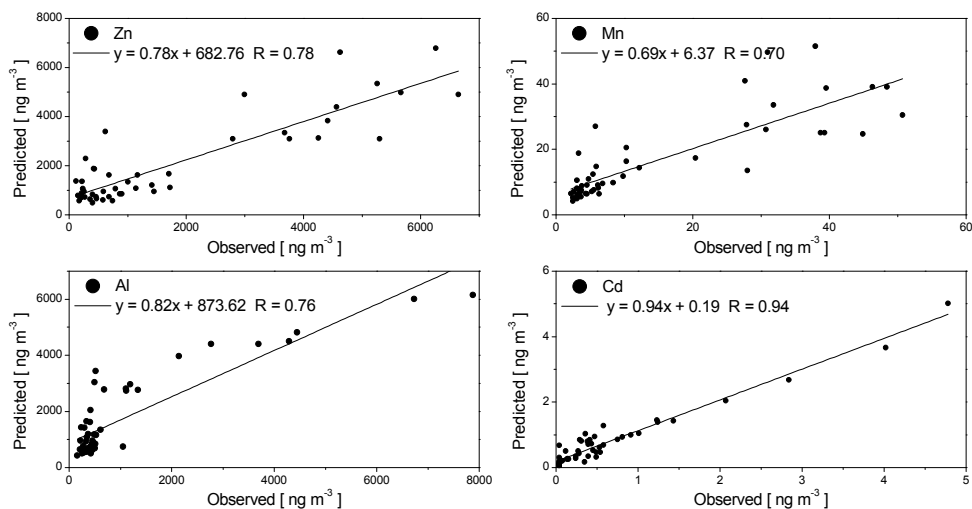Fig. 2. Unmix resolved source contribution in PM$_{2.5}$

Fig. 3. Scatter-plots of measured and Unmix predicted PM$_{2.5}$ element concentrations

4.2 PMF - Total Deposition

A total of 53 atmospheric deposit samples were collected monthly from June 2002 to December 2006 at FVM site, and element (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb) monthly fluxes were calculated. The statistical results of monthly element bulk deposition fluxes (BD), annual bulk deposition fluxes and seasonal variation are presented in detail by Tasić et al (2009). For source apportionment purpose, the PMF model was applied on element BD data set and resulted in six factors which have been identified as possible sources. The identified source profiles and time series plots of estimated monthly contributions for bulk depositions are presented on Fig 4.
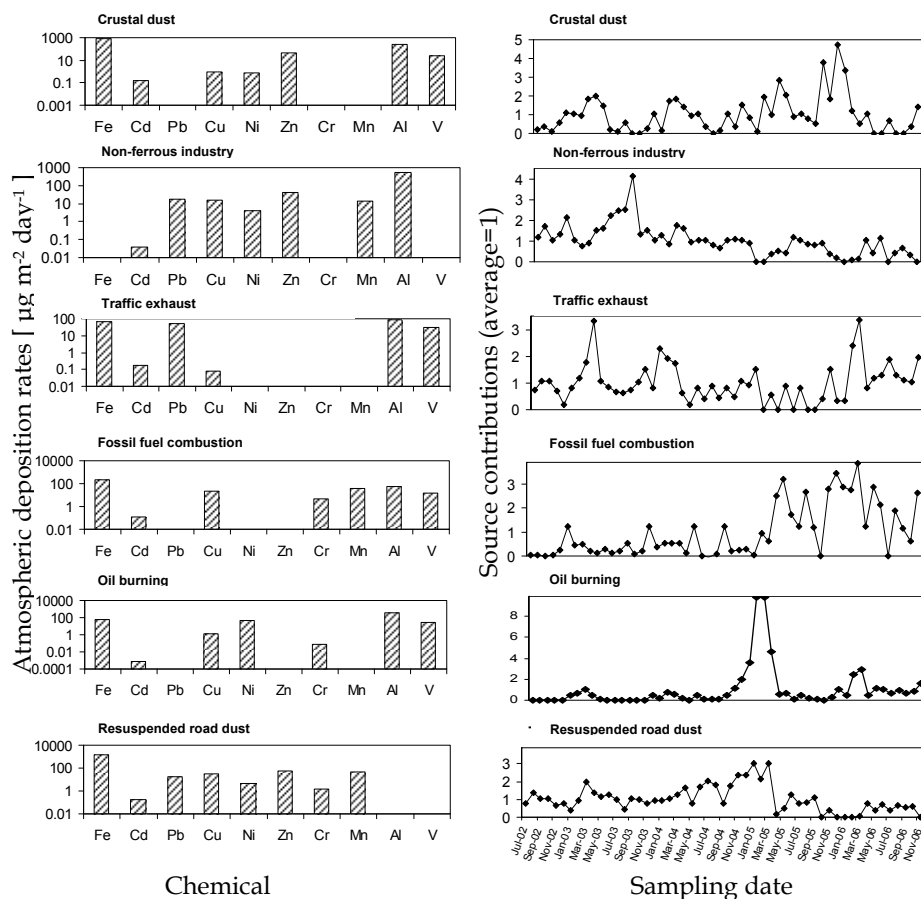
Fig. 4. Source profiles and time series plot of source contribution resolved from bulk deposition by PMF
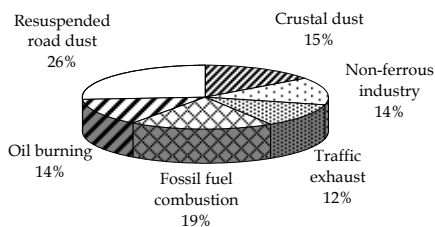

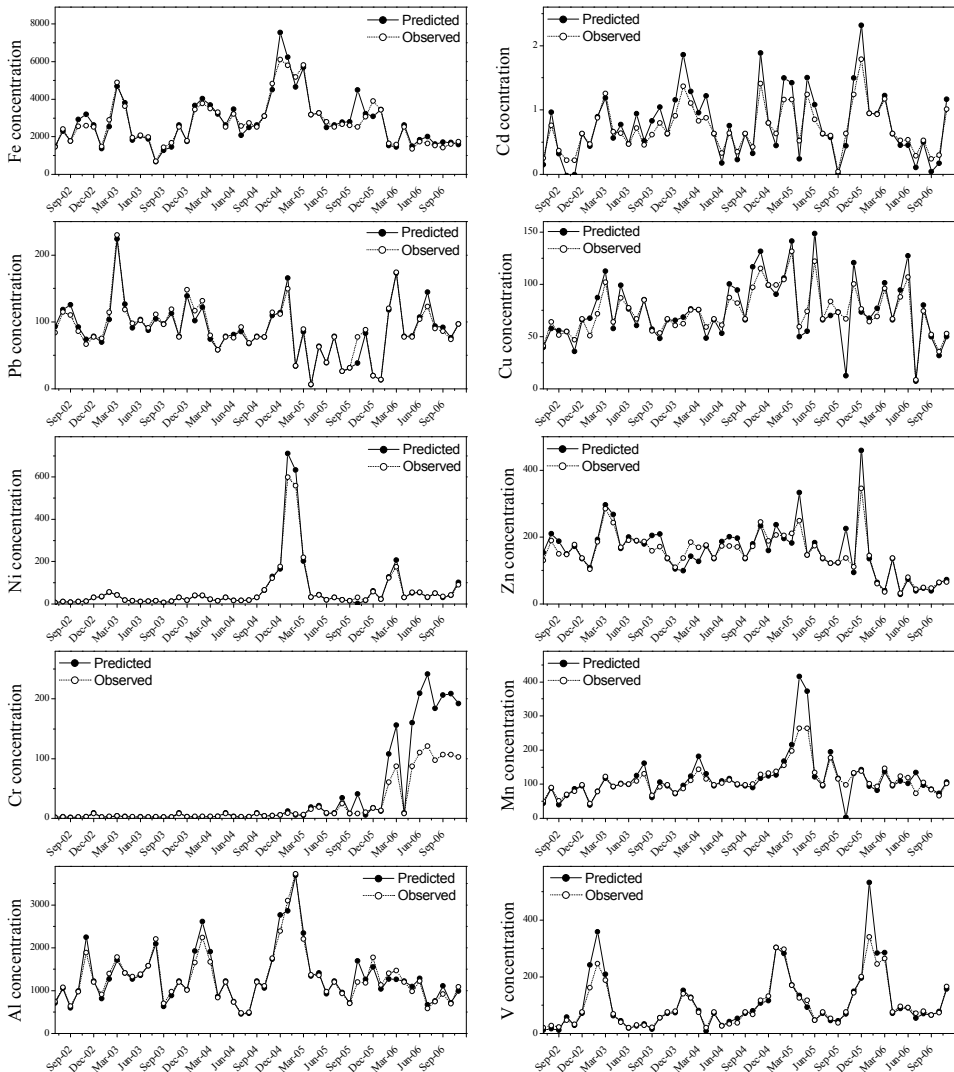Fig. 5. PMF source contribution in bulk deposition

Fig. 6. Time series plot of observed and PMF predicted element bulk deposition in Belgrade

The first factor dominated by Fe, Zn, Al, V and Cd accounted for 15% of the total variance and can be attributed to **crustal dust** contaminated with traffic related particles. Fe and Al are typical crustal elements; Zn is also one of the most common elements in the Earth crust. The second factor with high loadings of Al, Zn, Mn, Cu and Pb is related to **non ferrous metal industry** with contribution of 14%. The third factor resolved from the BD data is attributed to **traffic exhaust** source mostly loaded with Pb, V and Cd with overall contribution of 12 %. Pb probably comes from exhaust emission, since road vehicles use loaded gasoline or diesel fuel while Cd is related to fossil fuel combustion. The fourth factor

characterized by Cr, Cu, Cd, Mn and V. The greatest influence of Cr, can be attributed to the emission from **fossil fuel combustion**, probably mostly coal combustion. Manganese, typically dominated by crustal contributions, has been identified in the atmosphere from fossil fuel combustion and industrial emission sources as well. Emissions of chromium are mostly associated with particles emitted when burning fossil fuels, which includes power stations, cars and trucks. The emissions largely depend on the chromium content of the fuel, which varies with both the fuel type and source. Specific sources of chromium include metal smelting and foundries, cement production, etc. This factor contributes with 19% to the total data set. The fifth factor has high loadings of Ni and V, which are the fingerprint elements for fuel **oil burning** and most probably reflects urban region where residual oils are common fuels for utility and industrial sources. This factor associated to heavy oil burning has contribution of 14%. The sixth factor dominated by Fe, Mn, Cu, Zn, Pb, Cd and Cr has contribution of 26%. Fe and Mn are typical crustal elements, which may have been present in dust resuspended by traffic; Pb, Zn, and Cu are indicator elements of traffic emission; Cu, Fe and Zn are present in resuspended brake wear particles; Fe is also related to heavy-duty diesel emissions; the high Mn concentrations are related to motor vehicles that burn gasoline with the Mn additive. This factor was identified as **resuspended road dust**.

4.3 PSCF and CWT Results

Additional insights into the nature of the identified Unmix PM sources are provided through a trajectory based evaluation of the upwind locations associated with high concentrations of these sources. Five year PM_{10} data set (2004-2008) has been used in PSCF and CWT modelling. PM_{10} data were separated for summer and winter period, and then divided into the two groups, greater and lower of average values for specific period. Calculated PSCF values were subdivided into four categories: very weak (0.0–0.20), weak (0.20–0.40), intermediate (0.40–0.60) and strong (0.60–1.0). The results of PSCF are presented in Fig 7 (left). Based on the analysis of the whole trajectory data set, the most frequently arriving directions are west, north-west and south-west thus suggesting the sampling site might be under influence of several source regions. It can be seen that the highest PSCF values are from the west during summer period as well as during winter period. In addition, higher PSCF values are observed from north and south-east during winter period. The CWT method evenly distributes concentration along the trajectories similar to PSCF as presented on Fig. 7 (right). However, this method has an advantage over PSCF in that CWT distinguishes major sources from moderate ones by calculating concentration gradients. PSCF shows probabilities of potential sources based on samples with concentrations higher than the criterion, which does not distinguish between moderate and major sources. The results suggest that the major contribution to atmospheric PM_{10} concentrations comes from local and regional sources. There is evident a long – range transport from western countries which is sporadically (mostly in spring and summer) associated with African dust outbreaks in levels of both PM_{10} and $PM_{2.5}$ (Kubilay et al., 2000; Perez et al., 2008).
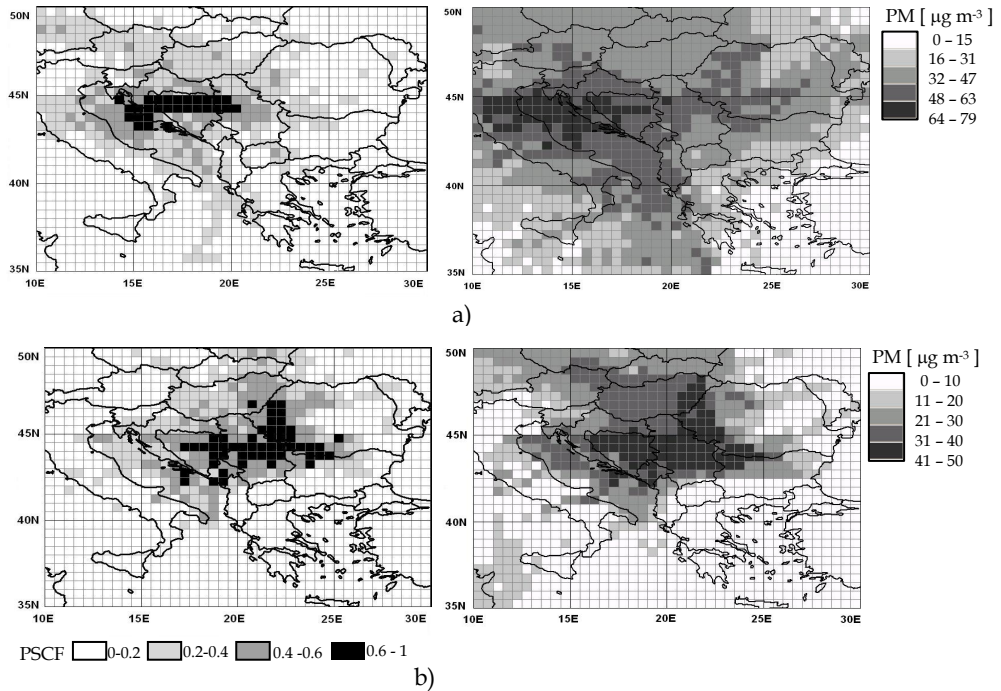
Fig. 7. Distribution of PSCF (left) and CWT (right) for PM$_{10}$ during a) summer and b) winter period 2004-2008.

4.4 SEM / EDX Characterization of Particles

Atmospheric particulate matter sampled in the urban area of Belgrade was analyzed with scanning electron microscopy coupled with energy-dispersive X-ray analysis. Particles were distinguished in terms of both particle morphology (rounded particles, mineral grains, etc.) and composition (determined by qualitative EDS analysis). Tens photomicrographs were arbitrarily taken under low resolution conditions and about 500 particles per PM sample were assessed for morphology and about 30 particles for the X-ray spectral analysis.

As the result of SEM images analysis particle size and shape distributions were determined for non-heating and heating periods and presented on Fig. 8.
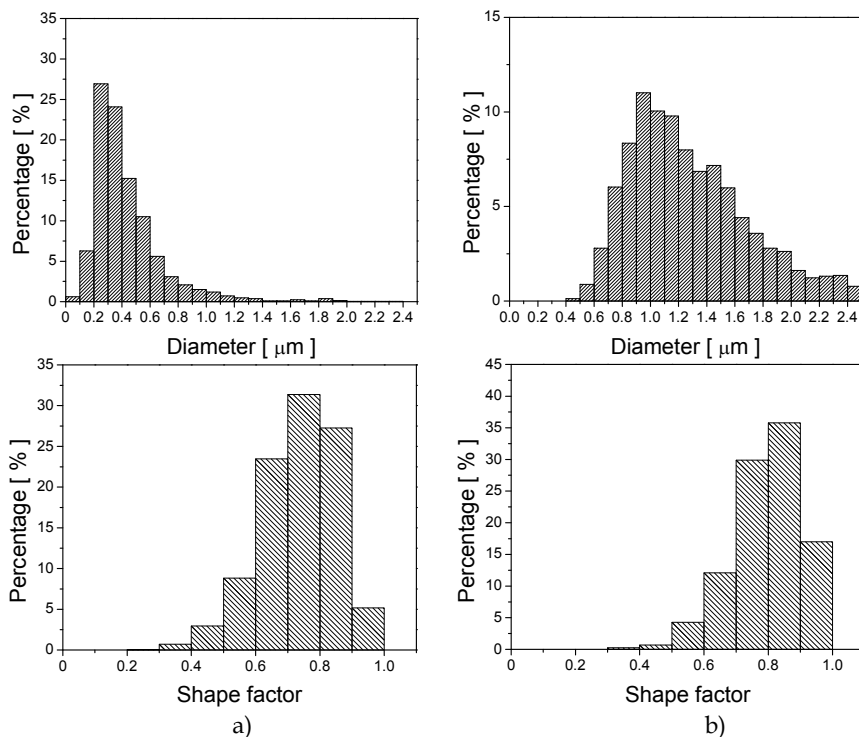
Fig. 8. Particle size distribution and shape factor of PM$_{2.5}$ samples in the a) non-heating and b) heating period.

The particle size distribution spans wider in the heating period than in the non-heating period with more coarse mean size value. Mean size value observed during heating period is 1.32 μm with standard deviation of 0.52 μm, while mean size value observed during non-heating period is 0.44 μm with standard deviation of 0.27 μm. Particles shape group with SF close to 1 (sphere like shape) obviously increase during the heating period and in the non-heating period more particles are square like. According to the morphology, two main particle categories were observed: particles of natural sources that include materials of organic origin (pollen, bacteria, fungal spores etc.) and anthropogenic particles.
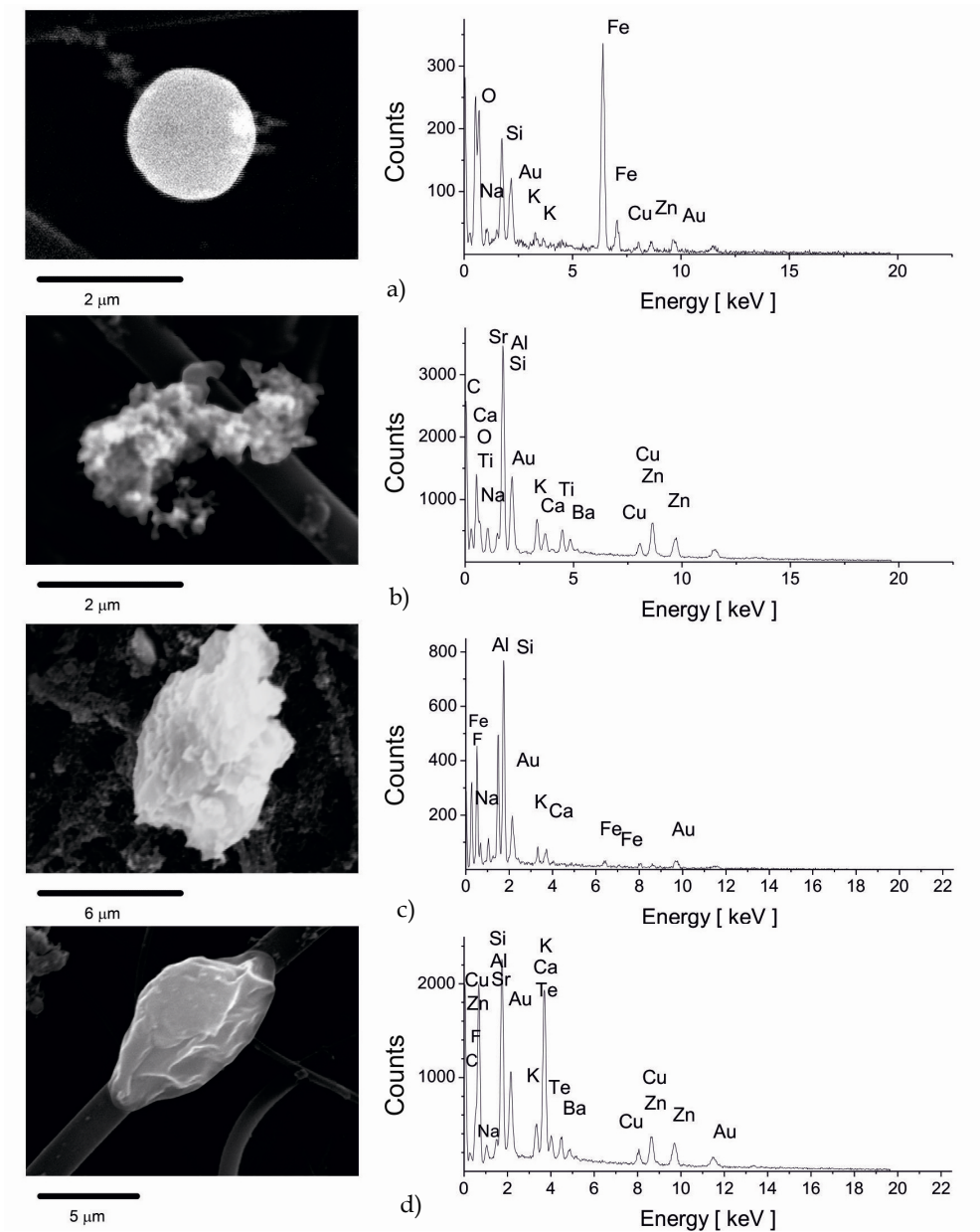
Fig. 9. SEM images of characteristic aerosol particles shape and corresponding X-ray spectra in Belgrade: (a) sphere; (b) soot agglomerate; (c) irregular; d) stick

This category also includes suspended soil dust (mostly minerals) such as the angular-shaped material. Particles from anthropogenic sources, mostly emitted from high

temperature combustion processes are characterized by their spherical shapes and smooth surfaces. This type of particles occurs as individual particles but also in an aggregate form, as agglomerates of similar-sized particles and individual large particles carrying several smaller attached particles (Tasić et al., 2006).

The elemental composition of selected particles in the secondary electron images was deduced from an energy dispersive X-ray spectrum in the energy range of 0 – 20 keV, collected from the selected particles for a spectrum acquisition time of 100 s. The elements observed were: Al, Si, C, S, N, Cl, P, K, Ca, Na, Mg, Cr, Fe, Cu, Zn, Ni, Cd, As, Ti, Te, Sr, F and V. The presence of Au lines on all spectra is due to Au coated samples. The SEM photomicrographs of some characteristic particles and their X-ray spectra are presented in Fig. 9 (a, b, c, d).

Rounded particles of complex compositions were interpreted as anthropogenic 'fly ash' particles, formed by high-temperature combustion processes. In most of the samples analysed, the spherical particles were mainly composed of Al-silicates and oxides of Fe, Zn, Cu, Ni, Pb, Ti. (Fig.9a).

Carbonaceous particles have been known to make up 50% of the aerosol in urban areas (Pandis et al., 1995) and principally consist of soot aggregates with irregular morphology of various shapes (Fig. 9b). Soot is present as agglomerates of many fine spherical primary particles originating mainly from petrol and diesel exhausts and contain C, O, Na, Si, Al, Cu, Zn, Sr, Ba, and Ti.

The most of silica particles (probably Si oxides) and aluminosilicates (containing Al, Si, K, Ca, Fe, F and Na) present in the coarse fractions have irregular forms and come from soil (Fig. 9c).

Sulphates are characterized by a strong S line in the X-ray spectrum and mostly by the presence of Ca, or Fe, Pb and K. These particles are formed as a result of the reaction in the atmosphere between sulphur compounds and other substances. Sulphate clusters, often with sharp edges are mainly composed of Ca sulphates.

Many particles, which could not be classified into one of these groups, in the coarse particle range, were mixed aggregates, irregularly shaped, consisting of soil and road dust: Si, Al with minor constituents such as C, Ca, Ba, K, Zn, Cu, Te, F and Sr, (Fig.9d).

5. Conclusion

In the field of atmospheric sciences receptor models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants based on ambient data measured at the monitoring sites. The information provided by receptor models is key to the design of effective mitigation strategies of the pollutant on the local and meso-scale. In addition, many epidemiological and health-related studies used the results obtained by receptor modelling. Because of widespread need there is growing information available on receptor modelling results from different countries, the type of models applied and the input data utilised. Short review of most popular receptor models used in source apportionment studies was presented in this paper.

Several receptor models (Unmix, PMF, PSCF, CWT) were applied to PM data set and bulk deposition fluxes in Belgrade urban area for pollution source apportionment. The Unmix model identified three sources of particulate matter $PM_{2.5}$: fossil fuel combustion (40%), metallurgical industry (13%) and resuspended road dust (47%). PSCF method indicates that

the most frequently arriving directions of PM_{10} transport are west, north-west and south-west thus suggesting the sampling site might be under influence of several source regions while the results of CWT analysis suggest that the major contribution to atmospheric PM_{10} concentrations comes from local and regional sources. The PMF analysis on bulk deposition fluxes resolved six sources: crustal dust, non ferrous industry, traffic exhaust, fossil fuel combustion and oil combustion.

Both methods, Unmix and PMF followed by characterization of individual particles by SEM/EDX analysis suggested that the road traffic, fossil fuel combustion and industry are the major sources of heavy metals in the Belgrade urban atmosphere.

Receptor models, of both the mathematical (PMF and Unmix) and trajectory (PSCF and CWT) types promise to be helpful tools for source attribution for atmospheric pollution ($PM_{2.5}$ and BD). The mathematical techniques objectively identify sources of influence on the data, but a good deal of subjective judgment is inevitably required in the interpretation of what these identified sources actually represent. The ensemble trajectory techniques produce only qualitative indications of predominant transport patterns and can be highly sensitive to the subjective metrics calculated from the gridded results.

The future direction should be related to the investigation of compatibility between receptor models and combination of back trajectory modelling with source apportionment analysis in order to improve the understanding of source receptor relationships, the confidence in the individual model results, and develop a better understanding of the underlying aerosol data. Models such as PMF, ME and Unmix are able to provide uncertainty estimates by applying a bootstrapping method. Such uncertainty estimations should thus be applied in future source apportionment studies.

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7. References

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