
Enhancing source apportionment with receptor models to foster the air quality directive implementation

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Abstract: Receptor models (RMs) identify pollution sources by solving a mass balance equation using measured chemical composition of samples either in combination with known source profiles or not. This approach has been extensively used in North America and South-Eastern Asia mainly on particulate matter (PM). Also, in Europe RMs found wide acceptance and contributed to the identification of sources in support of remediation measures development. With the aim of harmonising the activity on receptor modelling in Europe and supporting the implementation of Directive 2008/50/EC, a survey on the use of this methodology was carried out. In this study we discuss the sources of uncertainty in the input data, and the uncertainty contribution deriving from critical steps. We describe a methodology to assess RMs performance in intercomparison exercises developed and evaluated by the JRC within the framework of the forum for air quality modelling (FAIRMODE).

Keywords: source apportionment; intercomparison; particulate matter; mass balance; remediation measures; harmonisation; Europe; uncertainty; air quality directive; environmental pollution; receptor models; RMs.

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1 Introduction

The identification of pollution sources is required in many tasks concerning the air quality legislation (air quality assessment, development of action plans, identification of natural sources, etc.). Receptor models (RMs) are used to accomplish source apportionment by analysing chemical and physical parameters measured at one or more specific sites (receptor). RMs are based on the mass conservation principle and identify sources/factors by solving the mass balance equation given by:

$$x_{ij} = \sum_{k=1}^P g_{ik} f_{kj} + e_{ij} \quad (1)$$

where x_{ij} is the concentration of the j^{th} species in the i^{th} sample, g_{ik} is the contribution of k^{th} source to i^{th} sample, f_{kj} is the concentration of the j^{th} species in the k^{th} source, and e_{ij} is the residual for each sample/species. RMs that explicitly use source profiles (f_{kj}) to solve equation (1) are referred to as chemical mass balance methods (e.g., CMB) while models which solve the equation without using 'a priori' information on sources composition are called multivariate models [e.g., principal component analysis (PCA), UNMIX, positive matrix factorisation (PMF) and the other factor analysis (FA) models]. An intermediate category consists of multivariate models that can accommodate profiles of some sources and other constraints [e.g., COPREM and PMF solved with multilinear engine (ME)]. RMs are most commonly used to apportion particulate matter (PM) on the basis of its chemical composition. Typical input data are: major ions (e.g., nitrates and sulphates), carbonaceous fractions (organic and elemental carbon), trace elements and organic markers (e.g., levoglucosan and hopanes). Also, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), inorganic gases and aerosol size distributions have been used for source apportionment with RMs.

RMs process input data uncertainty and intrinsic model uncertainty in order to estimate the uncertainty in their output. This methodology is independent from emission inventories and is appropriate for urban and regional scales. Moreover, when wind speed and direction or backward trajectories are explicitly included in the analysis, RMs are suitable to study medium to long range transport (Hopke, 2009).

In this paper, we present a survey carried out to identify the RMs commonly used in Europe, discuss the main sources of uncertainty in these techniques and describe a new methodology to assess RMs performance in intercomparison exercises.

2 RMs used in Europe

A survey on the use of RMs for PM source apportionment in Europe between 2001 and 2010 is presented (studies performed in 2011 and available when the manuscript was submitted are also included). A total of 79 studies in 18 countries using 11 different model types were examined. In the 243 reported records the considered mass fraction spans from PM_{10} to PM_1 . About 60% of the studies were carried out in urban background sites, 16% in source oriented sites, 15% in rural sites, and the remaining 9% in either remote, suburban or residential sites.

The significance of RMs is evidenced by the dramatic increase in the number of scientific publications on this topic during the last decade and the increasing ready-to-use available tools. The highest increase rate in the number of studies coincides with the entry into force of the limit value for PM_{10} (Directive 1999/30/EC) and the target value for $PM_{2.5}$, (Directive 2008/50/EC), in 2005 and 2010 respectively (Figure 1). In the last decade, 36% of the receptor modelling studies on filed air quality data were performed with PMF and ME, 24% with CMB, 20% with PCA and absolute PCA (APCA or APCS), 9% with FA and absolute principal component factor analysis (APCFA), and the remaining 11% with either APEG model, COPREM, Lenschow (or incremental concentrations approach), UNMIX or mass closure (MC).

Figure 1 Time trend of RMs studies in Europe between 2001 and 2010 (see description in the text) (see online version for colours)

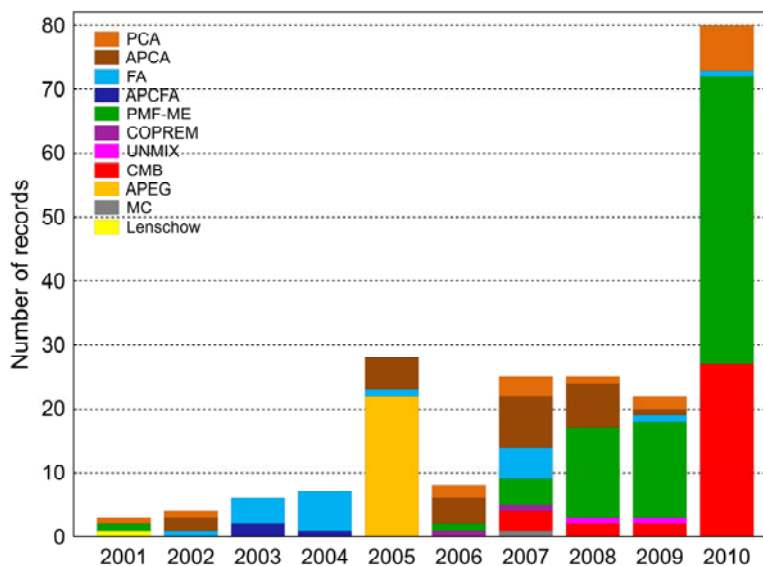


Figure 2 European source apportionment studies published between 2001 and 2010 (including some studies carried out in 2011) grouped by model type (see online version for colours)

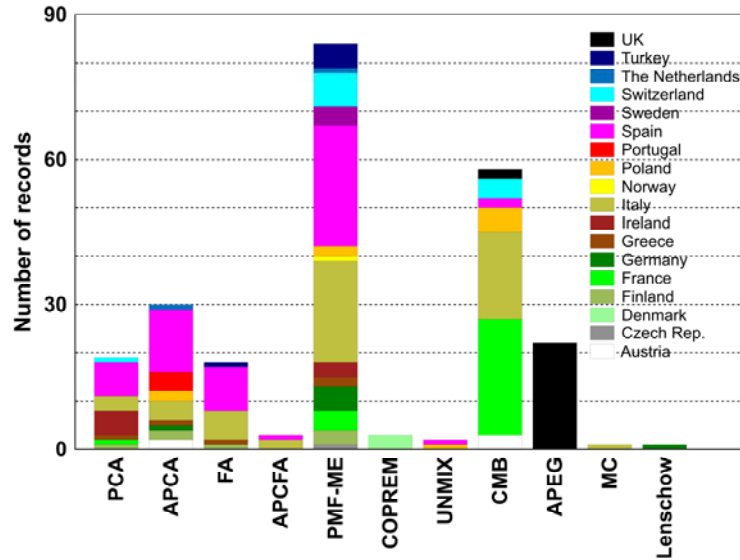
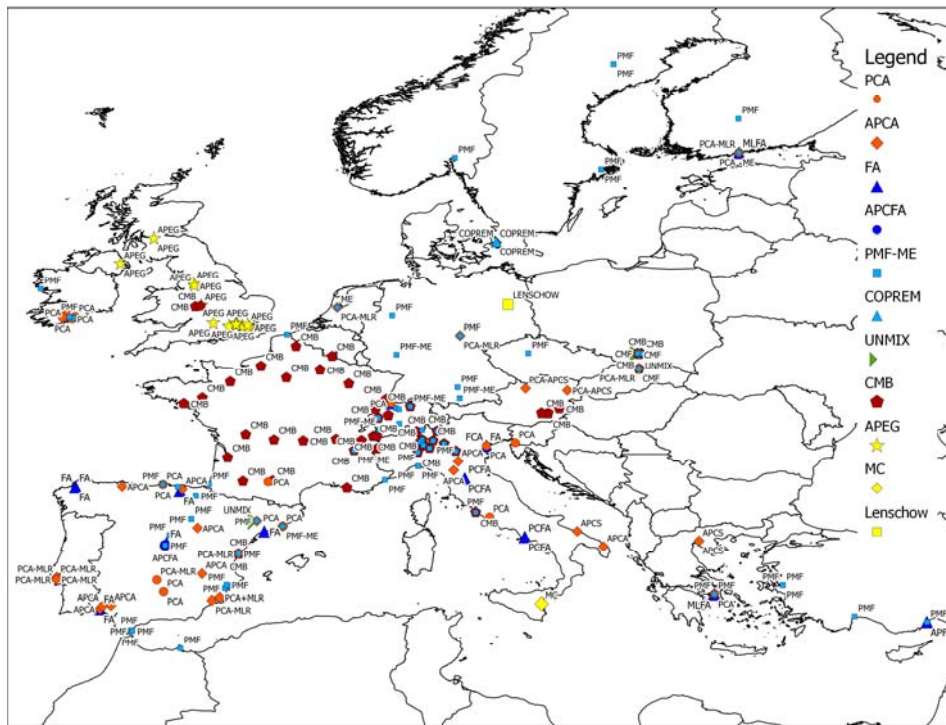


Figure 3 Geographic distribution of European source apportionment studies using RMs published between 2001 and 2010 (including some studies carried out in 2011) (see online version for colours)



The most common model (88 records) is PMF, which is sometimes solved using the ME platform. This kind of models became widespread especially after 2005 when the US-EPA made available user-friendly on line versions. The diffusion of PMF is also linked to its use in the elaboration of aerosol mass spectrometer (AMS) data, mostly oriented to the apportionment of the PM₁ organic particulate (nine studies). PCA and APCA family of models (50 records) are also very popular and dominate during the first part of the last decade. CMB and the FA models (FA and APCFA), are used in 59 and 22 records, respectively. Despite their good potentials UNMIX and COPREM aroused little interest among European experts.

There are conceptual models based on a number of empirical assumptions that have been used in specific geographic areas. APEG receptor model was developed by the 'Air Pollution Experts Group' in the UK and was used for extensive (preliminary screening) source apportionment studies on several cities. The Lenschow model was developed in Germany to estimate broad categories of sources combining different type of data from large cities and their surrounding area.

Spain and Italy are the countries with the highest number of receptor model records (58 and 56, respectively), followed by France (29), UK (24), Switzerland and Poland (12). A number of studies are also reported for Ireland (8), Germany (7), Finland and Turkey (6), Greece and Austria (5), Portugal and Sweden (4), Denmark (3), and the Netherlands (2). Only one record is available for Norway and Czech Republic (Figure 3).

The survey shows that different models and approaches (model implementations) are used in SA. In order to test whether the methodologies are suitable for the purpose of identifying sources, their performances should be assessed on the basis of quantitative criteria. Such criteria are commonly expressed as maximum accepted uncertainty. In the following sections the main sources of uncertainty and the methodology developed to test model performance in intercomparison exercises are discussed.

3 Sources of uncertainty

In RMs the uncertainty derives from both inaccuracy in the input data and model assumptions and ambiguities. Interpreting the results of a source apportionment study and comparing results from studies in different sites or in the same site with different models requires proper uncertainty estimation. In addition, there are models like PMF that weight data on the basis of their uncertainty. In this case, appropriate uncertainty estimation is a prerequisite for model execution. Moreover, improving the comparability of the model results requires harmonisation of the procedures according to international standards like the guide for the expression of uncertainty in measurements (GUM). Nevertheless, the analytical uncertainty is only the starting point to estimate the total uncertainty of the input data (Polissar et al., 1998).

3.1 Input data uncertainty

The identification of outliers and anomalous values is the first step to keep uncertainty under control. Also, criteria to report values below the minimum detection limit (MDL) need to be established. Certain models do not treat missing values; therefore, it is necessary to estimate them in order to avoid empty entries in the input data matrix.

Clearly, missing values and values below MDL have an impact on the quality of results since the uncertainty of estimated values is higher than the one of measured ones.

As previously mentioned, one of the most relevant components of input data uncertainty is the analytical one. The estimation of this component is carried out on the basis of the analytical method specifications. However, it often happens to deal with databases in which single entry uncertainties are unavailable or inconsistent. In these cases uncertainties may be estimated using equation-based approaches which rely on species MDL, empirical constants (k), species concentration (C) and/or coefficient of variation (CV).

Analytical uncertainty can be estimated by linear regression where σ_a is the uncertainty of the analytical procedure and m is the mass of the analyte, while σ_0 and α are fitting parameters (Anttila et al., 1995):

$$\sigma_a^2 = \sigma_0^2 + (\alpha m)^2 \quad (2)$$

In the estimated fractional uncertainties (EFU) method the error structures (s_{ij}) are (Kim and Hopke, 2005):

$$s_{ij} = [MDL] / 3 + kx_{ij} \quad (3)$$

When no empirical constants but MDL, and CV are used, the analytical uncertainty is (Chow et al., 2007):

$$\sigma_{i,t}^a = \sqrt{MDL_i^2 + (CV_i \times C_{i,t})^2} \quad (4)$$

Sampling contributes to the uncertainty of measured values due to sampling volume uncertainty, selective effect and other artefacts caused by the inlet, losses due to sample transport and conservation. These contributions can be assessed with field tests (e.g., collocated measurements and comparison with reference instrumentation). Other authors incorporated the sampling uncertainty into the input data uncertainty by considering the sampled volume (V_i) and a coefficient (β) to account for additional uncertainty sources (Amato et al., 2009):

$$\sigma_{ij}^2 = \sqrt{\frac{\sigma_A^2}{V_i^2} + (\beta x_{ij})^2} \quad (5)$$

The time representativeness of the model outputs depends on the amount and distribution of collected samples. Studies oriented to assess average levels use samples collected throughout the year, while studies interested in specific kind of events may concentrate the data collection in specific time windows (seasons, weeks).

The output of RMs like CMB, which use source profiles as input, could be seriously affected by their uncertainty. In order to prevent problems of collinearity, sources with similar chemical composition must be combined into source categories. The selection of sources to include in the final input should represent the local sources and their time variability in the study area. The suitability of source profiles may be checked with edge analysis and ratio-ratio plots (Robinson et al., 2006). Moreover, using measured local source profiles contributes to improve the model performance (Colombi et al., 2010).

3.2 *Uncertainty associated with model performance*

Considering that RMs rely on the mass conservation principle between source and receptor, substantial departures from this assumption due to evaporation, condensation or degradation of species, constitute a source of uncertainty. A way to deal with this kind of species is to increase their uncertainty according to their volatility or reactivity. Also, reactive species stray from the mass conservation principle. RMs often identify secondary inorganic aerosol assuming that ammonium sulphate and nitrate mainly derive from gaseous precursors. When quantitative information about the processes that precursor species undergo after emission is available, it is possible to introduce empirical coefficients [e.g., fractional aerosol coefficients, (Grosjean and Seinfeld, 1989)] to estimate the expected amounts of products at the receptor.

In multivariate models, the number of relevant factors and their correspondence with sources is unknown and represents another source of uncertainty. Estimating the number of factors is often performed with an iterative procedure by checking the influence of the number of factors on the model performance. A number of indicators such as, signal to noise, residuals, Q value (in PMF), are used to guide the selection of the number of factors. The procedure to establish a correspondence between the factors resulting from the analysis and the sources in the area may substantially contribute to the uncertainty of the output. This step shall consider the comparison of the factor profiles with measured local source profiles either visually or using statistical tests to identify the best fit (advisable).

Another contribution to the overall uncertainty in FA is the lack of a unique solution due to the large number of unknown variables. This limitation of FA, called rotational uncertainty (Paatero and Hopke, 2009), is partially removed by non-negativity constraints in PMF. Tests on residuals, Q^m parameter, FPEAK and analysis of edges can be used to identify the best rotation (Paatero et al., 2002). Moreover, introducing additional information about the sources and other constraints contributes to reduce or eliminate the rotational uncertainty. The most evolved tools include routine tests to evaluate the model performance and provide an estimation of the uncertainty associated to the source contribution estimations (SCE). As an alternative, overall model uncertainty may be assessed by performing intercomparison exercises.

3.3 *Intercomparison of RMs*

The intercomparison consists of comparing the results of source apportionment analyses performed by independent practitioners using the same or different RMs on the same dataset. The intercomparison main objectives are:

- a to gather information about the reproducibility between different approaches and scientific backgrounds
- b to assess whether the uncertainty of the model output (SCE) meets given quality criteria.

In real-world source apportionment studies it is not possible to validate the model outputs against measured values since the actual contributions from the sources are unknown. Different approaches have been used to compare the performance of different models on

the same dataset: visual comparison of models' SCE mean and standard deviation for each source type (Favez et al., 2010; Hopke et al., 2006; Larsen et al., 2008), correlation coefficient (Favez et al., 2010; Hopke et al., 2006; Sandradewi et al., 2008) and regression analysis between SCE provided by different models (Rizzo and Scheff, 2007; Sandradewi et al., 2008).

The methodology to evaluate intercomparison results presented below was developed on the basis of international standards for proficiency testing exercises (ISO 13528). The method consists of three milestones:

- a the reference value (X), that is the value to be compared with participant estimations
- b the standard deviation for assessment ($\hat{\sigma}$), that is the criterion to evaluate participants' performance
- c the algorithm to compare participants and reference values (z-score or z'-score).

The test is performed for every source category separately. The correspondence of sources identified by participants to each source category is tested by comparing its chemical profile (loadings) and time trend (scores) with all the other members of the same category and with measured source profiles, when available. The comparison is performed using Pearson correlation coefficient (P) and the weighted difference (WD):

$$WD_{ij} = 1/n \sum_{a=1}^n \frac{x_{ia} - x_{ja}}{\sqrt{s_{ia}^2 + s_{ja}^2}} \quad (6)$$

where x_i and x_j are the relative concentrations (or their logarithms) of the n species in the factor/source profiles i and j , respectively, and s_i and s_j are their uncertainties. Only factor/sources with median $P \geq 0.6$ and median $WD \leq 2$ are to be included in the following step.

When a synthetic database is used, the reference values (X) are the known source contributions. On the contrary, when the database consists of real-world measurements, X is the expected SCE for a given source and is generated by the robust analysis iterative algorithm (Analytical Methods Committee, 1989). The algorithm is applied to the participant's average values and provides the robust average (x^*) and the robust standard deviation (s^*).

The assessment criterion ($\hat{\sigma}$), may be either derived from Directive 2008/50/EC model quality objectives (50% for PM annual mean) or calculated by robust analysis (s^*).

The participants' scores are calculated using the z-score performance indicator (ISO 13528). The z-score indicates whether the difference between the participant measured value and the reference value remains within the limits of the specified criterion.

$$Z = \frac{x_i - X}{\hat{\sigma}} \quad (7)$$

If $|Z| \leq 2\hat{\sigma}$, results are considered coherent with $\hat{\sigma}$, if $2\hat{\sigma} \leq |Z| \leq 3\hat{\sigma}$, results are considered questionable, and if $|Z| > 3\hat{\sigma}$, results are considered not coherent with $\hat{\sigma}$.

4 Conclusions

The survey showed that RMs are widely used in Europe to identify pollution sources. The kind of outputs and the availability of ready-to-use tools evolve continuously and make this methodology suitable for providing reliable inputs for air quality policy planning and follow up. Nevertheless, quantitative assessment of model performances and definition of common criteria and procedures are required to set quality standards and improve the comparability of the studies across Europe.

Assessment and reporting of model input and output uncertainty is a prerequisite for model performance evaluation. In the present paper, input data inaccuracy and model assumptions and ambiguities are considered the main sources of uncertainty in receptor modelling. Moreover, in order to evaluate whether models meet given quality standards in intercomparison exercises, a methodology based on model output uncertainty is described.

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