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A review of

SOURCE APPORTIONMENT TECHNIQUES AND MARKER SUBSTANCES

AVAILABLE FOR

IDENTIFICATION OF PERSONAL EXPOSURE, INDOOR AND OUTDOOR SOURCES OF CHEMICALS

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The mission of Institute for Health and Consumer Protection is to provide scientific support to the development and implementation of EU policies related to health and consumer protection. The IHCP carries out research to improve the understanding of potential health risks posed by chemicals, biocides, genetically modified organisms, contaminants released from food contact materials and consumer products.

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Foreword

For the development and implementation of European policies protecting human health and the environment, the European Commission (EC) needs sound scientific knowledge on occurrence, source strengths, distribution and fate of the chemical substances, i.e. reliable exposure data. In the current stage of the development of the European Union (EU) strategy on chemicals (REACH; Registration Evaluation and Administration of Chemicals), there is abundant evidence among experts and policy makers, that human exposure data and specific source contributions represent a major bottleneck to any level of risk assessment. In 2002, the EU Council of Environmental Ministers has put forward a request to the European Commission to undertake action for eliminating existing deficiencies in exposure data. This gave the Joint Research Centre (JRC) a clear mandate to accurately evaluate the risk for European citizens deriving from the overall exposure to chemicals through different routes (food intake, air inhalation, skin contact, etc.) occurring in indoor and outdoor environments.

In the context of the EC 6th Framework Programme, the scope of the THEXAS-Chem (Total Human Exposure Assessment Study) action of the JRC's Institute for Health and Consumer Protection (IHCP), is the development, validation, harmonisation, and standardisation of assessment methods and models for quantifying total human exposure to chemical substances. In particular, experimental work is carried out in order to define robust parameters for realistic evaluation of risks. These methods and models are the most critical tools needed in exposure estimates and risk assessment regarding the environmental and health impact of chemicals.

In the context of THEXAS-Chem, the need to provide relevant data to evaluate human exposure to air pollutants guided the JRC research on indoor air pollution in recent years. This included, apart from specific measurements in selected confined spaces, such as homes, workplaces and schools, larger-scale monitoring campaigns at European level, such as the AIRMEX (Indoor Air Monitoring and Exposure Assessment) study. Campaigns were specifically designed to assess indoor and outdoor air quality and to assess personal exposures to pollutants in combination with time activity patterns. The information obtained from all these studies has been considered as crucial for a first evaluation of the overall situation in indoor environments, the possible sources and source strengths of pollutants, which humans are exposed to during working, commuting, and leisure time. However, the links between sources, emissions/releases of, and exposure to pollutants, as well as the impact of outdoor sources in indoor environments, especially in quantitative measures, need further studies.

As part of the aforementioned framework, the present report comprises a literature review on emission source tracers and source apportionment techniques providing supportive information for the development of harmonized exposure assessment practises and guidelines.

Summary

Introduction. The need of knowledge on occurrence, source strengths, distribution and fate of chemical substances is increasing. This knowledge is needed to effectively reduce levels of chemical substances in microenvironments that are harmful for human health and the environment. The only mechanism that ultimately will lead to cost effective reduction in population exposures is by the identification of sources that release these substances. Knowing the sources allows prioritization of substances/sources that most significantly contribute to target (sub)population exposures.

To apportion personal exposures to sources of substances present in indoor and outdoor air through daily time-activity patterns is a highly complex task. This requires reliable exposure data and the application of source apportionment techniques to all kinds of microenvironmental samples (indoor, outdoor and commuting). The present report provides an overview of the existing source apportionment techniques and source tracers and their respective data requirements and serves as a background and guidance document for the development of harmonized exposure assessment practises.

Methods. A literature survey was undertaken to identify source apportionment studies for two air pollutant groups, i.e. airborne particulate matter and volatile organic compounds. The results of this survey were used to compose an overview of the most commonly existing source apportionment techniques – also called receptor modelling - used to identify source contributions, including a description of the strengths and weaknesses.

Results. The fundamental principle of receptor modelling is based on the assumption that mass is conserved and that on this basis a mass balance analysis can be used to identify and apportion sources in the atmosphere. All techniques that were considered are based on assumptions regarding the source, chemical species and measurement methodology. They require a certain degree of knowledge about the source regarding the number of sources, source profile (which substances are emitted by which source) or source strength regardless the origin of the source (outdoors or indoors). Of all considered techniques, conventional factorization and chemical mass balances represent the two extremes. Conventional factorization requires little knowledge, while chemical mass balance strategies require exact knowledge about the source(s). Other techniques, such as Positive Matrix Factorization or UNMIX, can be considered as intermediate strategies and are based on partly overlapping or slightly different assumptions and source knowledge requirements.

Discussion and Conclusions. An ideal source apportionment study starts with selecting the trace elements or compounds representing the obvious sources that might contribute to the location where the measurements will be carried out. Consequently, the collection methods and chemical analyses should be selected in a way that the important marker species can be analyzed accurately. The number of samples is another major requirement for a successful source apportionment analysis. Typically at least tens of samples are needed for a reliable source apportionment analysis. From the methods considered in this report, chemical mass balance requires fewest samples, however, it requires the most detailed quantitative description of the number of sources and the respective chemical emission profiles. When identifying and interpreting emission sources of personal exposures or those of indoor air samples sufficient number of samples is required, i.e. preferably more than 50 samples for each receptor site.

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1. Introduction

Identification of sources of potentially harmful compounds in different microenvironments provides the only mechanism of reducing levels of these compounds in each microenvironment and ultimately leading to cost effective reduction in population exposures. More significantly it allows prioritization of those sources that contribute most significantly to exposures, and target subpopulations with elevated exposure levels (Edwards R.D. et al., 2001). The different existing source apportionment techniques, based on source markers, chemical mass balances, and statistical regression and factor analyses, numerically split air pollutant (mass) samples into (mass) fractions and chemical contributions from different sources. Apportioning personal exposures to sources in outdoor and indoor microenvironments and personal activities, including commuting, is a much more complex task and requires the application of source apportionment techniques to ambient, indoor and personal samples (Jantunen et al., 2003). The goal of this work was to “establish an updated review on source apportionment techniques and source tracers” that can be used as a background and guidance document to learn more about the existing techniques and various requirements and drawbacks.

Particulate air pollutants

Particulate matter (PM) consists of several elements and compounds deriving from a variety of sources. Previously, particles smaller than 10 µm in aerodynamic diameter (PM_{10}) have most often been collected and analysed. However, a study of associations between PM and mortality has suggested that fine particles (PM2.5; particles smaller than 2.5 µm in diameter) are more closely associated with day-to-day variations in mortality than the coarse fraction of PM10 (particles with diameter from 2.5 to 10 µm) (Schwarts et al., 1996). Also two cohort studies have suggested that ambient PM2.5 is closely associated with reduced survival (Dockery et al., 1993; Pope et al., 1995). PM_{10} is, for the most part, composed of suspended dust, such as crustal, marine and road dust. $PM_{2.5}$ rather originates of fine particles emitted from anthropogenic sources. Chemical reactions of precursor gases in the atmosphere and primary particle emissions from combustion processes are the main sources of $PM_{2.5}$ (Koistinen et al., 2002).

People spend about 90% of time in indoor environments (Jantunen M., 1999; Bruinen de Bruin et al., 2004; Eurostat, 2004). Studies have shown that indoor sources significantly contribute to personal exposure concentrations experienced in indoor microenvironments (Lanki et al., 2006; Bruinen de Bruin et al., 2005). Consequently, indoor sources cause a notable proportion of elements analysed from indoor air samples. The source apportionment will, therefore, probably be more complicated since the number of different factors influencing the elemental composition is greater (Koistinen et al., 2002).

Volatile Organic air pollutants

In the late 80s and early 90s two studies have indicated that the emissions of building materials and human activities – defined as those coming from household and consumer products, humans and office equipment- are major sources of VOCs in the indoor environment (Seifert et al., 1989; Wolkoff et al., 1991). There are several drawbacks of extrapolating results of studies performed in different parts of Europe, and the world, since little is known of how exposures to these compounds differ between European populations and between Europe and the United States. The composition or use of many housing materials, consumer products and cleaning chemicals may differ between these countries (Scott et al., 2001). In addition, behaviour of people and ventilation characteristics of homes in different latitudes may significantly affect the concentrations of pollutants in indoor environments and in personal exposures (Edwards et al., 2001).

2. Methods

A literature survey was undertaken to identify source apportionment studies for the most common air pollutants, such as airborne particulate matter and volatile organic compounds. The results of this survey were used to compose an overview of the most commonly existing source apportionment techniques used to identify source contributions including the strengths and weaknesses of the techniques considered.

3. Receptor Modelling

3.1 Principles

The fundamental principle of receptor modelling is based on the assumption that mass is conserved and that on this basis a mass balance analysis can be used to identify and apportion sources in the atmosphere (Hopke et al., 2006). Receptor models usually reduce the number of factors needed to describe the measured data. Typically, the relationship can be expressed as outlined in **Equation 1**:

$$x_{ij} = \sum_{p=1}^{P} g_{ip} f_{pj} + e_{ij}$$ **Equation 1**

where:
x_{ij} is the measured concentration of the jth species in the ith sample,
f_{pj} is the concentration of the jth species in material emitted by source p,
g_{ip} is the contribution of the pth source to the ith sample, and
e_{ij} is the portion of the measured elemental concentration that cannot be fit by the model (Hopke, 2003; Hopke et al., 2006).

Regardless of the source apportionment approach, receptor modelling procedures typically require the inclusion of an ‘error function’ (e_{ij} above) within the basic receptor model expression and the extraction of a ‘minimum error’ solution for the modelled dataset.

Various receptor modelling approaches have been used to rationalise this expression, of which conventional factorisation and Chemical Mass Balance (CMB) strategies perhaps represent the two extremes. Conventional factorisation strategies assume in principle little prior knowledge of either source profile or source strength. It extracts statistically valid solutions for both f_{pj} and g_{ip} matrices from a receptor site multiple species/multiple measurements matrix using a matrix algebra procedure, such as Principal Component Analysis (PCA). In contrast, CMB strategies assume that the number of sources and profile of each source (i.e., all f_{pj} values) are exactly known, and estimate source strengths, g_{ip} series, by pattern-fitting this information to the initial receptor site monitoring data, x_{ij} series. In addition, a number of ‘Intermediate’ strategies have been developed that use selected prior knowledge/assumptions about species behaviour and/or different sources, e.g., source ‘marker’ multiple linear regression, prior knowledge ‘targeted’ factorisation (e.g. Target Transformation Factor Analysis), and realistic behaviour and monitoring accuracy ‘restrained’ factorisation (e.g. Positive Matrix Factorisation) (University of Birmingham, 2002). When knowledge on sources is mostly missing the UNMIX method is another strategy that can be applied (Hopke, 2003; Paatero, 2005).

The fundamental principle is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne particulate matter in the atmosphere (generally referred to as receptor modelling). The approach to obtain a data set for receptor modelling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples. The next step is to write a mass balance equation to account for all chemical species in the total number of samples as contributions from all independent sources (El Shaarawi and Piegorsch, 2001).

3.2 Assumptions

The main assumptions for applying receptor models are: (Malm and Gebgart, 1996; Coulter C.T., 2004):

- compositions of source emissions are constant over the period of ambient and source sampling[1],
- chemical species do not react with each other (i.e., they add linearly)[1],
- the number of sources or source categories is less than or equal to the number of species[1],
- all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized[2],
- the source profiles are linearly independent of each other[3], and
- measurement uncertainties are random, uncorrelated, and normally distributed[4].

In reality the discrepancies from these assumptions occur, but the results of inter-comparison studies have shown that the effects of reasonable deviations can be tolerated.

1. Apply to all receptor models.
2. In the case of PCA, PMF and UNMIX a marker element of each source have to be included.
3. Apply to CMB.
4. Apply to PCA and UNMIX.

In the following paragraphs the modelling source apportionment techniques are described. The advantages and disadvantages of these techniques are presented in **Annex I**.

3.3 Modelling techniques

3.3.1 Multivariate methods

Multivariate analysis calculates loadings of elements into factors, which can be apportioned according to fingerprint elements and known source profiles. Wind direction, chemical compounds etc. can be combined with elemental data in factor analysis.

Multivariate analysis does not require information on source profiles and they can incorporate the time variation of ambient concentrations and source emissions (Henry et al., 1984). On the other hand large amounts of samples are needed. For source identification, information on marker species or combination of species is needed. However, the composition of a source determined at the receptor site is usually not the same as it is at the emission location.

Many multivariate methods are based on a factor analysis of individual pollutants or element components to identify underlying patterns that explain common variations among a set of variables, which represent physical properties causing changes in the trace metal concentration (Koistinen K. et al., 2004).

In the literature there are several multivariate methods used to apportion air pollution sources from air sample data (e.g. Henry 1984, Hosiokangas *et al.* 1996, Morandi *et al.* 1987, Hopke 1991). Multivariate methods can identify sources from ambient measurements alone. These models have been widely used in source apportionment of aerosol pollutants.

3.3.2 Factor analysis

Factor analysis is a mathematical tool which can be used to examine a various collection of data sets (Reese C.E. and Lochmüller C.H., 1994). The goal of factor analysis is to find out simple patterns in the pattern of relationships among the variables. It studies the patterns of relationship among many dependent variables, with the objective of discovering something about the nature of the independent variables that affect them, even though those independent variables were not measured directly. Thus, answers obtained by factor analysis are necessarily more hypothetical and tentative than is true when independent variables are observed directly. Specifically, it seeks to determine if the observed variables can be explained largely or entirely in terms of a much smaller number of variables, the inferred independent variables, called *factors*. A typical factor analysis suggests answers to four major questions (Darlington R.B., 1997):

1. How many different factors are needed to explain the pattern of relationships among these variables?
2. What is the nature of those factors?
3. How well do the hypothesized factors explain the observed data?
4. How much purely random or unique variance does each observed variable include?

A practical example of factor analysis: combining Two Variables into a Single Factor. The correlation between two variables can be summarized in a scatterplot. A regression line can then be fitted that represents the "best" description of the linear relationship between the variables. If a variable could be defined that would approximate the regression line in such a plot, then that variable would capture most of the "essence" of the two items. Subjects' single scores on that new factor, represented by the regression line, could then be used in future data analyses to represent that essence of the two items. In a sense the two variables are reduced to one factor. Note that the new factor is actually a linear combination of the two variables (Hill T. and Lewicki P., 2005).

The clearer the true factor structure, the smaller the sample size needed to discover it. But, it would be very difficult to discover even a very clear and simple factor structure with fewer than about 50 cases, and 100 or more cases would be much preferable for a structure that is less clear. In factor analysis it is allowed to have many more variables than cases. Generally speaking it can be stated that the more variables the better, however, as long as the variables remain relevant to the underlying factors (Darlington R.B., 1997).

Additional factor analysis methods are target transformation factor analysis (TTFA), factor analysis-multiple linear regression (FA-MLR) (Hopke, 1991). Target transformation is the technique used to relate the value of factor loadings derived from factor analysis to the value of mass fraction in the physical source emissions (Hopke, 1985, Chan et al., 1999). The number of contributing sources depends on whether the derived source profiles can be related to real sources and the goodness-of-fit results of source apportionment using the derived source profiles (Chan et al., 1999). Another simple model like MLR (multiple linear regression) (Turnbull and Harrison, 2000; Stedman et al., 2001) has also been used to calculate source contribution or chemical composition of pollutants. MLR techniques are used to relate the aerosol mass to the composition of certain tracer elements from the sources contributing in the aerosol samples (Gras et al., 1991; Chan et al., 1999).

Although factor analysis techniques have been widely used, Henry (1987) has shown how easily in-experienced users can reach serious errors in source apportionment and derived source compositions.

3.3.3 Chemical Mass Balance (CMB)

Chemical Mass Balance (CMB) is a widely used receptor model. The CMB can be applied when the number and profiles of the sources (*P and* f_{jp}*'s*) in a region are known. The remaining unknown is the mass contribution from each source to each sample (g_{ip}) that can be estimated using regression (Hopke et al., 2006). The advantage of the CMB method is that only a few measurements are needed (Koistinen et al., 2002**).** The disadvantage of the method is that it requires information on the number of sources and their chemical emission profiles. This is illustrated in **figure 1** below.

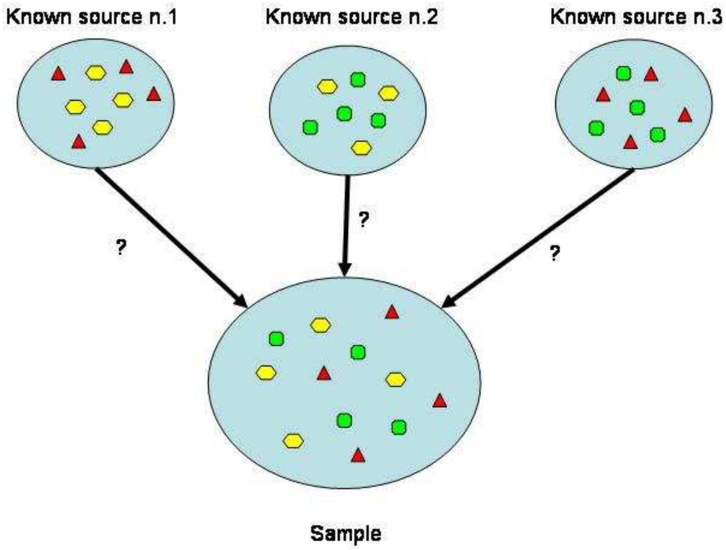

Figure 1. Illustration of the Chemical Mass Balance (CMB) source apportionment principle. Complete emission composition information for each source is required (design originates from Hildemann L.M., Stanford University, US).

3.3.4 Principle component analysis (PCA)

The practical example as described in the previous paragraph on factor analysis concerned the combination of two correlated variables into one factor. This example illustrates the basic idea of factor analysis and similarly of Principal Components Analysis. If the two-variable example is extended to multiple variables, then the computations become more involved, but the basic principle of expressing two or more variables by a single factor remains the same.

Classical PCE identifies sources components and the amount of variance explained by each source. However, a quantitative source apportionment of the pollution mass as presented in equation 1 is not directly provided without manipulation of the component solutions (Hopke et al., 2006). Basically, the extraction of principal components amounts to a variance maximizing (varimax) rotation of the original variable space. For example, in a scatterplot the regression line can be thought of as the original X axis, rotated so that it approximates the regression line. This type of rotation is called variance maximizing because the criterion for (goal of) the rotation is to maximize the variance (variability) of the "new" variable (factor), while minimizing the variance around the new variable (Hill T. and Lewicki P., 2005).

When the analysis concerns more than two variables, one could define them as a "space," just as two variables defined a plane. Thus, when there are three variables, a three- dimensional scatterplot could be drawn, and, again a plane could be fitted through the data.
With more than three variables it becomes impossible to illustrate the points in a scatterplot, however, the logic of rotating the axes so as to maximize the variance of the new factor remains the same (Hill T. and Lewicki P., 2005).

However, PCA suffers from several drawbacks:

1. the factors are rarely physically explainable and fully satisfactory rotation techniques have not been found (Henry,1987 ; Paatero,1997 ; Paatero et al.,2002) and
2. PCA models cannot properly handle missing and below detection- limit data that commonly occur during environmental measurements (Paatero et al., 2005).

A more detailed description and application experiences is provided by Henry, 1987, Paatero, 1997, Paatero et al., 2002, Paatero et al., 2005, Wolff et al.,1985, Gordon, 1998, Hopke, 1991.

It is possible to unscale and then uncenter the data after the PCA to provide a quantitative source apportionment using the procedure outlined by Thurston and Spengler (1985).

3.3.5 Positive Matrix Factorization (PMF)

Positive Matrix Factorization is a method developed by Paatero and Tapper (1993,1994) and has been actively under development during the last decade. The principles applied during the development were to find solutions for the problems arisen by the PCA method (Paatero et al., 2005) and to apply this method when source profiles are mostly unknown (Hopke P., 2003).

PMF does constrained maximization of a weighted object function. The main object function is a goodness-of-fit of the predicted mass contributions for each species, where the species are typically weighted by a measure of trust in the individual measurements. The measure of trust can be adjusted for closeness to the minimum detection level, filling in or missing values or other factors, as well as for sampling error. The results are constrained to be non-negative (although small negative values can occur) by adding penalty functions to the object function (Mane-VU, 2002).

Anderson et al. (2001) obtained high number of chemical specific personal exposure samples and tested the PMF method to apportion exposures to volatile organic compounds to sources. Although main sources of personal exposure to toxic VOCs could be identified, research need to continue to test the robustness of PMF as a source apportionment technique.

In addition, a more detailed description and application experiences is provided by Henry, 1987, Paatero and Tapper (1993,1994) Anderson et al., 2001; Paatero et al., 2005, Hopke, 1991, Kim and Hopke, 2004, and Hopke et al., 2006).

3.3.6 Unmix

Also Unmix is a method that has been actively under development during the last decade as a method to be applied when source profiles are mostly unknown (Hopke P., 2003). UNMIX has an advanced computationally intensive algorithm to estimate the number of sources than can be seen above the noise level in the data (Henry et al., 1999; Park et al., 2000). Unmix uses a base assumption that all the sources, except for those that can be ascertained with tracers species, occasionally have periods with near zero effect on the receptor. These periods generate “edges” in the multidimensional data set. These edges have a one-to-one correspondence with the solution profiles and, hence, generate an overall decomposition of source profiles and source contributions (Mane-VU, 2002, Paatero P., 2005). Unmix also provides some diagnostics for how many sources may be significant, but the decision for the number to search for is left to the user. Some special features of UNMIX are the capability to replace missing data and the ability to estimate large numbers of sources (up to 15) (Henry, 2005). The Unmix approach is available as a computer program and is described in more detail by Henry and Kim, 1999; Henry, 2005; Hopke et al., 2006).

4. Air pollutants; sources and markers

4.1 Particles

4.1.1 Natural sources of $PM_{2.5}$

Crustal and marine aerosols are the most common natural sources of fine particles. Resuspended dust is occasionally considered as a separate source of dust.

Crustal dust is often the major component of PM_{10}. In $PM_{2.5}$ soil dust is notable fraction of the particulate mass, as well. Particulate matter that originates from soil is usually wind-blown and, therefore, rather coarse particles. Al, Fe, Si and Sc have been used most commonly as crustal markers. (Lee *et al.* 1994, Chan *et al.* 1999; Janssen *et al.* 1997; Huang *et al.* 1994; Maenhaut *et al.* 1989)

Marine originated element i.e. sea salt contributes often to particulate matter. Na and Cl are almost without exceptions the fingerprint elements for sea salt. (Chan *et al.* 1999; Van Borm *et al.* 1990; Meanhaut *et al.* 1989; Harrison *et al.* 1996; Janssen *et al.* 1997) According to Pakkanen *et al.* (1996) large amounts of gaseous Br and I are known to evolve from sea in spring.

4.1.2 Coal burning

Biegalski *et al.* (1998) made a factor analysis on samples collected at Canada. The factor analysis of Burnt Island samples showed a factor that contained Ag, As and Se. Se is often associated with coal burning and fuel oils. Smelting activity, which was located near by the sampling site, could also cause the combinations of these three elements.

In Egbert, a factor containing Ag, Br, I, Sb, Se, V, W and Zn, represents urban sources including coal and oil burning. In Point Petre, analogous factor contained As, Br, Fe, I, Mn, Sb, Se and Zn. As and Se were associated to smelters. As, Ag and Se were highly enriched in all measurement sites. (Biegalski *et al.* 1998)

In Hong Kong, Fung and Wong (1995) used As and Se as the markers for coal-fired power plants. In their factor analysis this factor explained 15.3% of the total variance.

In Karachi, Pakistan, Parekh *et al.* (1987) identified a factor comprising Zn, Sb and Pb. This factor could originate from several sources, e.g. smelters or incinerators. Refuse incinerator and coal-burning plants operating in the area were the most probable sources.

Ag and Se were suggested as markers for coal combustion by Lee *et al.* (1994). Se could also derive from oil combustion, glass manufacturing, incineration and metal refining. The atmospheric concentration of Ag may often be too low to be analysed. It is present in Earth's crust and, is thus poorly applied as a trace element. Ojanen *et al.* (1998) found Mo to be suggested as a possible marker for coal burning in the literature.

Milford and Davidson (1985) gathered information of size distributions of various elements from the literature. The mass median diameter of As and Se were 1.11 and 0.68 µm, respectively. Both of the elements are, for the most part, derived from anthropogenic sources.

As a summary, As and Se can be used as markers for coal burning. Ag is also suggested as coal marker, but it often may not be possible to analyse due to its low concentration.

4.1.3 Combustion of oil

The most distinctive marker for oil combustion, identified in the literature, were vanadine (V) followed by nickel (Ni) (Cass and McRae, 1983; Huang *et al.* 1994; Janssen *et al.* 1997; Lee *et al.* 1994; Ojanen *et al.* 1998; Van Borm *et al.* 1990). However, Nickel may have other sources (e.g. petrol vehicles, asphalt) and it should be used with discretion (Ojanen *et al.* 1998). Morandi *et al.* (1987) selected V as marker for oil, since has less analytical uncertainty than Ni.

Studies performed by Hosiokangas *et al.* (1996) identified a factor comprising V, Ni and Cr associated with oil combustion. They concluded that the Cr was present as a heavy fuel oil marker. Morandi *et al.* (1987) identified a factor enriched with V and Ni, which indicated oil burning and partly space heating. Fung and Wong (1995) in their factor analysis identified that V and S were the markers for oil combustion sources.

Ojanen *et al.* (1998) correlated La and Sm with oil combustion and refining. La and Sm belong to so-called rare earth elements (REEs) which represent elements that are not generally found in the Earth's crust. Olmez *et al.* (1988) measured emissions of 46 elements on stacks of different sources. In emissions of oil-fired power plants V and Ni were present in high concentrations. La and Sm emission from plants were notably smaller than from fluid catalytic cracker. Instead, Mo and Co could be used as markers for oil burning.

Olmez and Gordon (1985) observed that La:Sm ratio and the concentration of V followed the same pattern. They concluded that REEs are suitable marker elements for oil in areas where there are several sources of oil burning. REE signature could arise from other sources as well in areas with only a few oil-burning plants.

In the Great Lakes area, V was combined with soil factors in each of the three measurement-sites (Biegalski *et al.*, 1998). Ni was not combined with V in any of the sites, instead it was found in a factor identified as an industrial factor. Both V and Ni were moderately enriched (i.e. $3<EF<30$), thus, both elements originate partly from crustal sources.

Parekh *et al.* (1987) identified a factor that combined V and Ni with the common soil elements (e.g. Ca and Mg). This could be caused by enrichment of V and Ni to the surface soil, since their sources had emitted them for years and years. Their enrichment factors were relatively low, what supported this statement.

In factor analysis performed by Harrison *et al.* (1996) on Birmingham aerosols, V and Ni were loaded in different factors. Ni and elemental carbon were identified in a coal factor with secondary compounds such as sulphate, nitrate and ammonium. V was present in two factors, road salt and secondary/oil combustion. Factor analysis of Antwerp winter samples showed that in fine particles V was related with typical traffic markers, Pb and Br. Ni, instead, was enriched in an industrial factor. (Van Borm *et al.* 1990)

According to Ojanen *et al.* (1998), bitumen consists of great amounts of V. Therefore, V can be a marker for asphalt, but since road dust is very coarse, it does not usually have influence on particles less than 15 µm in size. In the fine particles in Los Angeles 59% of V and 81% of Ni originated from residual fuel oil. 34% of V came from crustal sources (Cass and McRae, 1983).

The mass median diameter for V and Ni are 1.44 and 0.98 µm, respectively (Milford and Davidson, 1985). Both elements should thus be found in fine particles. Ojanen *et al.* (1998) discovered for more than 70% of V and Ni to be in particles less than 2.0 µm in diameter. On the other hand, Lyons *et al.* (1993) found Ni to be mainly in the range of 2-4 µm.

4.1.4 Refuse incinerators

The most distinctive markers for refuse incinerators, identified in the literature, were zinc (Zn) and copper (Cu) (Huang *et al.* 1994; Harrison *et al.* 1996; Parekh *et al.* 1987; Van Borm *et al.* 1990). Silver (Ag), indium (In) and antimony (Sb) have been suggested as refuse incinerator markers as well (Huang *et al.* 1994, Parekh *et al.* 1987).

Harrison *et al.* (1996) identified a factor highly loaded with Zn and Cu. Fine fractions of sodium and chlorine were accompanied moderately to this factor. This factor was identified as incinerator factor. Sodium and chloride were recognized clearly in another factor, which was identified as marine emissions and road salt factor. Possibly these two factors were partly mixed.

In Chicago, in factor analysis where wind directions were included, incinerator emissions comprised a factor with loadings of Zn, K and Pb. (Sweet *et al.* 1993). Zn was also present in factors originating from steel mill and zinc smelter.

Zn, Sb and Pb were loaded in same factor in Karachi, Pakistan (Parekh *et al.* 1987). The factor was not identified, since these elements are associated with many sources e.g. from coal-burning, smelting operations, automotive exhausts and incinerators. In Karachi, this factor originated from coal-burning plants and refuse incinerators.

Cu and Zn were identified in the same factor with Fe and Ni in Antwerp, Belgium (Van Borm *et al.* 1990). The elements suggested, that this factor represents refuse incinerator. This was supported by the fact that one refuse incinerator was located only 1 km from the sampling site. They remarked that Pb and K are often present in refuse incinerator emissions. In their results neither K nor Pb were present in incinerator factor, instead, K and Pb were found in other factors (soil/sulfate, soil/sulfate/auto and oil).

Zn may be problematic marker, since it has been suggested as traffic marker, too. The combination of Zn with other refuse originated elements (such as Cu, In) has proved to be applicable in source apportionment.

4.1.5 Smelters

Smelter activities can roughly be divided to ferrous and non-ferrous smelters. According to Sweet *et al.* (1993) Zn, Cd, Pb and Sn are emitted from zing smelter and Cu, Se, and P from copper smelter in particles smaller than 2.5 µm in diameter. Lee *et al.* (1999) found in source apportionment a factor containing Pb, Zn, and K^+. This factor originated probably from a non-ferrous metal smelter. Pio *et al.* (1996) identified a factor comprising As and Cu. The factor originated possibly from pyrite smelters.

Swietlicki *et al.* (1996) calculated Fe/Mn, Pb/Cu and Zn/Cu ratios for fine aerosols to clarify whether the ratio would be different for smelter emissions from ratio found in soil. Fe/Mn ratio for ferrous-smelter (10-15) was found to be significantly different from soil (approx. 60). In coarse road dust and traffic particles, the ratio was from 40 to 50. Pb/Cu and Zn/Cu ratios from smelter emissions were 9.2 and 15.6, respectively. The ratios for soil and coarse aerosols from road dust and traffic were notably smaller (<5).

4.1.6 Traffic

The traditional traffic marker, Pb, is no longer applicable in countries where leaded gasoline is no longer used (Huang *et al.* 1994). Several studies have been performed in order to identify reliable markers for motor vehicle exhausts. However, the fuel quality, fuel additives, and other factors may vary from country to country and thus the possible markers may not be universal.

According to Huang *et al.* (1994), Zn, Sb and Br could be used as markers for traffic. They recommended using these elements simultaneously. Ojanen *et al.* (1998) searched source elements from literature and concluded Zn, Sb and Br as traffic markers, too.

Janssen *et al.* (1997) made measurements near a street in the Netherlands and noticed that the concentration of Zn was only slightly higher by the street compared to urban background site. Because Zn was more dominant element in PM_{10} than in $PM_{2.5}$, they concluded that Zn's source was dust resuspension rather than anthropogenic.

Van Borm *et al.* (1990) correlated Zn with soil/sulphate factor in principal factor analysis. Incinerators and zinc smelters have been identified as Zn's source by Sweet *et al.* (1993). Parekh *et al.* (1987) identified a factor with Zn, Sb and Pb. The source of this factor was probably either coal burning or refuse incinerators.

Lyons *et al.* (1993) studied the size distribution of Zn. Zn originated partly from suspended particles, which caused weak modes in the area of 2-4 µm. When the influence of the suspended dust was subtracted, Zn was present mainly in the particles less than 1 µm in diameter. Milford and Davidson (1985) made a literature review and concluded that mass median diameter of Zn was 1.13 µm. The enrichment factor for Zn was 260, which indicated clearly anthropogenic sources for Zn. The mass median diameters for Sb and Br were 0.86 and 0.89, respectively, and the enrichment factor for Sb was 39.

In chemical mass balance (CMB), Sweet *et al.* (1993) correlated Pb with auto emissions, even though Pb's levels had already decreased by that time. Smelters were probably important sources of Pb, but this was not verified by the CMB because of inadequacies in source profiles. In wind trajectory analysis Pb was correlated with smelter emissions.

Huang *et al.* (1994) found high Al concentrations from catalyst-equipped vehicle exhausts. Al originated possibly from catalytic converters, which have γ-Al_2O_3 as a supporting substrate. Al was present in both fine and coarse particles. They studied also the possibility to use rare earth elements (REEs) as traffic markers. REEs did not prove to be suitable markers, because they were present in large particles, were emitted only moderately from motor vehicles, and were emitted by other sources, too.

Ojanen *et al.* (1998) studied diesel vehicle exhausts with using summer (DIK) and winter (DITC) type of diesel. They were able to analyse Al, Ba, Cu, Mg, Na, Pb, Sb and Zn from particle emissions. The emission rate of these elements varied between 20 □g/min (for Zn) to 0.1 µg/min (for Mn). Elemental carbon in Los Angeles mass balance analysis originated nearly entirely from diesel vehicles (Schauer *et al.*, 1996).

Ojanen *et al.* (1998) studied also the emissions from petrol vehicles. They identified Pb, Cd, V, Cu, Mn, Fe, Al, Na, K, Mg and Ca from particle emission samples. According to Ojanen *et al.* (1998) in source apportionment, marker elements should be in size range 0.03-0.2 µm. Only few of these elements were in this range. They concluded that greater amount of measurements are required to determine suitable markers for petrol vehicles.

In a roadside environment, when NO_x and particle count were used as tracers of road traffic emissions, the correlations of Cu, Zn, Mo, Ba, and Pb indicated a traffic source contribution for these elements (Harrison et al., 2003). Based on a tunnel study, Cu, Zn, Cd, Sb, Ba, and Pb are emitted from road traffic in considerable quantities (Sternbeck et al., 2002). In another tunnel study Al, Ba, Cr, Fe, Hg, La, Mg, Mn, Na, Sb, Sc, V, and Zn concentrations were found to be significantly higher than the background concentrations (Allen et al., 2001). On a motorway the black smoke concentration has been reported to be 300 % higher and on the street 100 % higher than at the background measurement site *(*Roemer and van Wijnen, 2001*)*. Based on tunnel studies Laschober et al. (2004) concluded that traffic and more precisely the brakes are a source of Zn, Cu, and Pb, while in another study brake wear was found to be a major emission pathway for, at least, Cu, Sb, and Ba (Sternbeck et al., 2002). In a tunnel study conducted by Chellam et al. (2005), Cu and Zn were connected to engine oil and brake wear, Zn to tyres, and Ba to brakes and diesel fuel. Yli-Tuomi et al. (2005) reported elevated concentrations of Cu, elemental C, Fe and Zn on traffic lane compared to urban background.

Particles produced by traffic correlate strongly with CO emissions. Between PM_{10} and CO following regression can be made: traffic PM_{10} = 17.69 * traffic CO. The r for the regression is 0.56. Both PM_{10} and $PM_{2.5}$ correlates with NO_x-emissions. In Birmingham measurement in winter time the correlation of $PM_{2.5}$ and NO_x in hourly data was: $PM_{2.5} = 0.103\ NO_x + 8.52$ and the r = 0.0.78. $PM_{2.5}$ is given in $\mu g/m^{-3}$ and NO_x in ppb. Data from summer time is consistent with winter data except for very high concentrations, which were present in winter. (APEG, 1999)

In Birmingham the correlation of PM_{10} and $PM_{2.5}$ in 96/97 was in daily data: $PM_{2.5} = 0.72\ PM_{10} + 0.99$ and in hourly data: $PM_{2.5} = 0.70\ PM_{10} + 0.60$. The correlation of the regressions were 0.95 and 0.94, respectively. (APEG, 1999)

Hydrocarbons have been suggested to traffic markers. The problem in using hydrocarbons is that they are reactive and may be altered between emission and sampling sites. (Huang *et al.*, 1994).

Duffy *et al.* (1999) studied hydrocarbon profiles from light-duty vehicles. They concluded that emissions from catalyst-equipped cars were 4-7 times smaller than the emissions from non-catalyst cars. In the study non-catalyst cars used leaded fuel, whereas catalyst-equipped cars used non-leaded fuel. Catalyst-equipped cars emitted greater amount of low molecular weight alkenes, but less substituted aromatics and alkenes than non-catalyst cars. The composition of emissions was quite different, but somewhat similar to the composition of fuel. Therefore, the composition of fuel can be used in evaluating the emissions.

Hopanes and steranes have been suggested as motor vehicle exhaust markers by Cass, 1998. They are found in both gasoline and diesel engine exhaust since they are present in lubricating oils. According to Schauer *et al.* (1996) hopanes and steranes in ambient air originate mainly from diesel and gasoline powered vehicles. Partly they originate from paved road dust and tire wear debris. Very good agreement was found between measured and calculated ambient concentrations for hopanes and steranes.

Schauer and Cass compared tailpipe emission from diesel engines to ambient concentrations for eicosane, pristane, phytane, 8,13-dimethyl-14-n-butylpodocarpane and 8,13-dimethyl-14-[3'-methylbutyl]podocarpane. Since good agreement was found between diesel-emissions and the ambient concentrations, these compounds can be used as tracers for diesel vehicles.

Doskey *et al.* (1999) studied non-methane organic compounds in the atmosphere in Cairo. They compared traffic emissions to petroleum refiners, lead smelter's and cast iron factory's emissions. In roadway emissions e.g. ethyne, benzene, toluene, p- & m-xylene, 2-methylbutaneand n-pentane had clearly higher weight-% than other emission sources. They developed source profiles of vehicle, petroleum refiner, lead smelter and cast iron factory emissions (**ANNEX II**).

Polycyclic aromatic hydrocarbons (PAHs) have been studied as vehicle exhaust markers, too. Rogge *et al.* (1993) analysed fine organic aerosol emissions from motor vehicles. Non-catalyst cars emitted more PAHs than catalyst-equipped cars or diesel trucks. Several PAHs were identified in each type of vehicles studied (e.g. dimethyl phenanthrene, and methyl anthracene). PAHs may not be reliable markers because the same compounds are emitted from other sources, too (e.g. wood burning). (Huang *et al.* 1994)

As a summary, no single reliable marker element have been identified in the literature reviewed in this paper. The combination of Zn, Br and Sb has been suggested as traffic markers. Zn has multiple sources, what can cause contradictory results in source apportionment. VOCs can be used to identify traffic emissions, particularly hopanes and steranes indicate motor vehicle exhaust emissions. Elemental carbon is applicable marker for diesel emissions. Also the relation of particulate matter and CO and NO_x can be used in source apportionment.

4.1.7 Secondary particles

Secondary particles are formed in the atmosphere within transportation from source to receptor. These elements and compounds are formed in gas/particle-phase conversion. NH_4^+, SO_4^{2-} and NO_3^- are typical secondary particles. (Pio *et al.*, 1998) Secondary particles size distribution shows that 90% of the concentration of ammonium, 60% of nitrate and 80% of sulfate is in $PM_{2.5}$ (APEG, 1998).

In Brisbane, Australia, 80% of the measured nitrate and ammonium sulfate in the fine particles was secondary. 63% of organics in fine particles was secondary in origin. (Chan *et al.*, 1999) Secondary ammonium nitrate and ammonium sulfate constituted 29-36% of the total particle concentration in 1988 at three measurement sites in California (Chow *et al.*, 1999).

According to Chan *et al.* (1999) most of the secondary organic compounds are related to motor vehicle exhausts in traffic environments. Olmez *et al.* (1988) compared fine particle emissions of several sources. Oil-fired power plants were the major sources of sulfate and ammonium. Also fluid catalytic cracker emitted large amount of sulfate. In principal component analysis applied to fine particles by Pio *et al.* (1998) nitrates were partly combined to traffic emissions. Ammonium, sulfate and nitrate, nevertheless, were present mainly in a secondary aerosol factor.

4.1.8 Indoor sources

Source profiles for indoor sources are not reported often. Özkaynak *et al.* (1996) created source profiles for indoor smoking and cooking. K, Cl and Ca were most common elements originating from smoking and Al, Fe, Ca and Cl from cooking. They did not found any indoor sources for S. Clayton *et al.* (1993) reported Cd as a marker for tobacco.

In three indoor particle studies done in U.S.A. reviewed by Wallace (1996), smoking caused the majority of particles. Cooking was the second primary particle source. Reviewed studies showed that cooking is the most important source for fine particles in non-smoking houses. Vacuuming and sweeping were sources of coarse particles. Studies showed that the indoor concentration of fine particles was approximately twice as high as outdoor particle concentration.

Some elements in indoor are primarily penetrated from outdoors. E.g. S, Ca, Fe, Pb and Br are elements which have indoor/outdoor (I/O) ratios smaller than 1 (Sexton and Hayward, 1987). Element having I/O-ratio below 1 may have also some indoor sources that are not very intensive.

During the EXPOLIS study indoor originated $PM_{2.5}$ was found to consist of crustal elements (Al, Ca, Si), salt (Cl, K) and cleaning product (P) (Koistinen et al., 2004).

Determinants and sources of $PM_{2.5}$ exposures among persons with coronary artery disease were studied in Amsterdam and Helsinki during the winter and spring of 1998-1999 (Brunekreef et al., 2005; Lanki et al, 2006). In Amsterdam, smoking in the living room contributed substantially to both the personal and indoor levels of PM2.5, absorption coefficient (a surrogate for elemental carbon), S, Zn, Fe, K, and Cl. In both cities, outdoor levels of $PM_{2.5}$ and absorbance were major determinants of personal and indoor levels. Cooking was associated with increased levels of both absorbance and $PM_{2.5}$, while cleaning activities increased the exposure to Cu.

Recently, a special online issue was released concerning the US Particulate Matter Supersites Program (Atmospheric Environment, Volume 40, Supplement 2, 22 September 2006, Pages 179-606). This program is an ambient monitoring research program that deals with the scientific uncertainties associated with fine particulate matter by focusing on fine particulate characterization, methods testing, and support to health effects and exposure studies (http://www.epa.gov/ttn/amtic/supersites.html). This issue includes 11 papers comprising additional information on the use of advanced statistical analysis methods to infer sources of ambient fine particles from ambient measurements (Bien et al., 2006; Buset et al., 2006; Dutkiewicz, et al., 2006; Hu et al., 2006; Lall and Thurston, 2006; Lee and Hopke, 2006; Liu et al., 2006; Ogulei et al, 2006; Pancras et al., 2006; Pekney et al., 2006; Qin et al., 2006).

A detailed overview of the single elements and assigned sources is presented in **ANNEX II**.

4.2 Organic compounds

Many sources emit certain organic compounds as well as certain elements. Organic compounds, usually volatile organic compounds (VOCs), can be used in source apportionment as markers.

In order to use organic compounds as traces, they need to fulfil certain requirements:

- compound must not be formed in atmospheric reactions,
- compound must survive transport from source to receptor, with other words the compound should not be highly reactive, and
- in case it concerns VOCs trapped on particles, the compounds must not evaporate into gas phase during transport (Cass, 1998).

Several polycylic aromatic hydrocarbons (PAHs) do not meet these requirements, since they are often semi-volatile and they react in the atmosphere in period of hours. PAHs are also emitted from practically all combustion sources (Cass, 1998). For example Schauer *et al.* (1996) excluded benzo[k]fluoranthene, benzo[b]fluoranthene and benzo[e]pyrene from their results since they had questionable stability.

Edwards et al. (2001a+b) and Jurvelin et al. (2003) identified common sources of target volatile organic compounds (VOCs) in residential outdoor, residential indoor and workplace microenvironments and personal 48-h exposure samples, as a component of the EXPOLIS study (Jantunen et al. 1999). Edwards et al. (2001) processed samples that were never exposed to ETS (Environmental Tobacco Smoke) using Principle Component Analyses and associated VOC classes to sources taking into account the percentage of variance accounted for. Alcohols and alkanals were assigned to cleaning products, fragrances, consumer products and particles board and accounted for 18% of the variance. Similarly another 9% could be assigned to carpets, rubber and adhesives. N-Alkanes, substituted aromatics and hydrocarbons were assigned to local traffic emissions and accounted for 18% of the variance. Aromatics were assigned to long-range transportation of mostly traffic related combustion sources and accounted for 17% of the variance. Esters, mainly 2-butoxyethanol, could be assigned to cleaning products and accounted 6% of the variance (Edwards et al., 2001; Pluschke P. 2004).

A detailed overview of the single compounds and assigned sources is presented in **ANNEX III**.

5. Discussion and Conclusions

An ideal source apportionment study starts with selecting the trace elements or compounds representing the obvious sources that might contribute to the location where the measurements will be carried out, i.e. in the receptor. Consequently, the collection methods and chemical analyses should be selected in a way that the important marker species can be analyzed accurately.

In case of organic compounds, the selected tracers should not be reactive during transportation from an emission source to a receptor since it becomes impossible to relate concentrations to sources if the variation of the concentration in a receptor does not reflect the variation of the emission strength in a source.

The number of samples is another major requirement for a successful source apportionment analysis. Some methods, for example CMB, can be applied with few samples, but typically at least tens of samples are needed for a reliable source apportionment analysis. Although, a clear minimum sample size could not be identified by studying the literature, in general it can be stated that higher sample numbers provide better input to obtain better statistical results. From the methods considered in this review CMB requires fewest samples, however, it requires the most detailed quantitative description of the number of sources and the respective chemical emission profiles.

In case of a few point sources in ambient air, it might be possible to have detailed emission data from the main sources, such as emissions from industrial point sources like factories or power plants. Typically, however, we do not have sufficient information on the major sources contributing to air quality, and thus we can not use such methods which for example require quantitative knowledge of emission profiles. When identifying emission sources of personal exposures or those of indoor air samples, we rarely know the quantitative emission profiles of their numerous sources originated from outdoor air, from potential indoor sources such as construction materials, smoking, gas stoves etc., or from consumer products. Therefore, typically we need to use such methods that require sufficient number of samples, i.e. preferably more than 50 samples.

The interpretation of the source apportionment results becomes easier if we have sufficient number of samples collected on one receptor rather than a pooled collection of samples from different locations.

The study design determines the methods that can be applied for the source apportionment; therefore it is critical to decide, prior to the data collection, what kind of source apportionment analyses will be applied.

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ANNEX I. Advantages and disadvantages of the reviewed source apportionment techniques.

Source Apportionment Technique	**Advantage**	**Disadvantage**
Chemical Mass Balance	Few samples needed (Minimum n ≥ 25)	Quantitative information is needed on the number of sources and their chemical emission profiles, assumptions are (Coulter C.T., 2004): - Compositions of source emissions are constant over the period of ambient and source sampling. - Chemical species do not react with each other (i.e.,they add linearly). - All sources with a potential for contributing to the receptor have been identified and have had their emissions characterized. - The number of sources or source categories is less than or equal to the number of species. - The source profiles are linearly independent of each other.
Factor Analysis	Extraction of underlying features/patterns of air pollutant distribution data is possible	- High number of samples needed (Minimum n ≥ 50-100). - Detailed information on the chemical emission profile is needed. - Compositions of source emissions are constant over the period of ambient and source sampling. - Chemical species do not react with each other (i.e.,they add linearly).

		- All sources with a potential for contributing to the receptor have been identified and have had their emissions characterized. - The number of sources or source categories is less than or equal to the number of species. - The source profiles are linearly independent of each other.
Principle Component Analysis	Extraction of underlying features/patterns of air pollutant distribution data is possible	- High number of samples needed (Minimum n 50-100). - The factors are rarely physically explainable and fully satisfactory rotation techniques have not been found (Henry,1987 ; Paatero,1997 ; Paatero et al.,2002). - PCA models cannot properly handle missing and below detection-limit data that commonly occur during environmental measurements (Paatero et al., 2005). - Some information must be available about the source profiles (Paatero et al., 2005). - The sources and their profiles are not clearly identified in detail, without costly chemical speciation data (Kim et al., 2004). - Compositions of source emissions are constant over the period of ambient and source sampling. - Chemical species do not react with each other (i.e.,they add linearly). - All sources with a potential for contributing to the receptor have been identified and have had their emissions characterized. A marker element of

		each source have to be included. - The number of sources or source categories is less than or equal to the number of species. - The source profiles are linearly independent of each other. - Measurement uncertainties are random, uncorrelated, and normally distributed.
Positive Matrix Factorization	Extraction of underlying features/patterns of air pollutant distribution data is possible	- High number of samples needed (Minimum n 50-100). - The sources and their profiles are not clearly identified in detail, without costly chemical speciation data (Kim et al.,2004). - Some information must be available about the source profiles (Paatero et al., 2005). - compositions of source emissions are constant over the period of ambient and source sampling. - chemical species do not react with each other (i.e.,they add linearly). - all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized. A marker element of each source have to be included. - the number of sources or source categories is less than or equal to the number of species. - the source profiles are linearly independent of each other.
Unmix	Extraction of underlying features/patterns of air pollutant distribution data is possible Features to replace missing data and ability to estimate	- High number of samples needed (Minimum n 50-100). - The sources and their profiles are not clearly identified in detail, without costly chemical speciation data (Kim et

	large number of sources (up to 15) (Henry., 2005)	al.,2004). - Compositions of source emissions are constant over the period of ambient and source sampling. - Chemical species do not react with each other (i.e.,they add linearly). - All sources with a potential for contributing to the receptor have been identified and have had their emissions characterized. A marker element of each source have to be included. - The number of sources or source categories is less than or equal to the number of species. - The source profiles are linearly independent of each other. - Measurement uncertainties are random, uncorrelated, and normally distributed.

ANNEX II. Summary of the reviewed outdoor source categories and marker elements identified from particles.

SOURCE CATEGORY	TRACE ELEMENT/COMPOUND	REFERENCE
Crustal	Sc, Ce, Sm, Fe, Al	Lee et al., 1994; Koistinen et al., 2004
Soil/crustal	Si	Chan et al., 1991
Soil-related	Si, Fe	Janssen et al., 1997
Soil	Mn, Al, Sc	Huang et al., 1994
Soil dust	Al, Si, Fe	Maenhaut et al., 1989
Sea salt	Na (soluble)	Chan et al., 1991
Sea salt	Cl^-	APEG, 1999; Koistinen et al., 2004
Marine	Na	Van Born et al., 1990
Sea salt	Na	Meanhaut et al., 1989; Koistinen et al., 2004
Marine	Na, Cl	Harrison et al., 1996
Sea salt (marine)	Na, Cl	Janssen et al., 1997
Traffic	Pb, Br, Sb, Zn, Cu, C	Ojanen et al., 1998
Traffic	Zn, Sb, Br	Huang et al., 1994
Catalyst cars	Al	Huang et al., 1994
Petrol vehicles	Cd, Ni, Cu, Mn, Fe, Al, Ca	Ojanen et al., 1998
Diesel vehicles	Al, Ba, Cu, Mg, Mn, Na, Pb, Sb, Zn	Ojanen et al., 1998
Non-catalyst vehicles	Pb, Br	Hildemann et al., 1991
Vehicle exhaust	Pb	Chan et al., 1991
Mobile sources	Volatile C, elemental C	Huang et al., 1994
Brake dust	SiO_2, Fe_2O_3, Mg^{2+}, Ba	Hildemann et al., 1991
Tire wear	Zn	Harrison et al., 1996
Tire dust	di-pentene(limolene), styrene	APEG, 1999

Road salt	Cl^-	APEG, 1999
Vehicle wear	Cu, Zn, Pb, Ba, Mo	Harrison et al., 2003
mainly from wear; Cu, Ba, Sb brakes	Cu, Zn, Pb, Ba, Cd, Sb, (Fe)	Sternbeck et al., 2002
TC, BC combustion; Cu, Zn, Pb brakes	TC, BC, Cu, Zn, Pb	Laschober et al., 2004
Traffic	Zn, Ba, Al, Cr, Fe, Hg, La, Mg, Mn, Na, Sb, Sc, V, OC, BC	Allen et al., 2001
Traffic	BC	Roemer and van Wijnen, 2001
Cu, Zn engine oil and brake wear; Zn tires; Ba brakes and diesel fuel	Cu, Zn, Ba	Chellam et al., 2005
Traffic	Cu, BC, Fe, Zn	Yli-Tuomi et al., 2005

Steal industry	Fe, Mn, Cr, Ca	Ojanen et al., 1998
Steal making	Fe, Mn	Huang et al., 1994
Sulphite smelting	In (chalcophiles)	Huang et al., 1994
Smelting works	In, Zn, Cu, Cd, Sn, Pb	Ojanen et al., 1998
Smelting	Fe, Zn, Pb, Mn	Swietlicki et al., 1996
Zinc smelter	Zn, Cd, Pb, Sn	Sweet et al., 1993
Copper smelter	Cu, Se, P	Sweet et al., 1993
Pyrite smelter	As, Cu	Pio et al., 1996

Refuse incineration	Ag, In	Huang et al., 1994
Refuse incineration	Cu, Zn	Van Borm et al., 1990
Incinerators	Zn, Cu	Harrison et al., 1996
Refuse incineration	Zn, Pb	Sweet et al., 1993
Refuse incineration	Zn, Sb	Parekh et al., 1987
Waste burning	Ag, In, Cl, Zn, K, Cu	Ojanen et al., 1998
Coal or oil burning	Se	Biegalski et al., 1998

Appendix 1. 2/2

Coal-fired powerplant	As, Se, S	Huang et al., 1994
Coal combustion	Ag, Se	Lee et al., 1994

Coal burning	As, Se, Mo, S	Ojanen et al., 1998
Coal burning	Zn, Sb, Pb	Parekh et al., 1987
Coal burning	Se, As, Cr, K	Harrison et al., 1996
Coal-fired powerplant	As, Se	Fung and Wong 1995

Oil burning	V, Ni, La, Sm, S	Ojanen et al., 1998
Burning of residual fuel oil	Ni	Cass and McRae, 1983
Residual oil combustion	V, Ni	Van Borm et al., 1990
Oil combustion	V	Janssen et al., 1997
Oil combustion	V	Lee et al., 1994
Oil-fired power plant	V, Ni, REEs	Huang et al., 1994
Oil combustion	V, S, (Ni, Cu)	Harrison et al., 1996
Oil refining	La, Sm	Ojanen et al., 1998
Heavy fuel oil	V, Ni, Cr	Hosiokangas et al., 1999

Wood burning	K, volatile C, elemental C	Huang et al., 1994
Wood burning	K	Janssen et al., 1997
Wood/crass burning	K, C	Ojanen et al., 1998
Biomass burning	Non-soil K	Chan et al., 1991

Long distance transport	S	Janssen et al., 1997
Secondary	S	Van Borm et al., 1990
Industrial processes	Hg	Lee et al., 1994
Limestone/concrete	Ca, Mg	Huang et al., 1994
Tobacco	Cd	Clayton et al., 1993

ANNEX III. Summary of the reviewed identified source categories from Volatile Organic Compounds.

SOURCE CATEGORY	TRACE ELEMENT/COMPOUND	REFERENCE
TRAFFIC		
(Local) traffic emissions	Decane, Formaldehyde, Hexane, Nonane, Propylbenzene, Undecane	Edwards et al., 2001a+b; Jurvelin et al., 2003; Edwards et al., 2005
Long distance transport of traffic emissions	Acetaldehyde, Benzene, Decylaldehyde, Ethylbenzene, m,p-Xylene, Naphthalene, Octylaldehyde , o-Xylene, Propylbenzene, Styrene, Toluene, Trimethylbenzene, Valeraldehyde	Edwards et al., 2001a+b; Jurvelin et al., 2003; Jurvelin et al., 2003

CONSUMER PRODUCTS		
Cleaning products	1-Butanol, 2-Butoxyethanol, 3-Carene, 2-Methyl-1-propanol, Acetone, Benzaldehyde, Butyraldehyde, Heptylaldehyde, Hexanal, Hexaldehyde, d-Limonene, Octanal, α-Pinene, Valeraldehyde	Knoppel and Schauwenburg, 1989; Cooper et al., 1995; Edwards et al., 2001a; Jurvelin et al., 2003; Edwards et al., 2005
Fragrances	1-butanol, 3-Carene, 2-methyl-1-propanol, Acetone, Benzaldehyde, Butyraldehyde, Heptylaldehyde, Hexanal, Hexaldehyde, d-Limonene, Octanal, α-Pinene, Valeraldehyde	Edwards et al., 2001a+b; Jurvelin et al., 2003
Soaps	d-limonene	Knoppel and Schauwenburg, 1989; Cooper et al., 1995
Particle board	1-butanol, 3-Carene, 2-methyl-1-propanol, Acetone, Benzaldehyde, Butyraldehyde, Heptylaldehyde, Hexaldehyde,	Edwards et al., 2001a; Jurvelin et al., 2003

	Hexanal, d-Limonene, Octanal, α-Pinene, Valeraldehyde	
Air refreshers	3-Carene, d-Limonene	Knoppel and Schauwenburg, 1989; Cooper et al., 1995; Edwards et al., 2001a
Adhesives	2-Butoxyethanol	Edwards et al., 2005
Waxes/polishes	α-Pinene	Edwards et al., 2001b
Oils, greases and lubricants	2-Butoxyethanol	Edwards et al., 2005
Plastics	1-Butanol	Edwards et al., 2001a
Paint	1-Butanol, 2-Butoxyethanol	Edwards et al., 2001a; Edwards et al., 2005
Paint thinners/removers	2-Butoxyethanol	Edwards et al., 2005
Spray lacquers	2-Butoxyethanol	Edwards et al., 2005
Enamels	2-Butoxyethanol	Edwards et al., 2005
Varnishers	2-Butoxyethanol	Edwards et al., 2005
Vinyl	Benzaldehyde	Edwards et al., 2001a
Carpet adhesives/glue	Benzaldehyde, Styrene	Edwards et al., 2001a
Rubber	Styrene	Edwards et al., 2001a
Building material (e.g. linoleum)	2-Ethylhexanol, Aceltaldehyde, Benzaldehyde, Octanal	Edwards et al., 2001a; Jurvelin et al., 2003

BIOLOGICAL SOURCES		
Vegatation (plants and trees)	Benzaldehyde, Decylaldehyde, Hexanal, α-Pinene	Edwards et al., 2001a+b; Jurvelin et al., 2003
Mould growth	1-Butanol, 2-Butoxyethanol, 2-Benzaldehyde, Ethylhexanol, Octanol	Edwards et al., 2001a
Bacterial growth	1-Butanol, Benzaldehyde	Edwards et al., 2001a
Fungal growth	2-Ethylhexanol, Benzaldehyde, Octanol	Edwards et al., 2001a+b

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Abstract

Introduction. The need of knowledge on occurrence, source strengths, distribution and fate of chemical substances is increasing. This knowledge is needed to effectively reduce levels of chemical substances in microenvironments that are harmful for human health and the environment. The only mechanism that ultimately will lead to cost effective reduction in population exposures is by the identification of sources that release these substances. Knowing the sources allows prioritization of substances/sources that most significantly contribute to target (sub)population exposures.

To apportion personal exposures to sources of substances present in indoor and outdoor air through daily time-activity patterns is a highly complex task. This requires reliable exposure data and the application of source apportionment techniques to all kinds of microenvironmental samples (indoor, outdoor and commuting). The present report provides an overview of the existing source apportionment techniques and source tracers and their respective data requirements and serves as a background and guidance document for the development of harmonized exposure assessment practises.

Methods. A literature survey was undertaken to identify source apportionment studies for two air pollutant groups, i.e. airborne particulate matter and volatile organic compounds. The results of this survey were used to compose an overview of the most commonly existing source apportionment techniques – also called receptor modelling - used to identify source contributions, including a description of the strengths and weaknesses.

Results. The fundamental principle of receptor modelling is based on the assumption that mass is conserved and that on this basis a mass balance analysis can be used to identify and apportion sources in the atmosphere. All techniques that were considered are based on assumptions regarding the source, chemical species and measurement methodology. They require a certain degree of knowledge about the source regarding the number of sources, source profile (which

substances are emitted by which source) or source strength regardless the origin of the source (outdoors or indoors). Of all considered techniques, conventional factorization and chemical mass balances represent the two extremes. Conventional factorization requires little knowledge, while chemical mass balance strategies require exact knowledge about the source(s). Other techniques, such as Positive Matrix Factorization or UNMIX, can be considered as intermediate strategies and are based on partly overlapping or slightly different assumptions and source knowledge requirements.

Discussion and Conclusions. An ideal source apportionment study starts with selecting the trace elements or compounds representing the obvious sources that might contribute to the location where the measurements will be carried out. Consequently, the collection methods and chemical analyses should be selected in a way that the important marker species can be analyzed accurately. The number of samples is another major requirement for a successful source apportionment analysis. Typically at least tens of samples are needed for a reliable source apportionment analysis. From the methods considered in this report, chemical mass balance requires fewest samples, however, it requires the most detailed quantitative description of the number of sources and the respective chemical emission profiles. When identifying and interpreting emission sources of personal exposures or those of indoor air samples sufficient number of samples is required, i.e. preferably more than 50 samples for each receptor site.

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