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Results of the European Intercomparison exercise for Receptor Models 2011-2012. Part I

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Executive summary

The quantification of pollution sources contributions to ambient atmospheric pollutants is a key element for the development of any effective air quality management policy.

Source apportionment is explicitly or implicitly needed for the implementation of the Directives on Air Quality (Directive 2008/50/EC and 2004/107/EC, hereon AQD). Pollution source information is required, for instance in: identifying exceedances due to natural sources or to road salting and sanding, preparing air quality plans, quantifying transboundary pollution, and in demonstrating eligibility for postponement of PM₁₀ and NO₂ limit value attainment (COM/2008/403).

In order to achieve a better understanding of the comparability and performance of different source apportionment methodologies, an intercomparison exercise (IE) was organized by the European Commission's Joint Research Centre (JRC) as part of the initiative for the harmonization of source apportionment with receptor models that was launched by the JRC in collaboration with the European networks in the field of air quality: FAIRMODE (modelling) and AQUILA (measurements). Facing such a challenging task was possible thanks to the collaboration of many European experts in the field that accepted to participate.

The IE was organized to fill a gap in the knowledge about the quantitative assessment of source apportionment model performances. The main objective was to assess whether the estimations of source contributions in terms of mass (ng/m³) compared with a reference value are consistent with a quality standard expressed as maximum accepted uncertainty. A database was distributed to the participants, including information on air pollutant concentration, their uncertainties and the emission inventory information.

Due to the lack of a specific methodology to assess receptor model performances in IEs, the organizers developed a battery of tests, partially based on existing international standards, and defined quality criteria (more details in Karagulian & Belis, 2012).

In the overall evaluation were also considered: a) the ability of models to reconstruct the measured PM mass, and b) the capacity of models to identify the number of sources. These two tests are, however, to be considered a complement of the main performance test.

The test to assess models' performance was divided in two stages: a) a preliminary stage aiming at assessing the similarity of the factor/source profiles reported by participants, mainly based on their fingerprints and their uncertainties, and b) a second stage targeted at evaluating whether the bias in the quantification of the solutions is consistent with the established quality standards.

The preliminary test was passed by a 90% of the tested factor/sources. APCS and COPREM were the models with the highest rate of rejected profiles (44% and 33% respectively). Of the 167 scores (z-scores) calculated in the final performance test, 144 (86%) complied with the 50% standard uncertainty quality criterion. Only 7% of the factor/source profiles were rated as unsatisfactory while 6% were ranked as questionable.

Concerning the subordinate tests, the majority of the solutions reproduced the PM mass in an acceptable manner, however, a number of solutions presented either an overestimation or an underestimation.

The average number of factors/sources identified by participants was 9. Nevertheless, this value varied considerably between solutions. The CMB type models presented an average of 8.3 sources per solution while the factor analysis type models average was 9.2 factors per solution. These values are in good agreement with the 10 sources identified in a previous study on the same database (Lee et al., 2006).

As a whole the IE results indicate a good general agreement between the performances of the different participants and models. Participants demonstrated good skills in dealing with complex real-world data. The next step of the IE consists in the use of a synthetic database containing known source contributions for the evaluation of the solutions.

Glossary

Source: a source of air pollution is any activity that causes pollutants to be emitted into the air.

Source category: is a group of sources that emit pollutants with similar chemical composition and time trend.

Source Apportionment (SA): is the practice of deriving information about pollution sources and the amount they emit from ambient air pollution data.

Source profile or fingerprint: is the average relative chemical composition of the particulate matter deriving from a pollution source, commonly expressed as the ratio between the mass of every species and the total PM mass.

Factor: is a calculated independent theoretical variable obtained by linear combination of many measured dependent variables used to describe their patterns of relationship.

Factor/source: is the pollution emitting entity identified in a SA study. Depending on the type of used model the output may be a factor (factor analysis type) or a source (CMB type).

Factor/source profile: a chemical profile or fingerprint identified and reported by a participant in a SA exercise disregarding the model from which it derives.

Reference source profile: source profile determined by chemical characterization of the particulate emitted by a specific source and available from public repositories, scientific publications or technical reports.

Chemical Mass Balance (CMB): models that solve the mass balance equation using effective variance least square used when the number and composition of sources are known.

Factor Analysis methods: a family of models used when there is no information on source number and composition. The most common methods to solve the mass balance equation are eigenvector analysis, explicit least squares fit, and conjugate algorithm.

Solution: is the output of a model run reported by one participant using a specific model setup.

Receptor Models (RM) abbreviated names:

APCS: Absolute Principal Component Scores

COPREM: Constrained Physical Receptor Model

CMB: Chemical Mass Balance

ME2: Multilinear Engine version 2

PCA: Principal Component Analysis

PMF: Positive Matrix Factorization (two versions used in this exercise EPA PMF 3.0 and PMF2)

1. Introduction

The quantification of pollution sources contributions to ambient atmospheric pollutants is a key element for the development of any effective air quality management policy.

Source apportionment is explicitly or implicitly needed for the implementation of the Directives on Air Quality (Directive 2008/50/EC and 2004/107/EC, hereon AQD). Pollution source information is required, for instance in: identifying exceedances due to natural sources or to road salting and sanding, preparing air quality plans, quantifying transboundary pollution, and justification for postponement of limit value attainment for PM₁₀ and NO₂.

Different methodologies for identifying sources are available. However, establishing to what extent a methodology is appropriate for a specific purpose and expressing the reliability of the results quantitatively is complex. This is mainly due to the fact that the actual source contributions in a specific point are unknown. In addition, there is a need for harmonization of the techniques aiming at making the results of the different studies comparable. In order to address the challenges connected to the use of modelling techniques in estimating pollution sources, the JRC launched in 2010 an initiative for the harmonization of receptor models used to identify pollution sources in Europe (Figure 1.1).

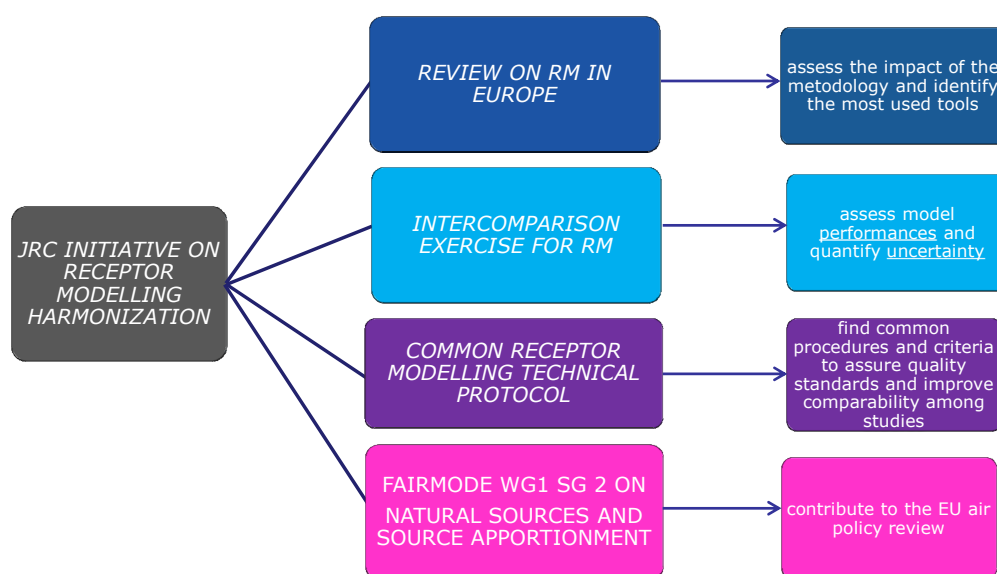


Figure 1.1: JRC Initiative for Receptor Model Harmonization

Two main approaches are used to determine and quantify the impacts of air pollution sources:

- receptor-oriented models (top-down approach)
- source-based models (bottom-up approach)

Dispersion models (not discussed in this report) estimate source contributions by miming the physical and chemical processes in the atmosphere based on the input from emission inventories and meteorological data.

Receptor-oriented methods (receptor models) estimate pollution sources contributing to the ambient air in a specific site using multivariate statistical analysis. Receptor models (RMs) solve a mass balance equation using the concentration of pollutants measured at the receptor and the

sources relative chemical compositions, also known as fingerprints (reference source profiles).

The mass balance equation solved by receptor models assumes that the concentration of every chemical species in a given sample depends on both its concentration in every source and the contribution of each source to the pollution at the monitoring site (receptor) where the sample is collected. This concept is summarized in the following expression:

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

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 known as multivariate models [e.g. Principal Component Analysis (PCA), UNMIX, Positive Matrix Factorization (PMF) and 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)).

According to the survey on the use of receptor models for PM source apportionment in Europe between 2001 and 2010, carried out as first step of the JRC’s initiative, 36% of the receptor modelling studies were performed with PMF and ME, 24% with CMB, 20% with PCA and Absolute PCA (APCA), 9% with FA and Absolute Principal Component Factor Analysis (APCFA), and the remaining 11% with other models (Karagulian & Belis, 2012).

RMs apportion Particulate Matter (PM) on the basis of its chemical composition. Typical input data are: major ions (e.g. nitrates, sulphates), carbonaceous fractions (organic and elemental carbon), trace elements and organic markers (e.g. levoglucosan, hopanes). Also volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), inorganic gases and aerosol size distributions have been apportioned to sources using RMs. In addition to species concentrations, many RMs process input data uncertainty and intrinsic model uncertainty in order to estimate the uncertainty of their output.

RM 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). Nevertheless, the application of RMs is more critical in conditions severely straying from the mass conservation assumption.

2. Intercomparison of Receptor Models

One of the outcomes of the preliminary survey was the need for harmonization in the evaluation of receptor models performance across Europe. In order to cope with this gap it was decided to launch an intercomparison exercise involving experts in source apportionment from different European Countries.

Comparing the results of source apportionment analyses performed by independent practitioners using the same or different RMs on the same dataset makes it possible a) to gather information about the reproducibility within and between different approaches and b) to evaluate the model output source contribution estimations (SCE) by testing the conformity with 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. Therefore, comparing the results of different models on the same dataset is a common method to validate

them and quantify their variability. 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, correlation coefficient and regression analysis between SCE provided by different models (e.g. Viana et al., 2008; Belis et al., 2011).

ORGANIZATION	COUNTRY
<i>IDAEA CSIC</i>	<i>Spain</i>
<i>Univ. Aarhus</i>	<i>Denmark</i>
<i>University of Genoa</i>	<i>Italy</i>
<i>Finnish Meteorological Institute</i>	<i>Finland</i>
<i>INERIS/LSCE</i>	<i>France</i>
<i>University of Birmingham</i>	<i>United Kingdom</i>
<i>Norwegian Institute for Air Research (NILU)</i>	<i>Norway</i>
<i>Dep. of Physics University of Florence</i>	<i>Italy</i>
<i>University of Milan Bicocca</i>	<i>Italy</i>
<i>C.N.R. I.I.A</i>	<i>Italy</i>
<i>Dept. of Physics - University of Milan</i>	<i>Italy</i>
<i>C.N.R. - I.S.A.C.</i>	<i>Italy</i>
<i>IUTA e.V.</i>	<i>Germany</i>
<i>NCSR Demokritos, Environmental Research Laboratory</i>	<i>Greece</i>
<i>Paul Scherrer Institut Laboratory of Atmospheric Chemistry</i>	<i>Switzerland</i>
<i>European Commission – Joint Research Centre</i>	<i>European Union</i>

Table 2.1: List of participants' affiliations

In the present intercomparison exercise, the uncertainty in the SCE was evaluated using a methodology developed on purpose to assess receptor models performance in proficiency tests (Karagulian & Belis, 2012).

The intercomparison exercise involved 16 participants from research institutes and universities in 10 European countries. The participating organizations are listed in Table 2.1.

Participants were asked to apply the source apportionment method they selected on a common real-world database of PM_{2.5} concentrations and relative chemical composition. They received information on the analytical methods and a local emission inventory. However, location, sampling time and meteorological variables were not disclosed to them.

Intercomparison exercise stages

10th June 2011: the organizers distributed the intercomparison package to the experts who had sent an Expression of Interest (EoI). The intercomparison package contained:

- database (DB) with concentrations and uncertainties
- analytical Minimum Detection Limits (MDLs) and uncertainties
- emission inventory of the study area
- instructions
- application form
- results reporting form

8th September 2011: the organizers sent a technical note to answer participant's questions

14th September 2011: the organizers released an "errata corrige" on organic MDLs

31st October 2011: deadline for submitting results

At the delivery of the solution the organizers sent a questionnaire to each participant asking them to describe their expertise and the methodology applied.

3. The database

3.1. The study site

Saint Louis is a densely populated and industrialized area located in the State of Missouri (United States) on the banks of the Mississippi river, at the border with the State of Illinois (Figure 3.1.1). The independent city's population is more than 300.000 inhabitants in an area of only 170 km². However, the whole urban area, known as "Great-Saint Louis", totalizes ca. 2.8 million inhabitants. The main economic activities in the area are services, manufacturing, trade, transportation of goods and tourism.

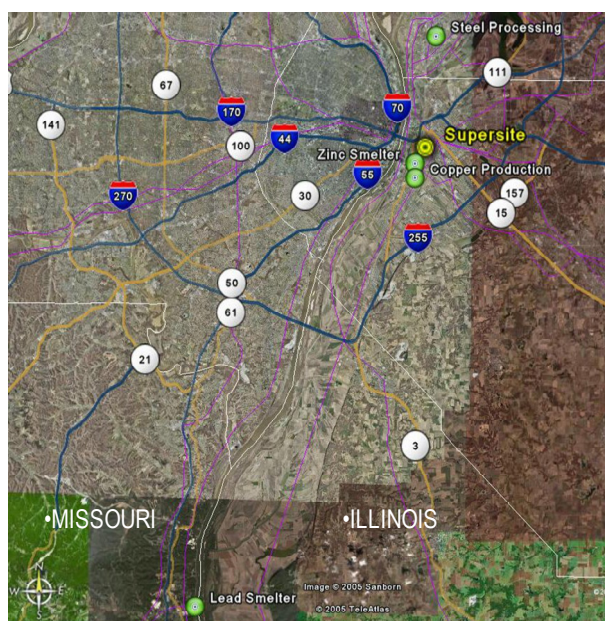


Figure 3.1.1: Location of the St. Louis Supersite where PM_{2.5} samples were collected from 2001 to 2003 (map source Google Earth).

Schauer et al.(2006) identified and reported specific factor profiles for three industrial sites that mostly influenced the PM_{2.5} collected at the St. Louis Supersite: a copper production plant, a zinc smelter and a steel mill (Figure 3. 1.1).

Previous work carried out by Lee et al. (2006) applied Positive Matrix Factorization (PMF2) finding **10 sources** categories including (study average contribution to the PM_{2.5} mass in parentheses): secondary sulfate (33%), carbon-rich sulfate (20%), gasoline exhaust (16%), secondary nitrate (15%), steel processing (7%), airborne soil (4%), diesel emissions/railroad traffic (2%), zinc smelting (1.3%), lead smelting (1.3%), and copper production (0.5%).

3.2. Structure of the database

A database (DB) composed of PM_{2.5} mass and chemical species sampled in the St. Louis Midwest Supersite (U.S.A.) was created for the intercomparison by merging two existing

databases.

One of the original databases consisted of 710 PM_{2.5} samples collected on a daily basis between 2001 and 2003. This dataset was composed of trace elements, inorganic ions and organic and elemental carbon (OC, EC) divided by analytical steps. The second database, including organic compounds, was sampled during the same time window but at a frequency of 1 every 6 days.

For the purpose of the proposed intercomparison, the two sets of data were merged selecting only the days for which both inorganic and organic data were available. The final DB consisted of 178 24 hour samples with following inorganic species: *SO₄, NO₃, NH₄, Al, As, Ba, Ca, Co, Cr, Cu, Fe, Hg, K, Mn, Ni, P, Pb, Rb, Se, Si, Sr, Ti, V, Zn, Zr, OC1, OC2, OC3, OC4, OP, EC1m, EC2, EC3*) (Lee et al., 2006) and the organic compounds: indeno(cd)pyrene, benzo(ghi)perylene, benzo(a)anthracene, fluorantene, pyrene, coronene, benzo(b,k)fluoranthene, benzo(j)fluoranthene, dibenzo[a,h]anthracene, and levoglucosan (Jaeckels et al., 2007).

One of the objectives of the intercomparison exercise was to collect information about the methodology applied by participants in order to better understand differences between results from different groups. No specific indication on how to treat the data was made. Participants were simply asked to perform all the necessary steps in order to prepare data for the analysis properly and to execute their models reporting all the methodological choices taken during data analysis and interpretation.

The database provided to the participants already contained the uncertainties for each entry. Nevertheless, to allow participants wishing to check or make their own estimation of uncertainties (facultative), minimum detection limits (MDL) and analytical uncertainties were provided.

A summary of the emission inventories of the districts surrounding the monitoring site (St. Louis city, St. Louis county, St Clair county and Madison county) was distributed with the intercomparison package.

For the source profiles, participants were asked to refer to the US database SPECIATE (<http://www.epa.gov/ttnchie1/software/speciate/>).

Missing values and values below detection limit (BDL) had been treated in the inorganic species dataset. On the contrary, missing values and BDL were not processed in the dataset with organic species. In this case, participants were expected to perform preliminary data evaluation and treatment.

3.3. Database pre-treatment

In the original DBs quality checks had been carried out to assess the data consistency and when the results of the tests fall beyond the acceptability criteria actions had been taken.

Some species composing the DB had been excluded when:

- Signal noise ratio (S/N) ≤ 0.2
- $\geq 90\%$ below MDL

Some samples had been excluded when:

- PM_{2.5} mass concentration value was missing or invalid
- firework took place (that was on July 4th and 5th)

In the inorganic database, BDL values had been replaced by $\frac{1}{2}$ MDL and missing values had been replaced by the geometric mean.

Despite the care put by the practitioner in removing noise from the data, real-world datasets contain inconsistencies that can be associated with the variability of parameters, sampling errors and data processing slips.

For illustrative purposes, some remarks about the structure of uncertainties are reported below:

- Inorganic ions presented a relatively high uncertainty.
- *Co, Cr, Hg, Ni, Rb, Ti, V, Zr*, and PAHs showed a high proportion of values below detection limit (BDL)
- *Ca, Fe, Zn, K* uncertainties were below 5%
- For every chemical species were used more than one MDL, most probably due to different analytical batches.

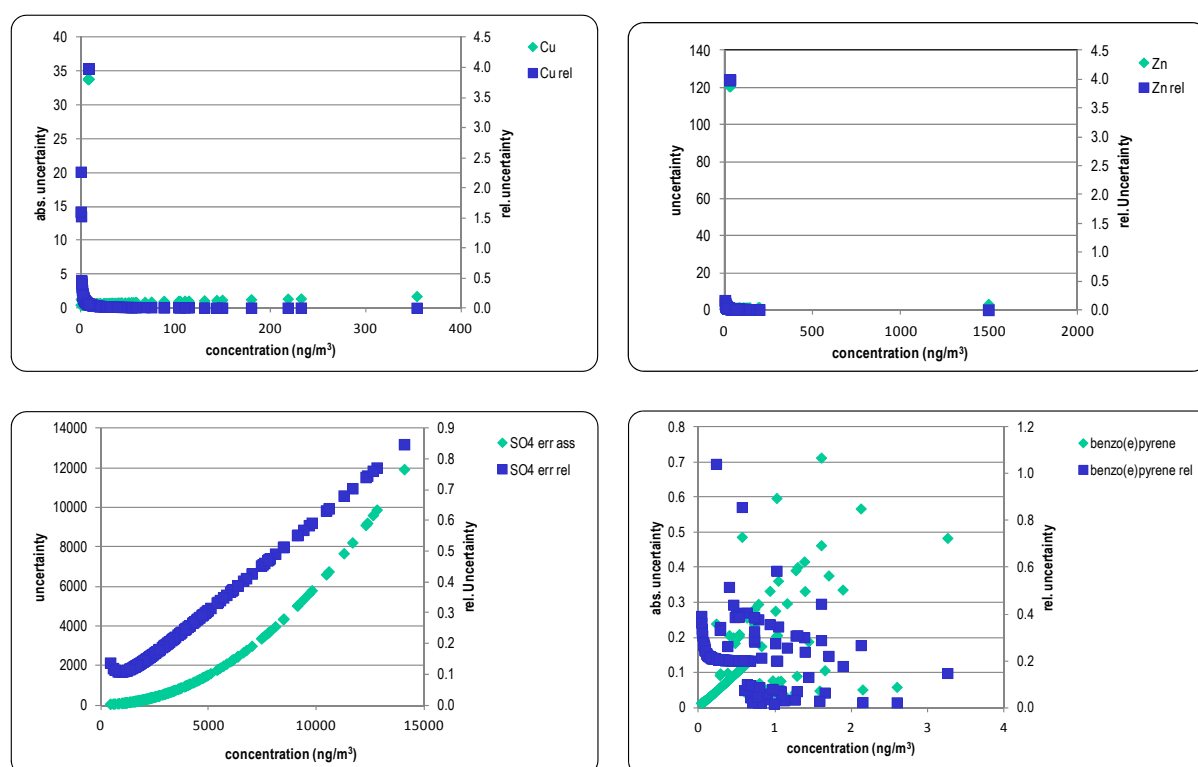


Figure 3.3.1: Examples of uncertainty structure in organic and inorganic species.

In Figure 3.3.1 samples of uncertainty structures for metals, inorganic ions and organics are shown. As already explained above, they varied among the different species.

4. Methodological approach for the evaluation of solutions

The ultimate objective of the intercomparison is to quantify the differences between the solutions reported by participants and a reference value, and compare this difference with a criterion of acceptability. In this exercise is applied a methodology developed on purpose (Belis & Karagulian, 2012) adapted from the standard ISO 13528 on proficiency test assessment. According to this approach, the assessment of the source contribution estimation (SCE) is made for each factor/source separately. The method consists of a two-stage procedure. The first stage includes a number of preliminary tests to assess whether the factors/sources belong to the same source category. The test is carried out comparing factor/sources using both

their chemical composition (fingerprint) and the trends of their contributions in time. The Pearson coefficient is commonly used in literature to compare SCE. However, Pearson coefficient may be influenced by few species with high leverage (e.g. high contribution to the PM mass). In order to keep under control the influence of species in the high range of concentrations, Pearson is calculated also on log-transformed data. Moreover, in order to take into account the uncertainty of the considered factor/source profiles provided by participants, a test based on the Weighted Difference (WD) index was introduced (Karagulian and Belis, 2012). In synthesis, the first step comprises 7 preliminary tests to check the comparability of the factor profiles within a factor category (Figure 4.1). If one factor/source fails in 4 or more of those tests, then it is considered dubious and the factor/source is removed from the source category under examination.

The second stage is the proficiency test using the methodology proposed in ISO 13528 (2005) (z-score) which is explained in detail in Chapter 6.

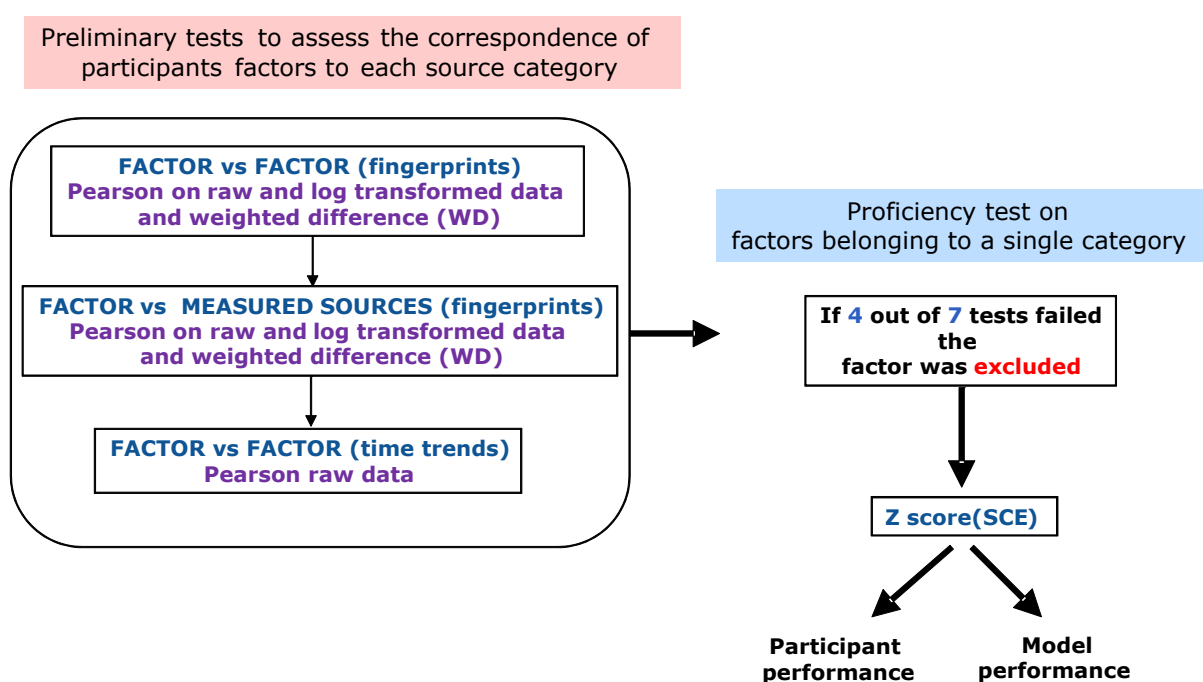


Figure 4.1: Diagram representing the methodology followed in this intercomparison.

5. Preliminary tests

5.1. Mass Closure test

An indirect test commonly used to assess the performance of a source apportionment exercise is to observe the match between the measured gravimetric mass and the sum of the masses of all the factors /sources identified in the analysis. In principle, the sum of the SCE should account for all the measured mass within the uncertainty of both the sum and the measured mass. A difference between observed and estimated mass above 20% may indicate problems in the source attribution e.g. relevant sources are missing, or quantification errors. On the contrary, a good mass closure does not necessarily mean that the source apportionment is properly done. In this analysis the match between observed and estimated (sum of factors) $PM_{2.5}$ mass in every sample was assessed for each solution using linear regression analysis (Chapter 8).

5.2. Correlation between factors/sources

For each source category, a correlation matrix was calculated for all participants' relative factor profiles (sources for CMB solutions). Pearson product-moment correlation coefficients (R) were calculated with the software STATISTICA 10[®]. The correlation involved all possible pairs of factor profiles and the statistical significance was set to $p < 0.05$.

The median, minimum, maximum, 25th and 75th percentile of the Rs of each factor/source profile *versus* all the other factors/source profiles and reference source profiles in the same source category were calculated.

The criterion of $R \geq 0.6$ was used for the median value of the Pearson coefficient to establish whether a factor profile was, on average, comparable to all the other factors/sources profiles in the same category.

In order to test if a correlation is determined only by those species with the highest mass contribution in the factor/source profiles, correlation was also performed on log transformed data. For that purpose, relative contribution data were converted into logarithmic data avoiding negative values and values below zero ($-1/\ln[x]$).

Tests using Pearson coefficient:

- Correlation between factor/source profiles (both raw and log transformed data) reported by participants.
- Correlation between factor/source profiles reported by participants and source profiles from literature, SPECIATE (USA), Lee et al. (2006) and Larsen et al. (2012) (both raw and log transformed data).
- Correlation between factor/source contributions per sample (time trends) estimated by participants (only raw data).

5.3. Weighted Difference test

The Weighted difference (WD) is the average ratio of the difference between relative species concentrations of all possible pairs of factor profiles and the sum of the respective uncertainties according to the following equation (Karagulian and Belis, 2012):

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

where x_i and x_j are the relative concentrations of the n species in the source profiles i and j , respectively, and s_i and s_j are their uncertainties. This index is used to test the relationship of the distance between two factors/sources and their uncertainty. The range of acceptability is set between 0 and 2 ($WD_{ij} \leq 2$) denoting that distances up to twice the uncertainty are considered acceptable. By comparing WD and Pearson it is possible to establish whether the uncertainties attributed to the factor/source profiles by participants are coherent with the observed reproducibility.

6. Performance Test

In order to evaluate the conformity of SCEs with reference to an established quality objective, a performance test based on the proficiency test of the ISO 13528 (ISO 13528, 2005) was applied. The key elements of this test are:

- The assigned value X (source contribution estimation; SCE) and its uncertainty uX as reference value to compare with participant's run average x_i .
- The standard deviation for proficiency assessment (σ_p) as criterion to evaluate participants' performance.
- z-score indicator

The source categories were evaluated separately. A reference value X for each source category was generated by applying the robust analysis iterative algorithm (Analytical Methods Committee 1989a, 1989) to the average SCE of all solutions included in it.

The standard deviation for proficiency assessment criterion (σ_p) was set at 50% taking as reference the model quality objectives for PM_{10} annual mean laid down in Directive 2008/50/EC.

The participants' scores are calculated using the z-score performance indicator (ISO 13528, 2005). The z-score indicates whether the difference between the participant measured value and the reference value remains within the limits of specified criteria.

$$Z_{(SCE)} = \frac{x_i - X}{\sigma_p} \quad (3)$$

where x_i is the SCE of every solution belonging to a given source category. The factor/source performance is then evaluated as follows:

- $|Z| \leq 1$ SCE is **optimal** \Rightarrow performance 'Excellent'
- $1 < |Z| \leq 2$ SCE are **coherent** \Rightarrow 'Acceptable'
- $2 < |Z| \leq 3$ SCE are **questionable** \Rightarrow 'Warning'
- $|Z| > 3$ SCE are **unsatisfactory** \Rightarrow 'Action'.

The test is applied to demonstrate that the results obtained by participants do not exhibit a level of bias beyond the set criteria with respect to the reference value. Proficiency test results can therefore give recommendations on the use of SCE factors in the real world.

Nevertheless, the reference value obtained by consensus from all participants, while useful to quantify the differences between participants' solutions, may not detect a common bias in the used methodologies with respect to the "true" value. Worth to mention that the above approach assumes that participants have generally similar repeatability in their model runs.

7. Factor /Source Profiles (Fingerprints)

Considering that the output of factor analysis are factors (to which a source name was attributed) while CMB outputs are sources, in this report the expression “factor/source” is used to refer to the profiles identified by participants regardless of the model used. Sometimes the term “factor” is used for the sake of brevity (e.g. factor vs factor graph) but the meaning is the same as above. On the other hand, “reference source profiles” are source fingerprints obtained from third sources and used as reference in the tests.

In general, participants presented one solution each but some presented more than one. In order to standardize and simplify the nomenclature of factor/source profiles a letter was assigned to each participant followed by a numeric index to identify the different solutions presented by some of them.

Participants C, D, E, H, I, and J used PMF 3.0 while F, L, M and Q used PMF2. Participants A and K solutions were made with APCS and COPREM, respectively.

Participant **B** presented 4 solutions with different receptor models: ME2, EPA PMF 3.0, PMF2 and PCA. Therefore, four different labels were assigned to this participant: **B1, B2, B3** and **B4**. Participant **G** performed 2 runs: one with EPA PMF3.0 (**G1**) and one with PMF2 (**G2**).

Participant **N** performed 3 runs with CMB (**N1, N2**, and **N3**) and reported the input profiles used for the runs. In this way were generated alphanumeric codes to identify the 22 reported solutions:

A1, B1, B2, D, E, C, G1, H, I, J, B3, G2, F, L, M, Q, K, B4, N1, N2, N3, S.

The codes listed above were used to identify the factor /source profiles reported in every solution following the scheme reported in Table 7.1

Similarly codes were introduced to identify the reference source profiles retrieved from the literature used for the validation of participants’ solutions. The code “**_P**” was given to reference source profiles reported by Shauer et al. (2006). The names of the European reference source profiles reported by Larsen et al. (Larsen et al., 2012) were kept as reported in the original publication. The code **_Lo** was added only in few cases. Codes **_SPEC** and **_Lee** were assigned to source profiles obtained from the EPA SPECIATE database and from Lee et al. (2006).

Reference	Assigned label
Participants	Factor name_ CC
Schauer et al. (2006)	Source name_ P
European source profiles (Larsen et al. 2012)	Source name_ Lo
EPA SPECIATE	Source name_ SPEC
Lee et al. (2006)	Factor name_ Lee

Table 7.1: Nomenclature rules used to label factors/sources in the intercomparison exercise.

EPA SPECIATE	Label
Draft Residential Wood Combustion: HardSoft - Composite	HardSoft_Wood_Comp_SPEC
Brake Lining Dust – Composite	Brake_Comp_SPEC
Transportation – Composite	Transp_Comp_SPEC
Transportation – Composite+tire and brakes	Trans_Comp+Tire+Brake_SPEC
Draft Paved Road Dust – Composite	Road_Dust_Paved_Comp_SPEC
Draft Industrial Soil – Composite	Dust_Ind_SPEC
Crustal Material – Composite	Crustal_Comp_SPEC
Cement Production – Composite	Cement_Comp_SPEC
Cement	Cement_SPEC
Lead Smelters – Average	Pb_smelt_SPEC
Lead Production – Composite	Pb_product_comp_SPEC
Lead Processing – Composite	Pb_process_comp_SPEC
Oil-Fired Power Plant Composite	Oil_Power_SPEC
Steel Production – Average	Steel_prod_SPEC

Table 7.2: Reference source profiles from the US database SPECIATE (2011).

In this section are listed the source profiles used in the preliminary tests to validate factor profiles reported by participants.

In Table 7.2 are reported the source profiles obtained from the EPA SPECIATE Version 4.2. European source profiles selected from Larsen et al. (2012) are listed in Table 7.3.

European Source Profiles	Label
Biomass Burning	REALLWO_NP
	50W350OF1_NP
	REWOOD1_NP
Re-suspension	REBITUM
	PAVRD-1
Traffic	REVEHI
Traffic Exhaust	D75EXH
Traffic Brakes & Tires	BRTIR-CO
Marine Vessel	MARVES1
Metallurgy	IRON_Lo
Fuel combustion	FUEL_Lo
Coal combustion	Coal_Lo

Table 7.3: Reference source profiles from Larsen et al.(2012).

Source profiles of tailpipe emissions from diesel, gasoline zinc smelting, copper metallurgy and lead smelting were taken from Schauer et al. (2006) and are shown in Table 7.4.

Schauer et al. (2006)	Label
Diesel	Diesel_P
Gasoline	Gasoline_P
Zn smelter	Zn Smelter_P
Pb smelter	Pb Smelter_P
Cu metallurgy	Cu Metallurgy_P

Table 7.4: Reference source profiles from Schauer et al. (2006).

Source profiles used in the reference paper on source apportionment identification of airborne PM_{2.5} at the St. Louis Super Site (Lee et al., 2006) were included in the list of reference source profiles (Table 7.5):

Lee et al. (2006)	Label
Carbon rich sulphate	C-rich sulfate_Lee
Lead smelter	Pb_Lee
Copper production	Cu_Lee
Airborne Soil	Soil_Lee
Secondary nitrate	Nitrate_Lee
Zinc smelting	Zinc_Lee
Gasoline exhaust	Gasoline_Lee
Diesel emissions/railroad traffic	Diesel_Lee
Secondary sulfate	Sulfate_Lee
Steel processing	Steel_Lee
Carbon rich sulphate	C-rich sulfate_Lee

Table 7.5: Reference source profiles

On the basis of a) the solutions reported by participants and b) a review on source apportionment studies with receptor models carried out in the last decade in Europe, the factor/sources reported by participants were allocated to the 15 “source categories” listed below:

- **Biomass Burning**
- **Gasoline**
- **Diesel**
- **Brakes**
- **Traffic**
- **Dust**
- **Sulphate**
- **Nitrate**
- **Secondary sources**
- **Zinc smelter**
- **Copper production**
- **Lead smelter**
- **Steel processing**
- **Industry & Combustion**
- **Ship emissions**

Factor/source profiles reported by participants were allocated into source categories on the basis of the name given to them by the participant taking into account the chemical composition. The identification of the typical chemical composition of the source categories is the result of a review of the following papers (Begum et al., 2009; Belis et al., 2011; Harrison et al., 1997; Hopke, 2010; Hopke et al., 1995; Kim and Hopke, 2004; Lee et al., 2006; Lenschow et al., 2001; Lewis et al., 2003; Marcazzan et al., 2003; Moreno et al., 2006; Piazzalunga et al., 2011; Putaud et al., 2010; Querol et al., 2004; Viana et al., 2008). Nevertheless, the definitive allocation of factors/sources to source categories was done after the preliminary analysis described in the previous chapters.

For the purpose of data processing, factor profiles provided by participants are expressed in mass concentration. Relative factor profiles were calculated by dividing the mass concentration of each chemical species in the source profile by the total PM_{2.5} mass apportioned by the model.

The number of solutions that reported each source categories is indicated between brackets:

1. Biomass Burning (22)
2. Dust - Re-Suspended Soil (21)
3. Traffic (16)
4. Industry -combustion (16)
5. Copper metallurgy (14)
6. Zinc smelter (11)
7. Sulphate (10)
8. Nitrate, Diesel (9)
9. Lead metallurgy smelter, Steel processing, Secondary (8)
10. Gasoline, Brakes, ships (≤ 6)

8. Results: Mass Closure test

In figure 8.1 are presented the regression parameters of the total $PM_{2.5}$ mass concentration estimated from the sum of factor/source mass in the solutions versus the measured $PM_{2.5}$ mass concentration. Displaying slope and the intercept in abscissa and ordinate respectively, makes it easier to appreciate the relationships between the points representing the solutions performance. For a better interpretation of the graph, symbols and colors are used to represent the models and the determination coefficient (R^2) of each solution. The majority of the solutions (12) present low intercepts ($< 3000 \text{ ng/m}^3$) and slope between 0.7 and 0.95. These points also show high determination coefficient $0.8 < R^2 < 1$. A second group of solutions (5) presents a still good determination coefficient $0.7 < R^2 < 0.8$ but high intercepts ($5500 - 7500 \text{ ng/m}^3$) and low slopes ($0.4 - 0.6$). These are solutions that were able to reproduce the time trend of the mass fairly well but tend to overestimate at low concentrations and to underestimate a high concentrations. On the other extreme, there is a small group of two solutions with intercepts higher than 8000 ng/m^3 and slopes higher than 1.2 that denote serious quantification problems. The last group, in an intermediate position between the first and the second, includes two solutions with low determination coefficients (< 0.7) indicating a poor time trend reproducibility. No relationship between mass closure performance and the kind of receptor model used in the generation of the solution emerges from figure 8.1, with the exception of a slight tendency to underestimation in CMB solutions. In addition, an influence of the operator experience and the methodological choices adopted in the execution of the analysis cannot be excluded.

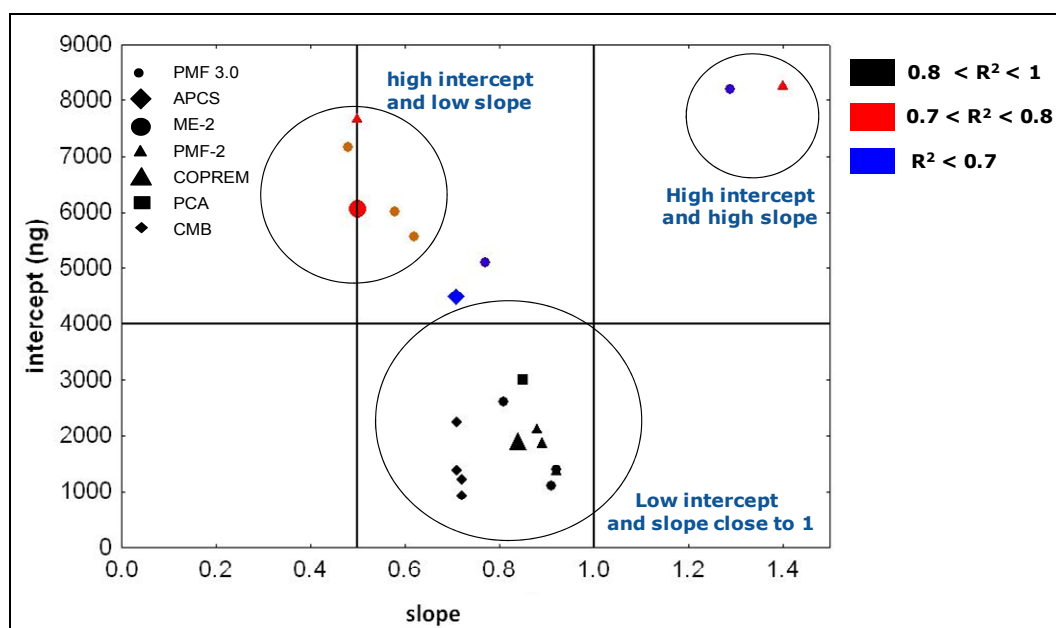


Figure 8.1: Regression of calculated $PM_{2.5}$ mass concentration versus observed $PM_{2.5}$ mass for each solution.

9. Results: Preliminary Tests

In this chapter the results of the preliminary tests described in subchapters 5.2 and 5.3 are presented. In order to summarize the huge amount of results, box and whisker plots, representing the distribution of all the indexes obtained from the comparison of one factor/source profile with all the others in the same category, are used. The names of the factor/source profiles are reported in abscissa and the value of the index is shown in ordinate. The boxes represent the quartiles of the distribution of the indexes while the lines (whiskers) represent the minimum and maximum values. In every graph there is a horizontal line to indicate graphically the limit of acceptability that was used to evaluate whether the considered factor/source profiles passed a given test or not.

9.1 Preliminary test I: Correlation between factor/source fingerprints

In this section the Pearson coefficients between factor/source profiles (fingerprints) of each source category are reported. In factor vs. factor plots, the correlations of the reference source profiles with the factors/sources in the source category is reported for illustrative purpose on the right side. However, they are not considered in the assessment of the correlation between participants' factor/source profiles. The test includes also comparison of reference source profiles obtained from the literature with all the factor/sources in the source category. The horizontal line denotes the acceptability limit set at 0.6. Calculations were performed with both raw and log-transformed data.

9.1.1 Biomass Burning

Biomass Burning (BB) factor/source was identified by all the participants (16) in all the solutions. **REALWO_NP**, **50W350OF1_NP**, **REWOOD1_NP** and, **HardSoft_Wood_Comp_SPEC** were chosen as “reference source profiles”.

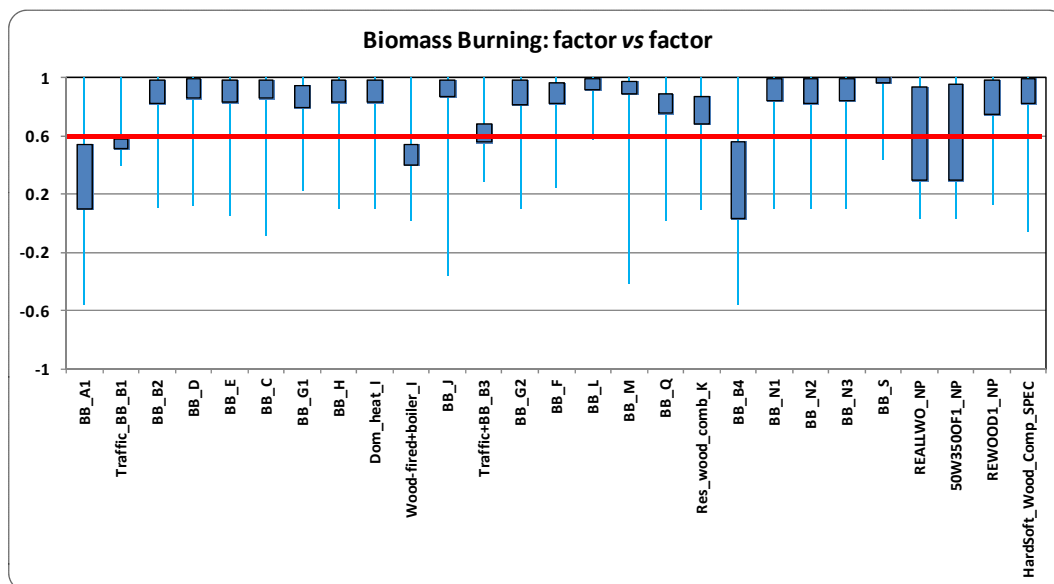


Figure 9.1.1.1: Correlations between Biomass Burning factor/source profiles using raw data.

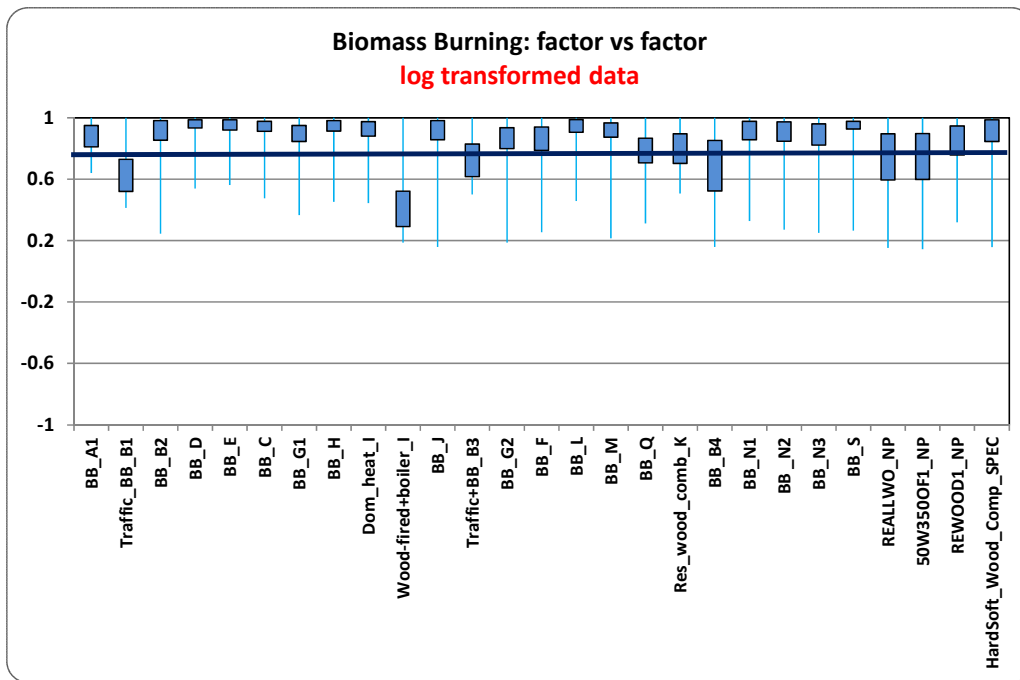


Figure 9.1.1.2: Correlations between Biomass Burning factor/source profiles using log transformed data.

The analysis of the correlation coefficients between factor/source profiles raw data shows that factors **BB_A1**, **Wood-fired-boiler_I** and **BB_B4** are not correlated with the majority of the factor/sources in this category. These factors present the full inter-quartile range below the limit of acceptability ($R = 0.6$; Figure 9.1.1.1). A similar analysis using log-transformed data shows that only **Wood-fired-boiler_I** is not correlated with the other factor/source profiles in the same category (Figure 9.1.1.2). Instead, **BB_A1** and **BB_B4** in this test meet the criterion of comparability. This is probably an indication that there are species in these profiles that influence the correlation coefficient more than others due to their high contribution to the mass.

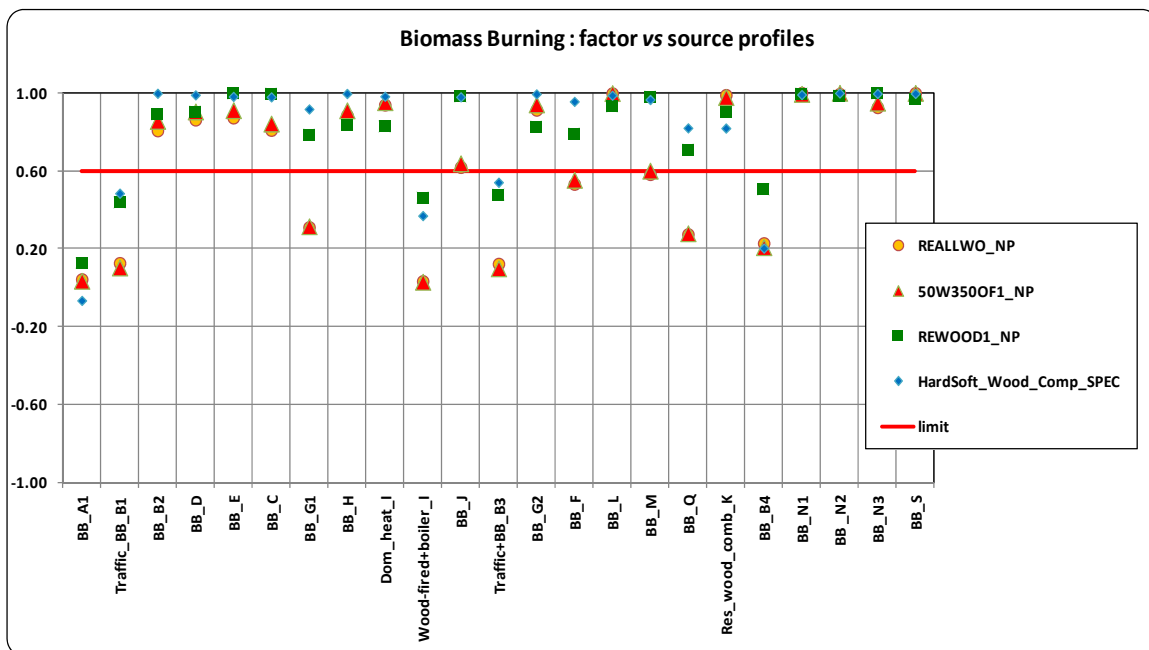


Figure 9.1.1.3: Correlation between Biomass Burning factor/source profiles and reference source profiles using raw data.

Figure 9.1.1.3 shows that factors **BB_A1**, **Traffic_BB_B1**, **Wood-fired+boiler_I**, **Traffic+BB_B3** and **BB_B4** are not correlated to any reference source profile. On the other hand, all the other factors/sources are correlated to one or more reference source profiles. The analysis of log-transformed data confirms that **Traffic_BB_B1**, **Wood-fired+boiler_I** and **Traffic+BB_B3** are poorly correlated with the reference source profiles (Figure 9.1.1.4), while **BB_A1** and **BB_B4** meet the criterion of comparability with reference sources. In conclusion, the study of correlations makes it clear that mixed factors for traffic and biomass burning (**Traffic_BB_B1** and **Traffic+BB_B3**) are not comparable with the other factor/sources assigned to biomass burning.

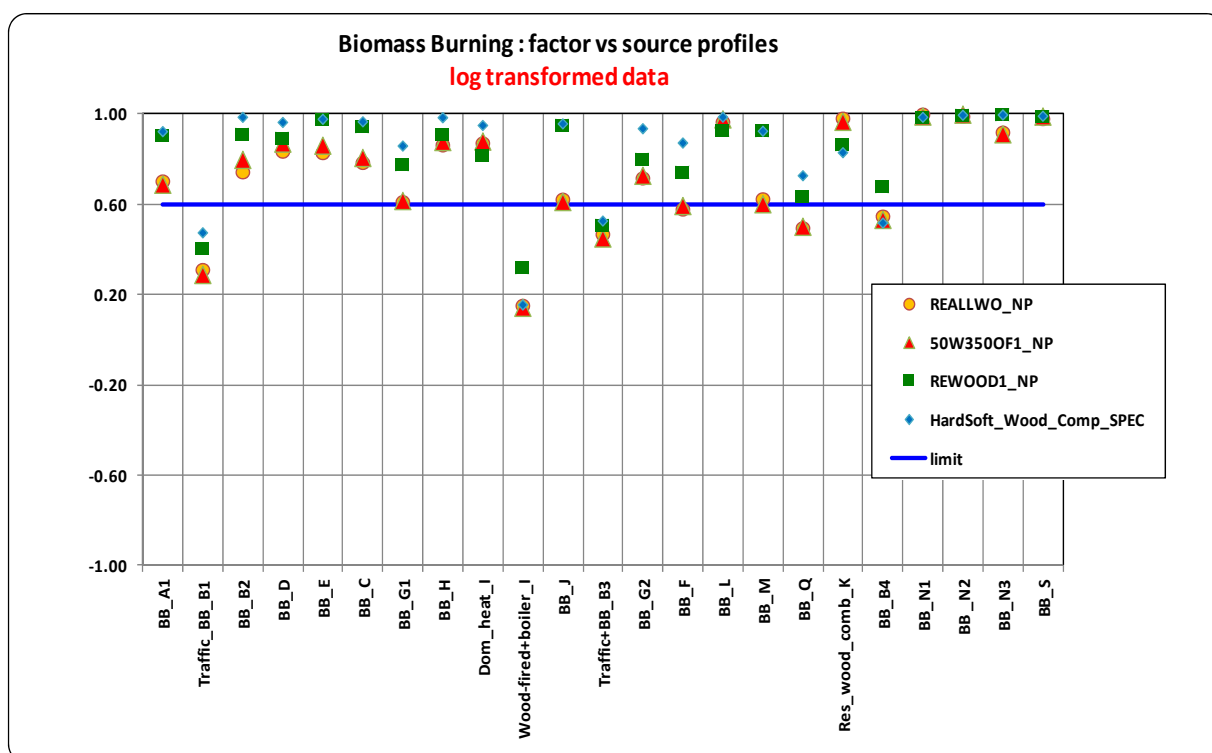


Figure 9.1.1.4: Correlation between Biomass Burning factor/source profiles and reference source profiles using log transformed data.

9.1.2 Gasoline

Gasoline factor/source was identified by only 7 participants. **Gasoline_P** and **Gasoline_Lee** were chosen as “reference source profiles”.

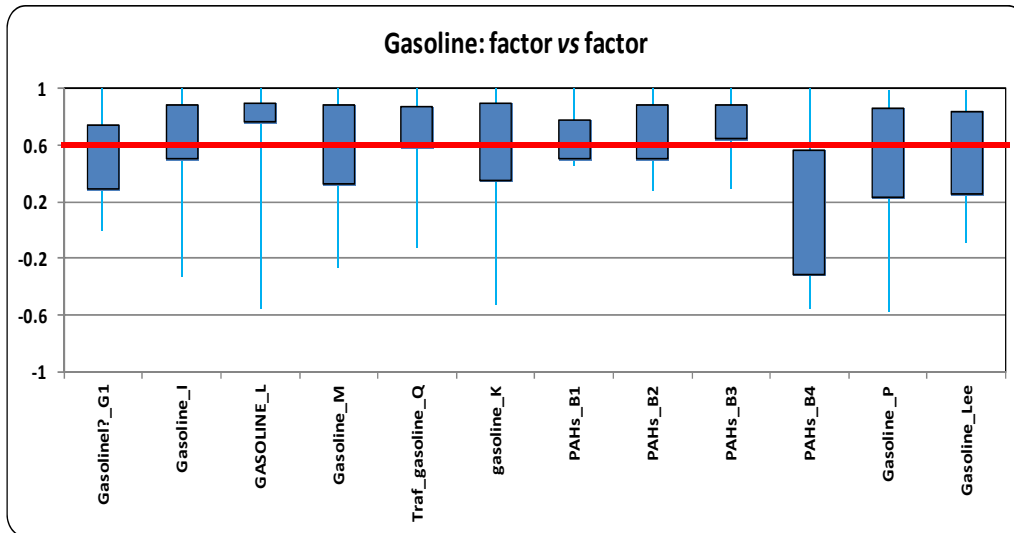


Figure 9.1.2.1: Correlation between Gasoline factor/source profiles using raw data.

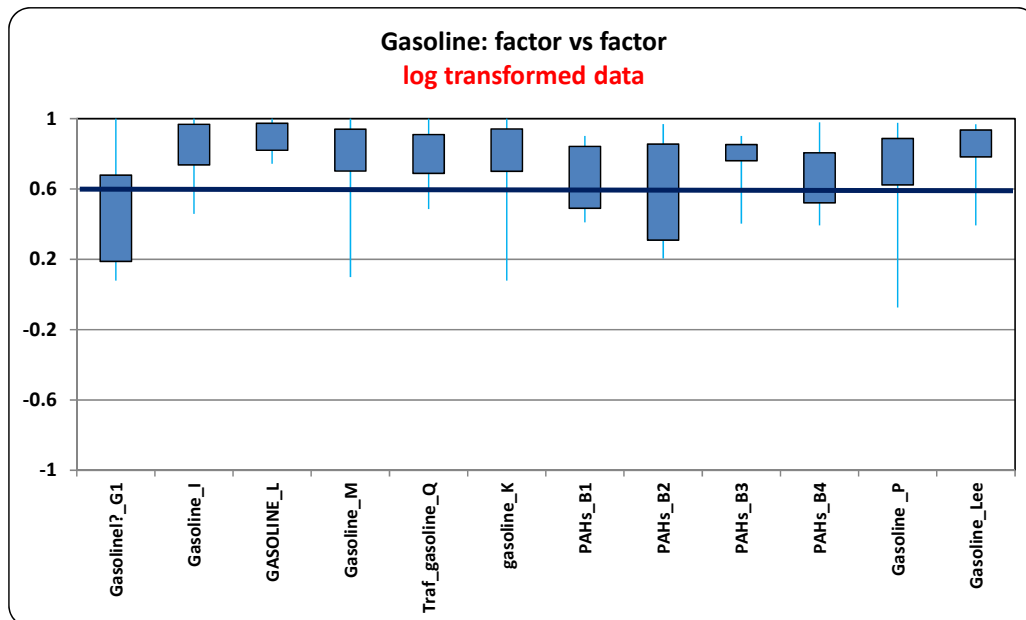


Figure 9.1.2.2: Correlation between Gasoline factor/source profiles using log transformed data.

Gasoline?_G1 and **PAHs_B4** (PAHs = Polycyclic Aromatic carbons) were not correlated with factor/sources profiles of the same category reported by other participants (Figure 9.1.2.1). Further analysis with log transformed data excluded **Gasoline?_G1** and **PAHs_B2** from the source category (Figure 9.1.2.2).

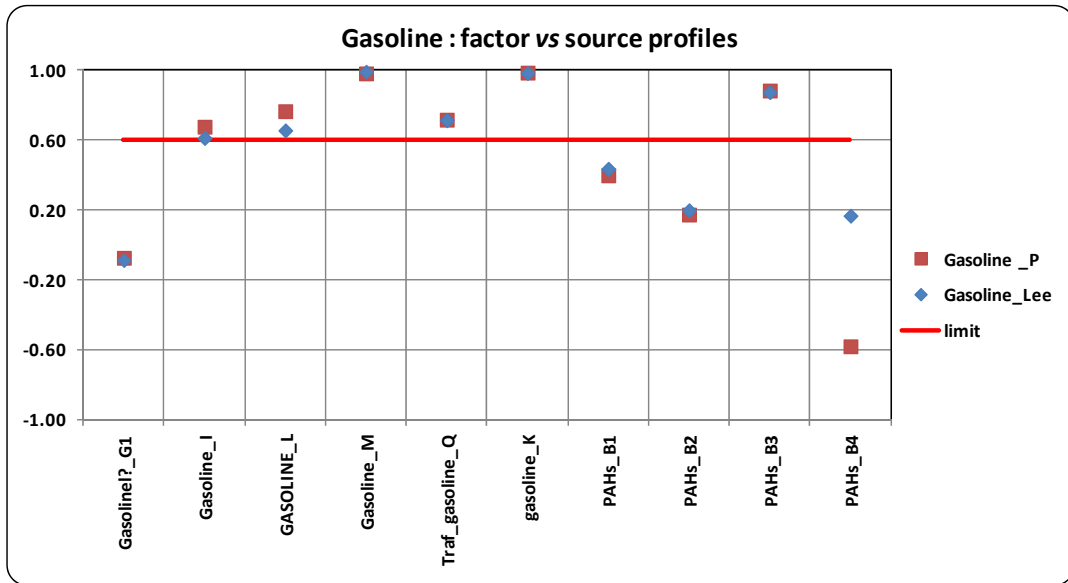


Figure 9.1.2.3: Correlation between Gasoline factor/source profiles and reference source profiles using raw data.

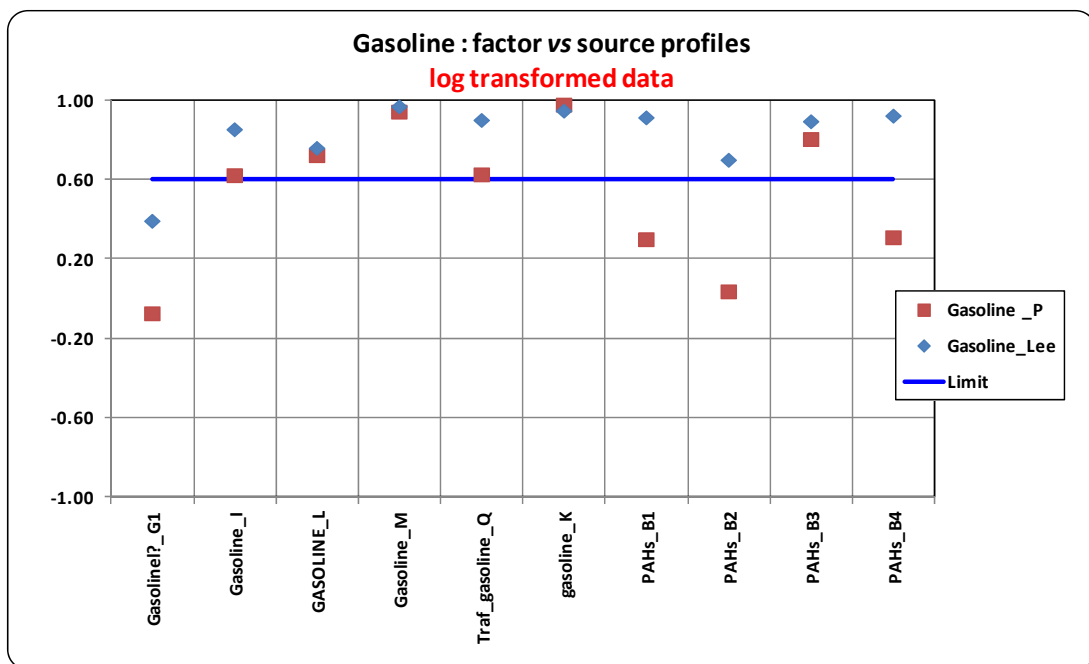


Figure 9.1.2.4: Correlation between Gasoline factor/source profiles and reference source profiles using log transformed data.

Correlations between raw data of factor/source profiles and reference profiles for Gasoline show that **Gasoline?_G1**, **PAHs_B1**, **PAHs_B2** and **PAHs_B4** are poorly correlated with reference source profiles (Figure 9.1.2.3). However, analysis with log transformed data sorts out only **Gasoline?_G1** as poorly correlated with reference source profiles (Figure 9.1.2.4).

9.1.3 Diesel

Diesel factor/source was identified by 8 participants. **D75EXH_NP**, **Diesel_P** and **Diesel_Lee** were chosen as “reference source profiles”.

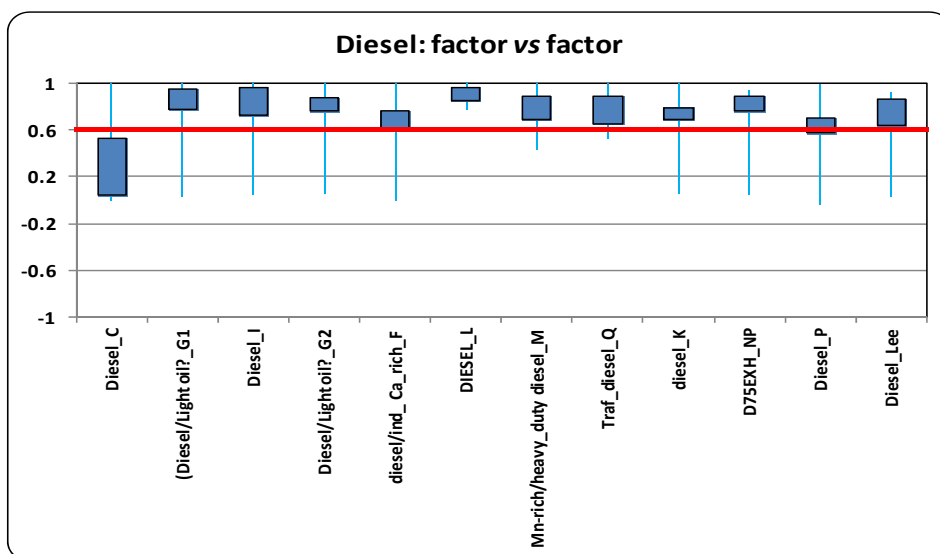


Figure 9.1.3.1: Correlation between Diesel factor/source profiles using raw data.

Analysis with raw and log transformed data showed that only **Diesel_C** was poorly correlated with factor/sources of the same category (Figure 9.1.3.1, Figure 9.1.3.2).

Correlation between raw data of factor/source profiles and reference profiles for Diesel showed that **Diesel_C** was the only factor poorly correlated with the reference source profiles (Figure 9.1.3.3). The same result was confirmed by correlation performed with log transformed data (Figure 9.1.3.4).

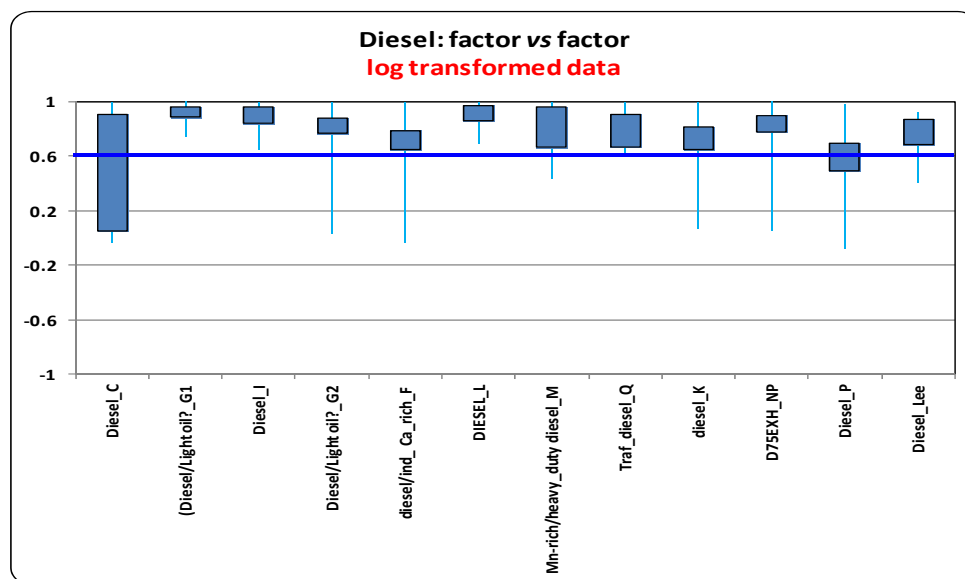


Figure 9.1.3.2: Correlation between Diesel factor/source profiles using log transformed data.

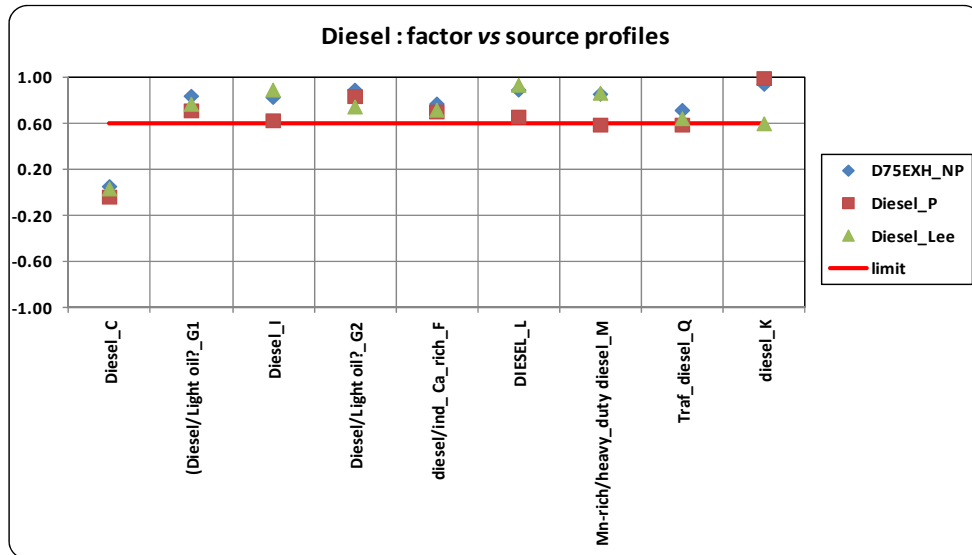


Figure 9.1.3.3: Correlation between Diesel factor/source profiles and reference source profiles using raw data.

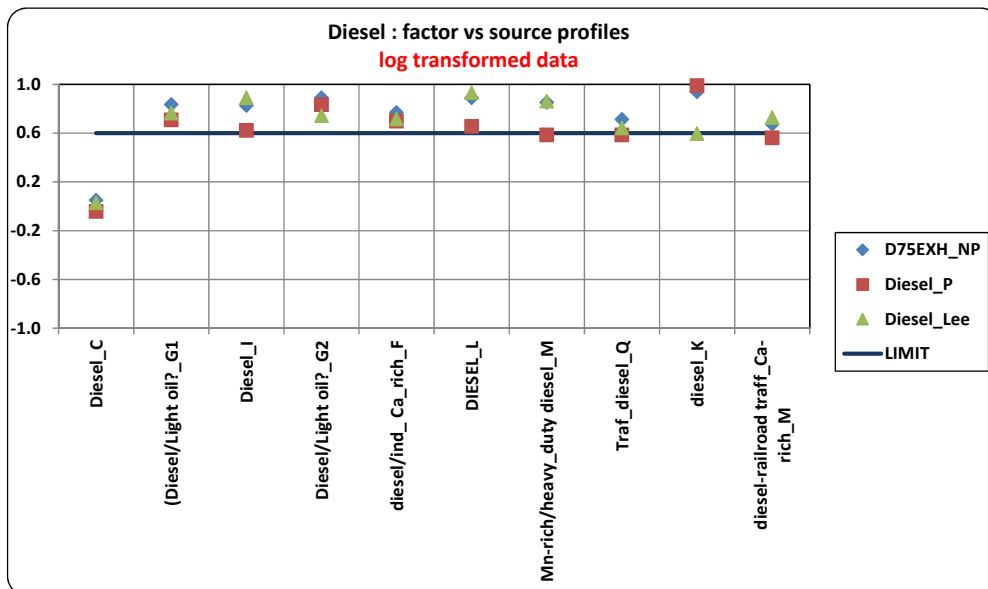


Figure 9.1.3.4: Correlation between Diesel factor/source profiles and reference source profiles using log transformed data.

9.1.4 Brakes

Six factors/sources compatible with Brakes description were identified by 3 participants. **BRTIR-CO_NP** (Brakes and Tires) and **Brake_Comp_SPEC** were chosen as “reference source profile”.

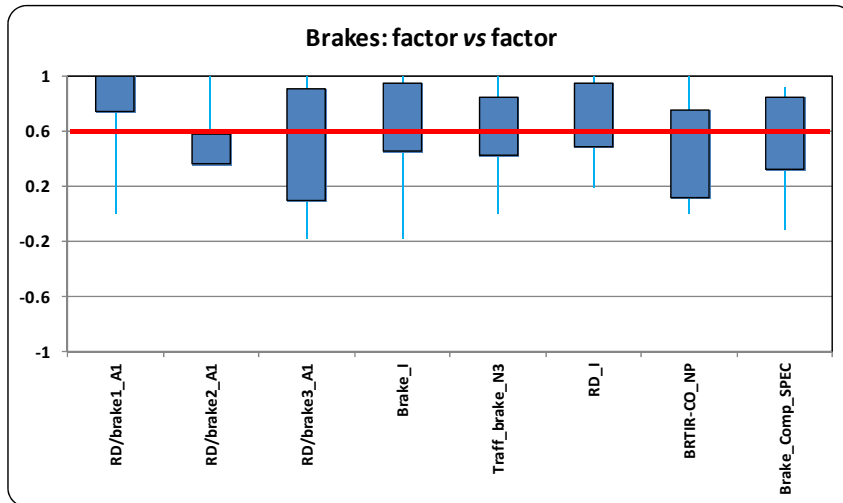


Figure 9.1.4.1: Correlation between Brakes factor/source profiles using raw data.

Raw and log-transformed data analysis showed that only **RD/brake3_A1** (RD =road dust) was poorly correlated with the factor/sources reported by the other participants (Figures 9.1.4.1 and 9.1.4.2). For the analysis with log-transformed data it was not possible to convert relative mass concentrations into logarithmic data for the factor profile **RD/brake2_A1** because of some relative values bigger than 1.0.

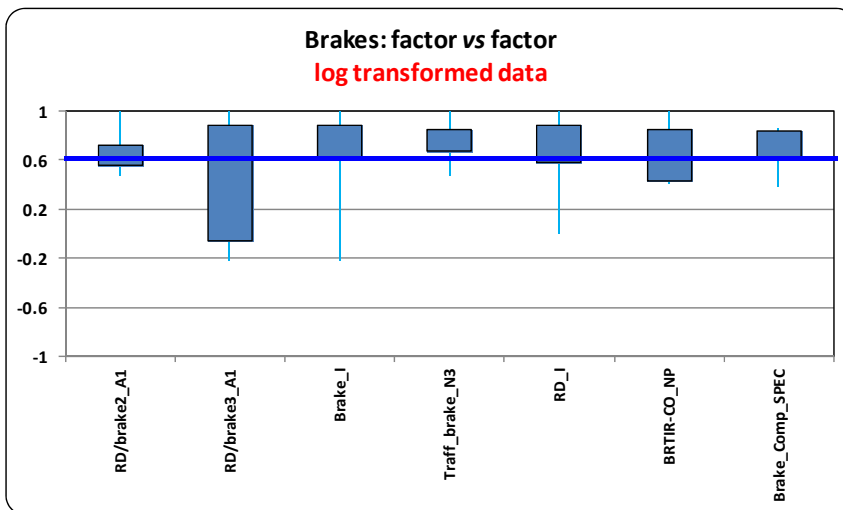


Figure 9.1.4.2: Correlation between Brakes factor/source profiles using log-transformed data.

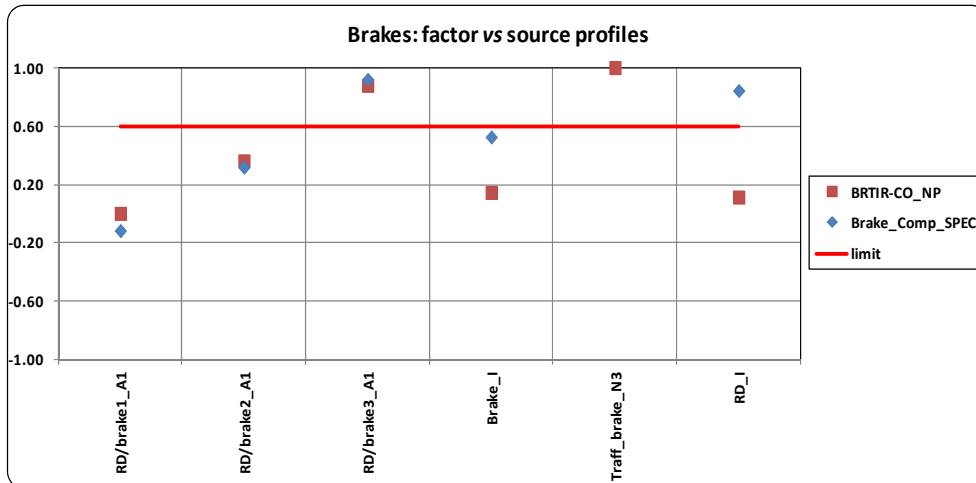


Figure 9.1.4.3: Correlation between Brakes factor/source profiles and reference source profiles using raw data.

Correlation analysis of raw data of factor/source profiles and reference profiles for Brakes showed that **RD/brake1**, **RD/brake2_A1** and **Brake_I** were poorly correlated with reference source profile (Figure 9.1.4.3). **RD/brake2** could not meet the criterion of acceptability even in the correlation with log-transformed data (Figure 9.1.4.4).

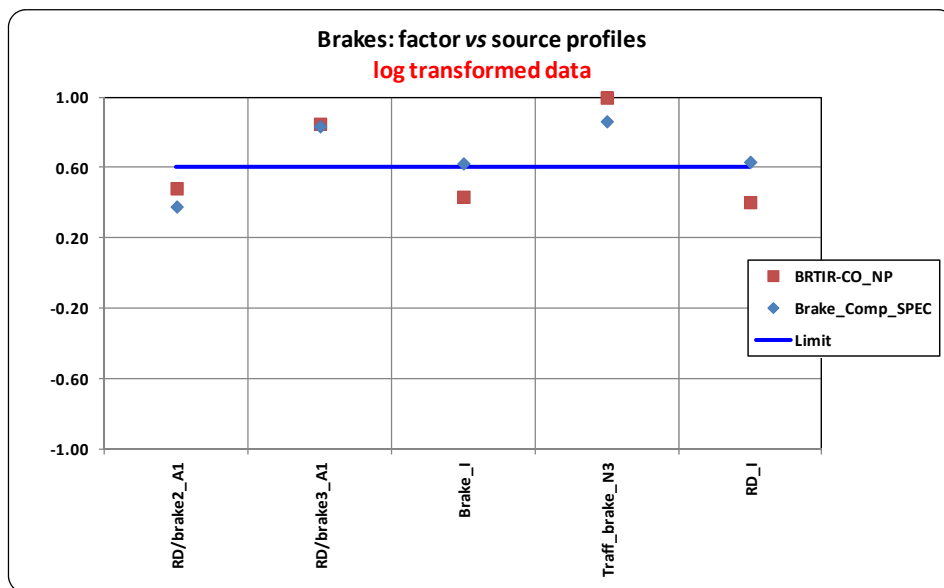


Figure 9.1.4.4: Correlation between Brakes factor/source profiles and reference source profiles using log-transformed data.

Missing points (as for the missing correlation value between **Traffic_brake_N3** and **Brake_Comp_SPEC** in Figure 9.1.4.3) are due to the lack of minimum number of data pairs to run a correlation.

9.1.5 Traffic

Eighteen factors/sources attributed to traffic were identified by 12 participants. **REVEHI_NP** (Re-suspended dust from vehicles), **Traffic_SP**, **Transp_Comp_SPEC** (from transport), **Trans_Comp+Tyre+Brake_SPEC** and **Road_Dust_Paved_Comp_SPEC** (from paved road) were chosen as “reference source profiles”.

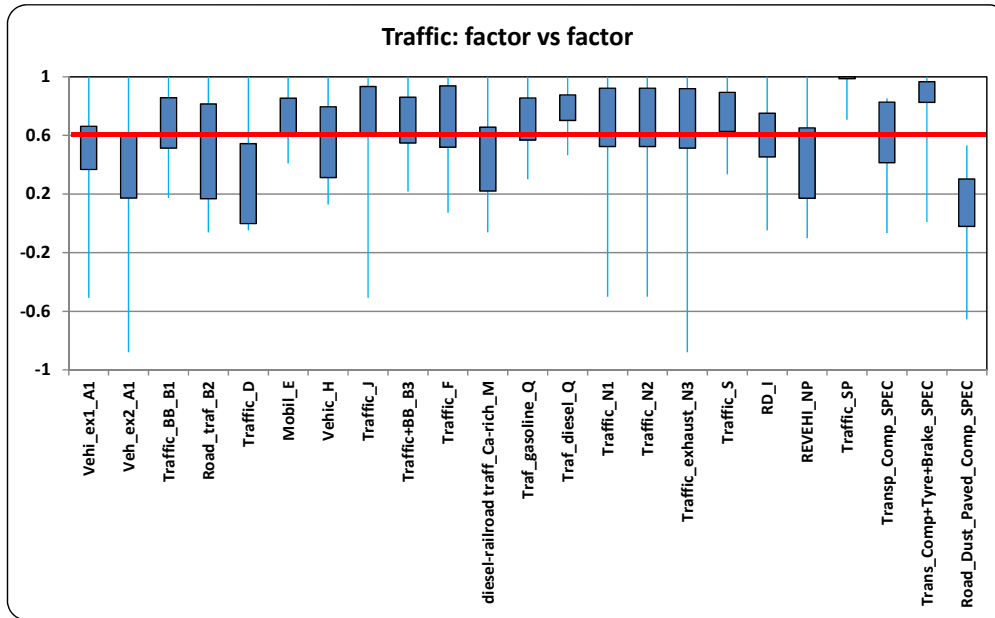


Figure 9.1.5.1: Correlation between Traffic factor/source profiles using raw data.

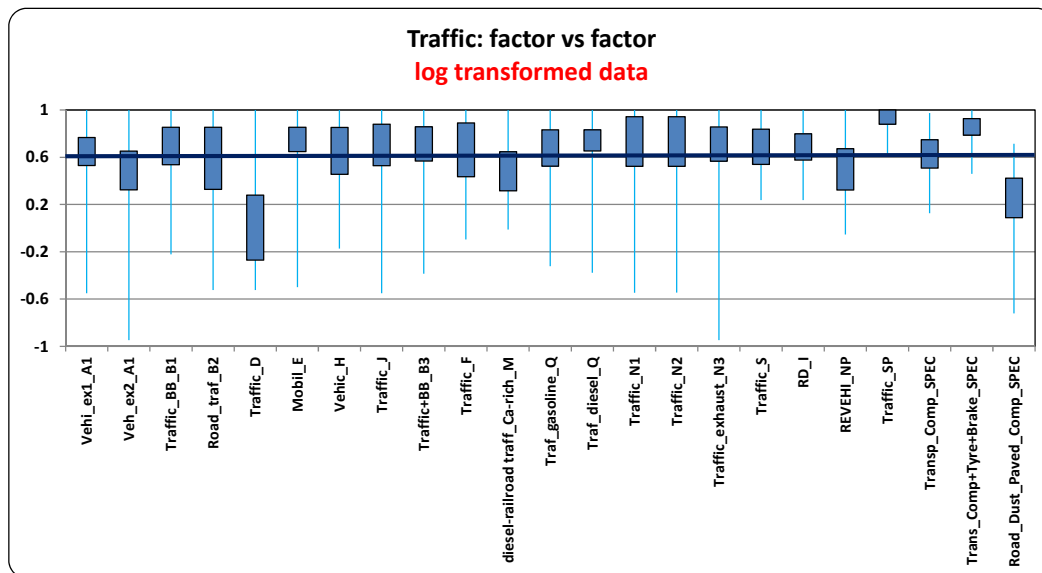


Figure 9.1.5.2: Correlation between Traffic factor/source profiles using log-transformed data.

Correlation analysis using raw data shows that **Veh_ex1_A1**, **Veh_ex2_A1** (vehicle exhaust), **Road_traf_B2**, **Traffic_D**, **Vehic_H** and **diesel-railroad traff_Ca-rich_M** (Carbon-rich) profiles are poorly correlated with factor/sources profiles of the same category found by other participants (Figure 9.1.5.1). However, analysis performed with log-transformed data, shows that

only Veh_ex2_A1, Traffic_D and diesel-railroad traff_Ca-rich_M are poorly correlated with other factor/source profiles (Figure 9.1.5.2).

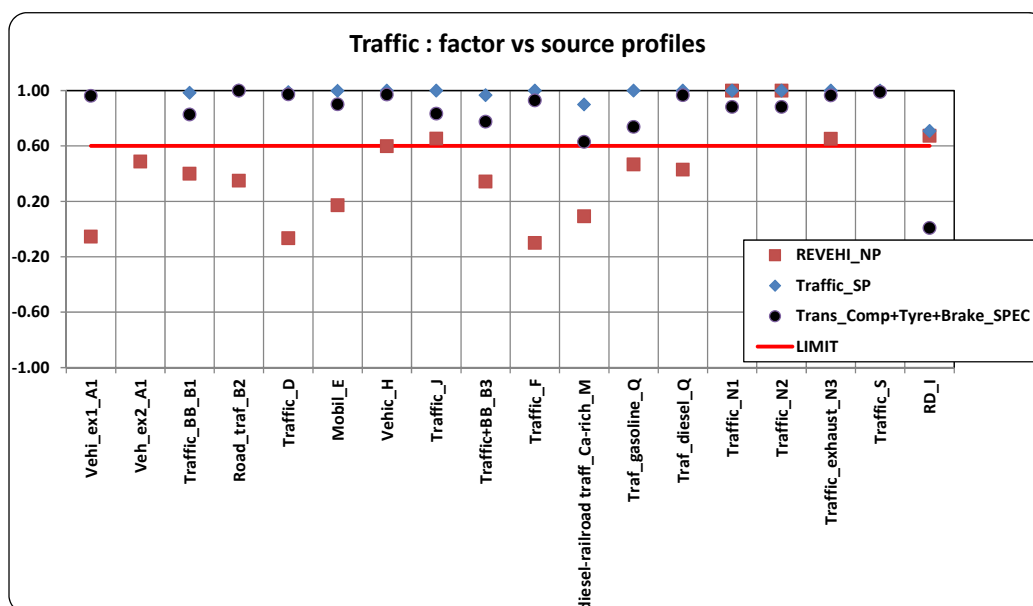


Figure 9.1.5.3: Correlation between Traffic factor/source profiles and reference source profiles using raw data.

With the exception of Veh_ex2_A1, all factor/source profiles are correlated with reference source profiles (Figure 9.1.5.3). On the other hand, all factor/source profiles are correlated with reference source profiles (Figure 9.1.5.4) when log-transformed data are used.

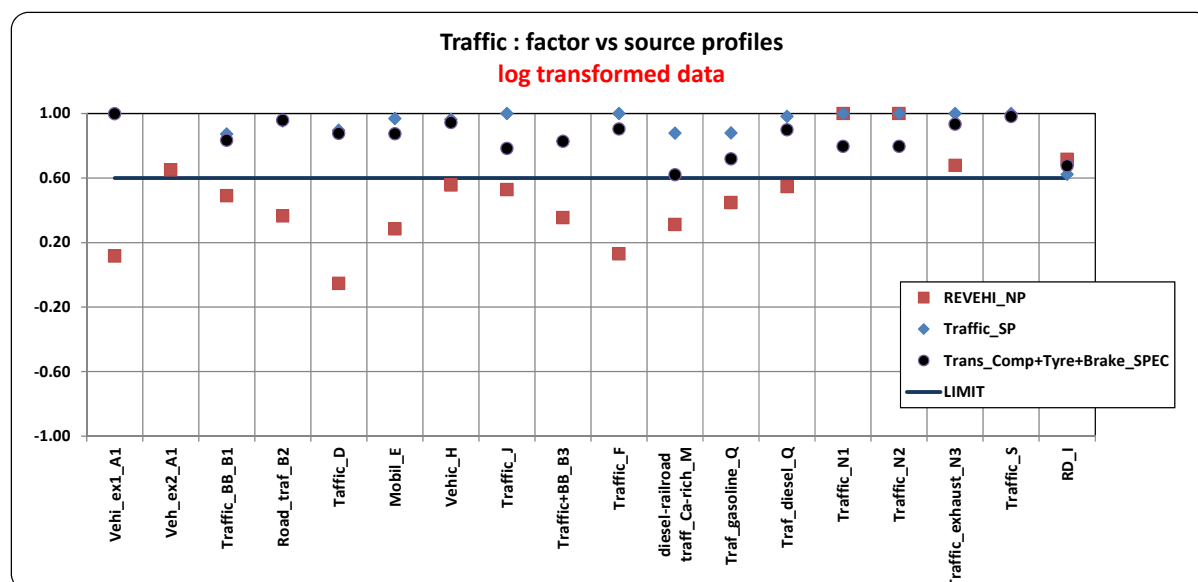


Figure 9.1.5.4: Correlation between Traffic factor/source profiles and reference source profiles using log-transformed data.

9.1.6 Dust – Re-Suspended Soil

Dust – Re-Suspended Soil factor/source was identified by all 16 participants and is present in all the solutions. REBITUM_NP (re-suspended bitumen), PAVRD-1_NP (paved road),

Dust_Ind_SPEC (industrial dust), Crustal_Comp_SPEC and Soil_Lee were chosen as “reference source profiles”.

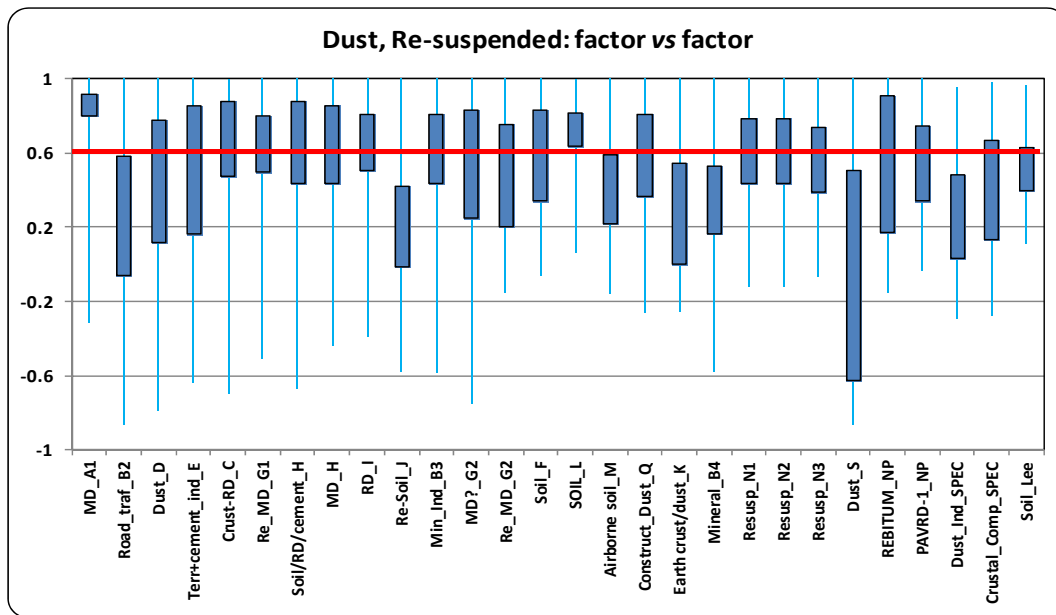


Figure 9.1.6.1: Correlation between Dust factor/source profiles using raw data.

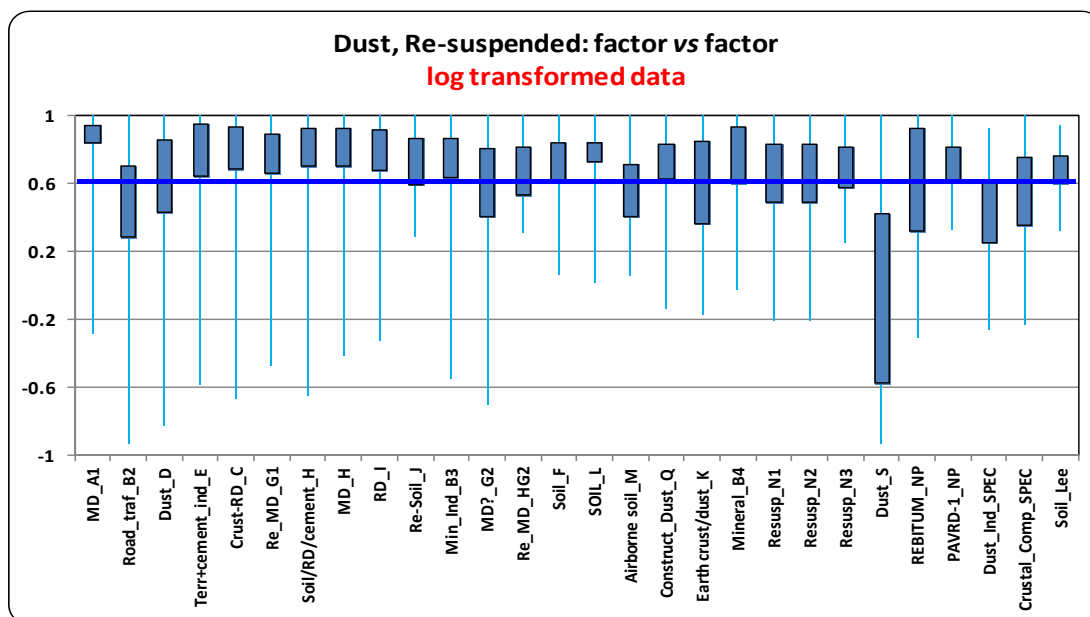


Figure 9.1.6.2: Correlation between Dust factor/source profiles using log-transformed data.

Correlations performed with raw data show that several factor/source profiles (**Road_Traf_B2**, **Dust_D**, **Terr+cement_ind_E** (plant debris mixed with cement), **Re-Soil_J**, **MD?_G2**, **Re_MD_G2**, **Soil_F**, **Airborne_Soil_M**, **Constuct_Dust_Q** (dust from construction), **Earth crust/dust_K**, **Mineral_B4**, **Resusp_N3** and **Dust_S**) are poorly correlated with the majority of the other factors/sources in the same category (Figure 9.1.6.1). On the other hand, the same analysis performed with log-transformed data shows that only **Road_traf_B2** (Road traffic) and **Dust_S** are poorly correlated with factor/source profiles of the same category (Figure 9.1.6.2).

Such a difference between raw and log-transformed data may indicate a dominant influence of species with high mass contribution into this factor/source.

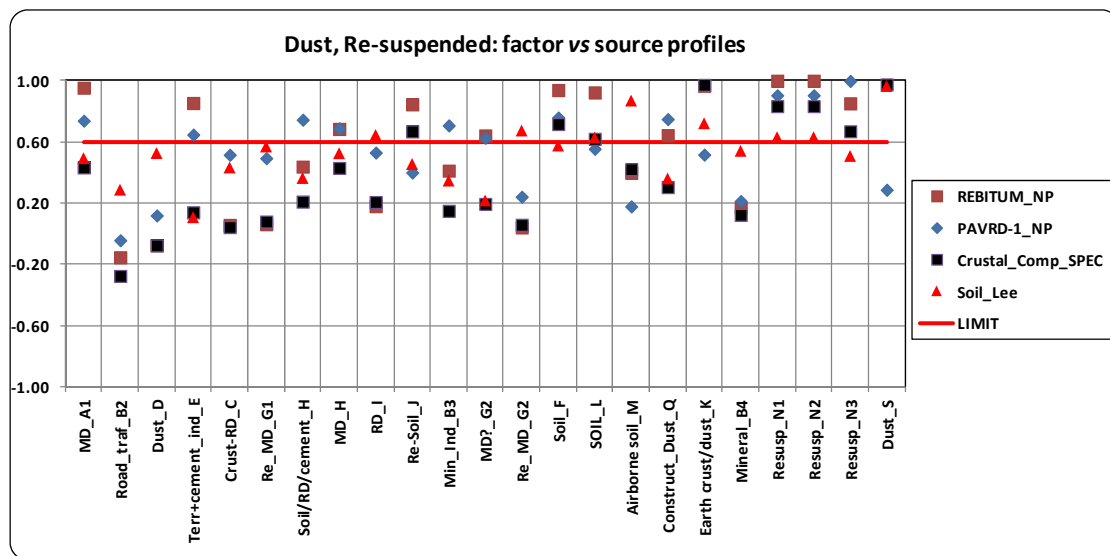


Figure 9.1.6.3: Correlation between Dust factor/source profiles and reference source profiles using raw data.

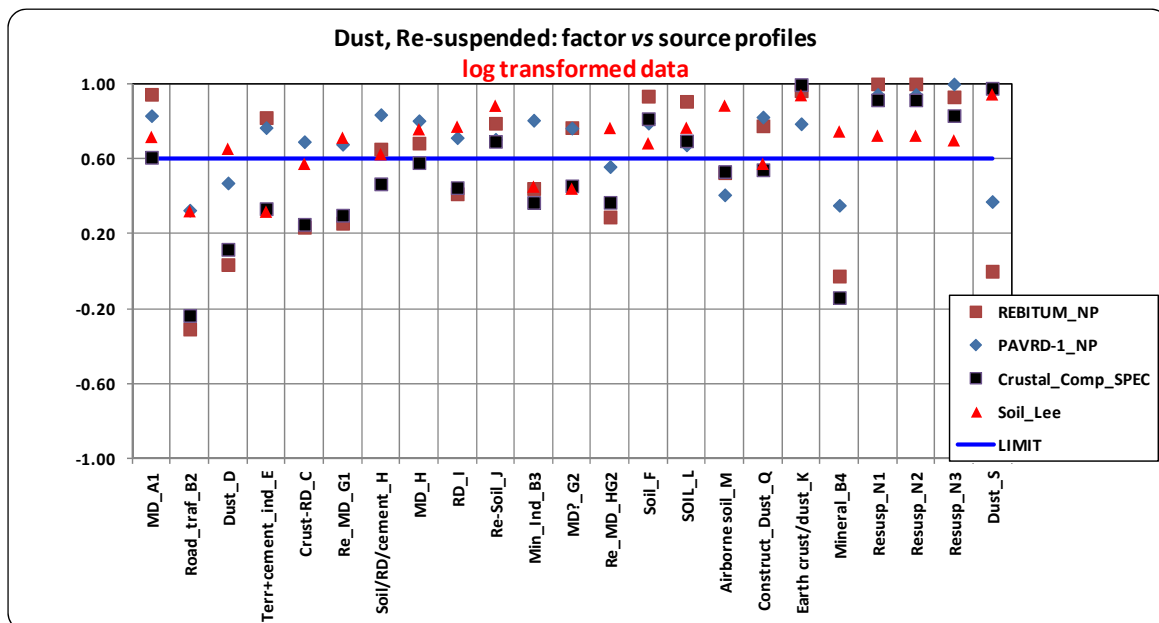


Figure 9.1.6.4: Correlation between Dust factor/source profiles and reference source profiles using log-transformed data.

The analysis of the correlations between factor/source profiles and reference source profiles reveal that **Road_Traf_B2**, **Dust_D**, **Crust-RD_C**, **Re_MD_G1** and, **Mineral_B4** are poorly correlated with all the reference source profiles (Figure 9.1.6.3). However, analysis performed with log-transformed data shows that only **Road_traf_B2** is not correlated to any reference source profiles (Figure 9.1.6.4).

9.1.7 Secondary aerosols

Secondary aerosols factor/source was identified by 6 participants. No reference source profile is available for this source category. No secondary sources were identified in the original publication of the source apportionment study carried out on these data, (Lee et al., 2006).

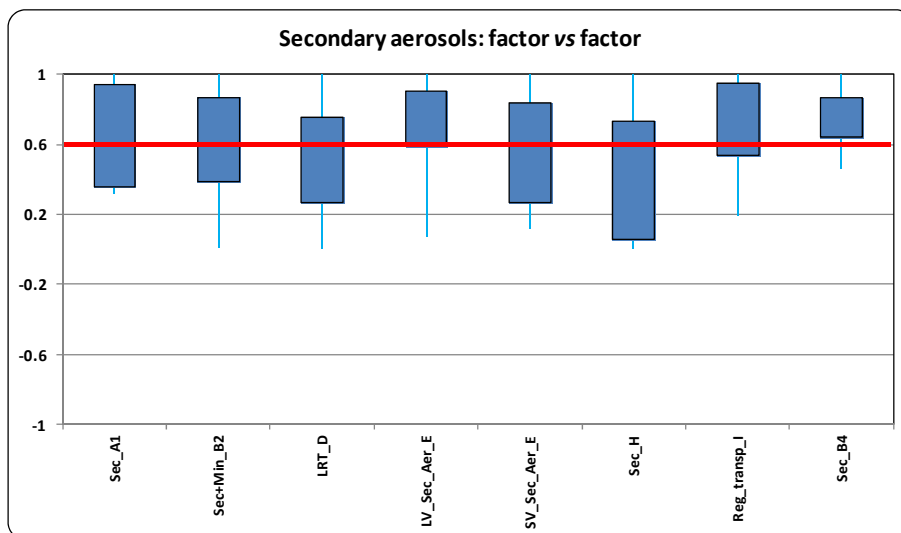


Figure 9.1.7.1: Correlation between Secondary aerosols factor/source profiles using raw data.

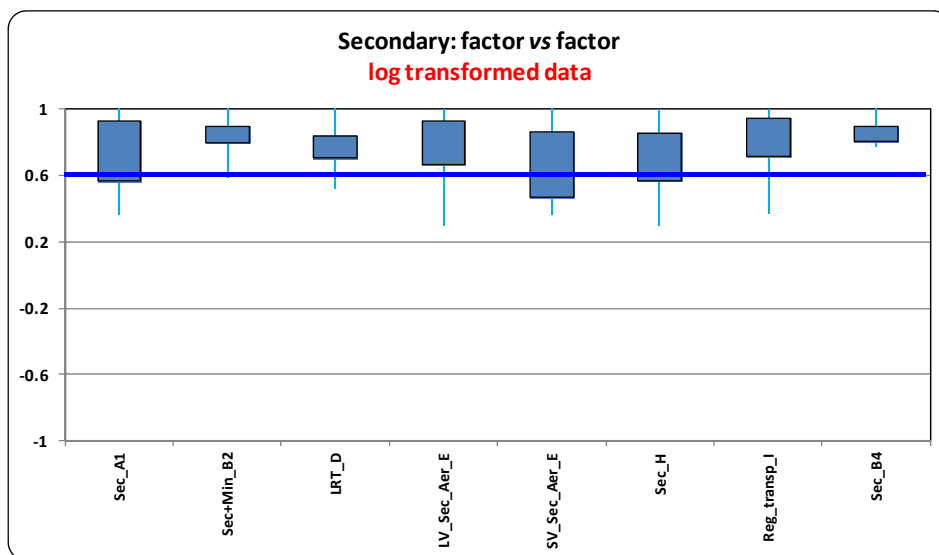


Figure 9.1.7.2: Correlation between Secondary aerosols factor/source profiles using log-transformed data.

Correlation analysis performed with raw data showed that **LRT_D** (long range transport), **SV_Sec_Aer_E** (semi volatile secondary aerosols) and **Sec_H** (secondary) were poorly correlated with the other factor/source profiles in the same category (Figure 9.1.7.1). On the other hand, correlation analysis performed with log-transformed data showed that all the

factor/source profiles identified by the participants are correlated between each other (Figure 9.1.7.2).

9.1.8 Sulphate

Sulphate factor/source was identified by 8 participants. **Sulfate_Lee** is the only “reference source profile” used to test this source category.

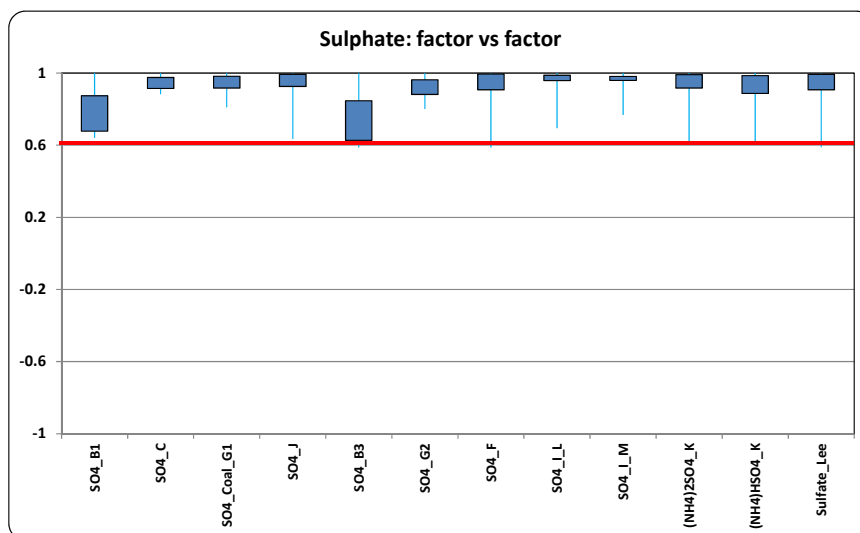


Figure 9.1.8.1: Correlation between Sulphate factor/source profiles using raw data.

Both correlations performed with raw and log-transformed data showed that all factor/sources profiles identified by the participants were correlated among each other and to the reference source profile **Sulfate_Lee** (Figures 9.1.8.1, 9.1.8.2, 9.1.8.3, and 9.1.8.4).

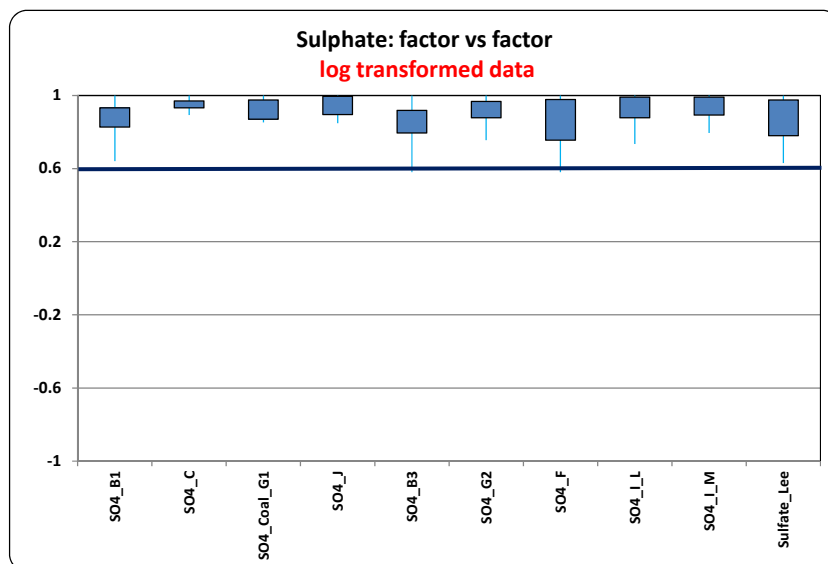


Figure 9.1.8.2: Correlation between Sulphate factor/source profiles using log-transformed data.

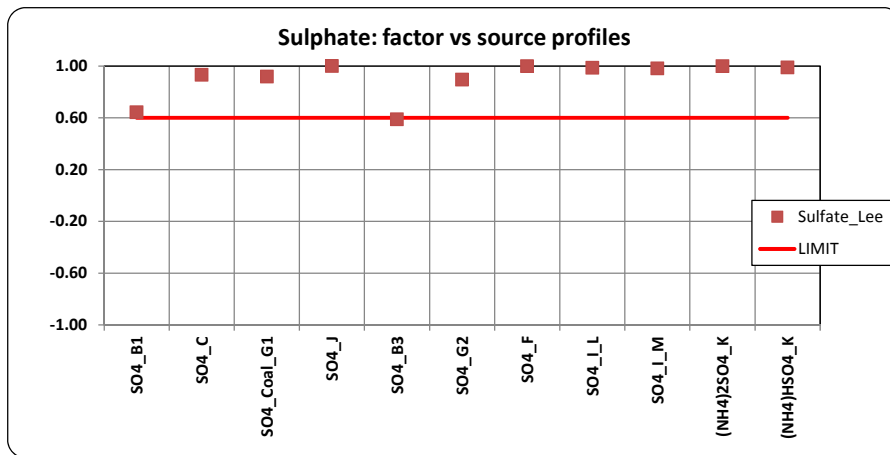


Figure 9.1.8.3: Correlation between Sulphate factor/source profiles and reference source profiles using raw data.

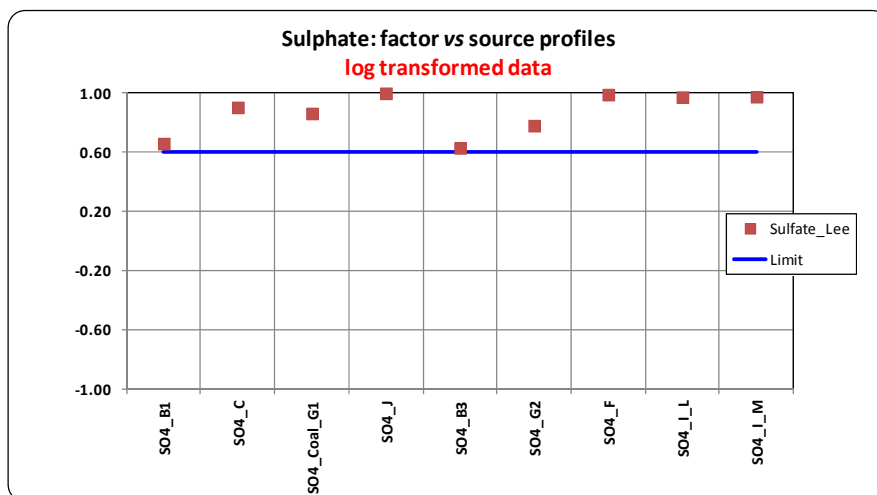


Figure 9.1.8.4: Correlation between Sulphate factor/source profiles and reference source profiles using log-transformed data.

9.1.9 Nitrate

Nitrate factor /source was identified by 8 participants. **Nitrate_Lee** was the only “reference source profile” used to test this factor/source.

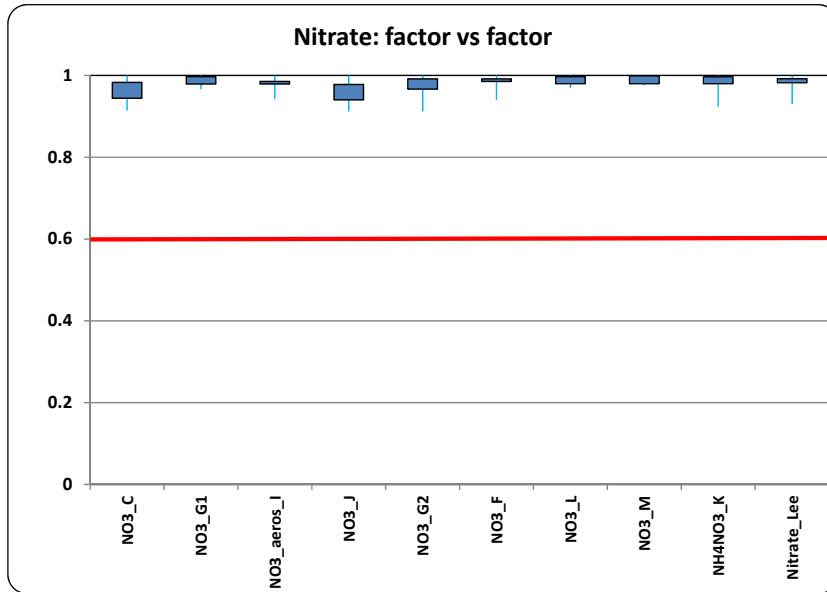


Figure 9.1.9.1: Correlation between Nitrate factor/source profiles using raw data.

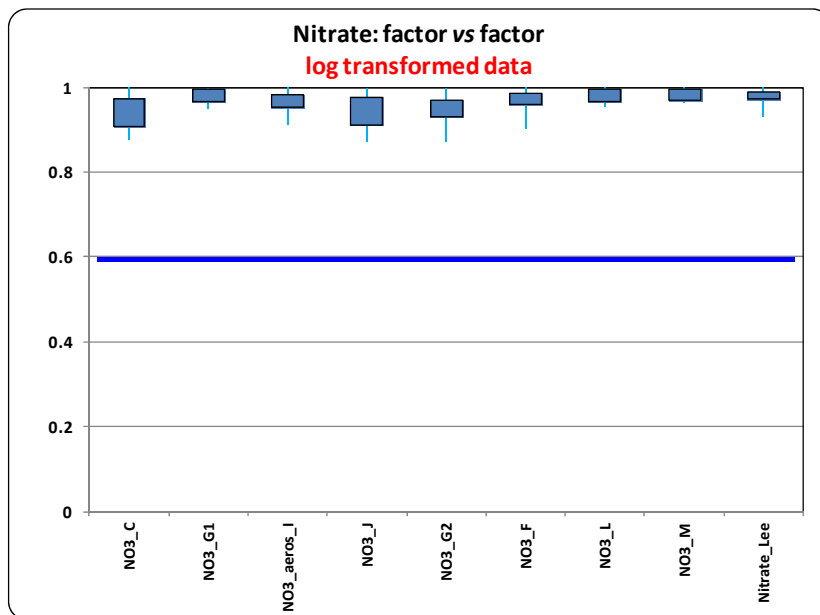


Figure 9.1.9.2: Correlation between Nitrate factor/source profiles using log-transformed data.

As for the Sulphate source category, both correlations performed with raw and log-transformed data showed that all factor/sources profiles identified by the participants are highly correlated among each other and with the reference source profile **Nitrate_Lee** (Figures 9.1.9.1, 9.1.9.2, 9.1.9.3, and 9.1.9.4).

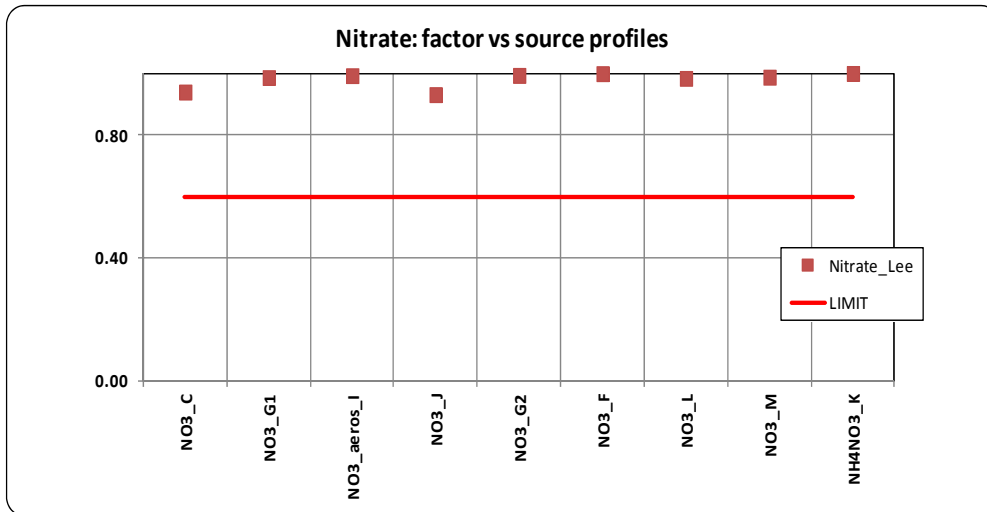


Figure 9.1.9.3: Correlation between Nitrate factor/source profiles and reference source profile using raw data.

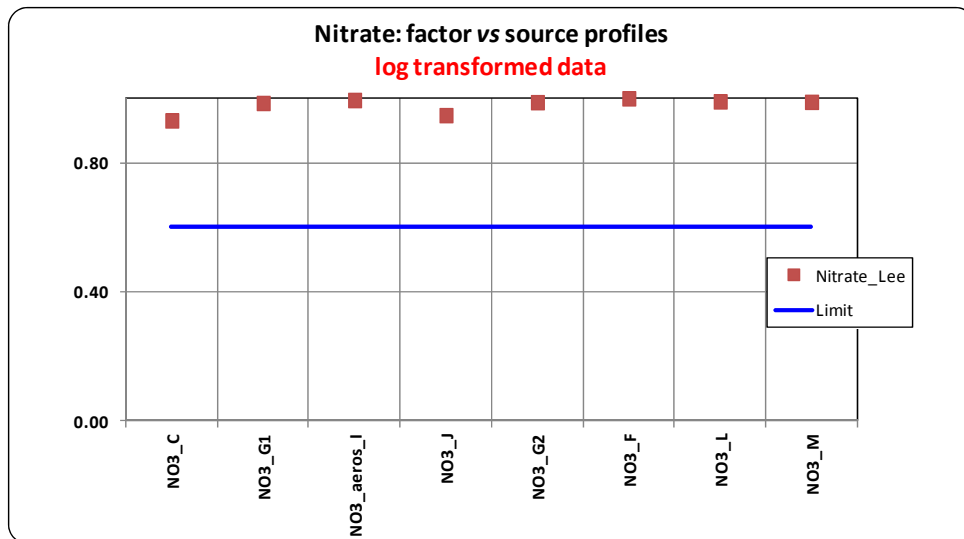


Figure 9.1.9.4: Correlation between Nitrate factor/source profiles and reference source profile using log-transformed data.

9.1.10 Zinc smelter

Zinc smelter factor/source was identified by 9 participants. **Zn Smelter_P** and **Zinc_Lee** were chosen as “reference source profiles”.

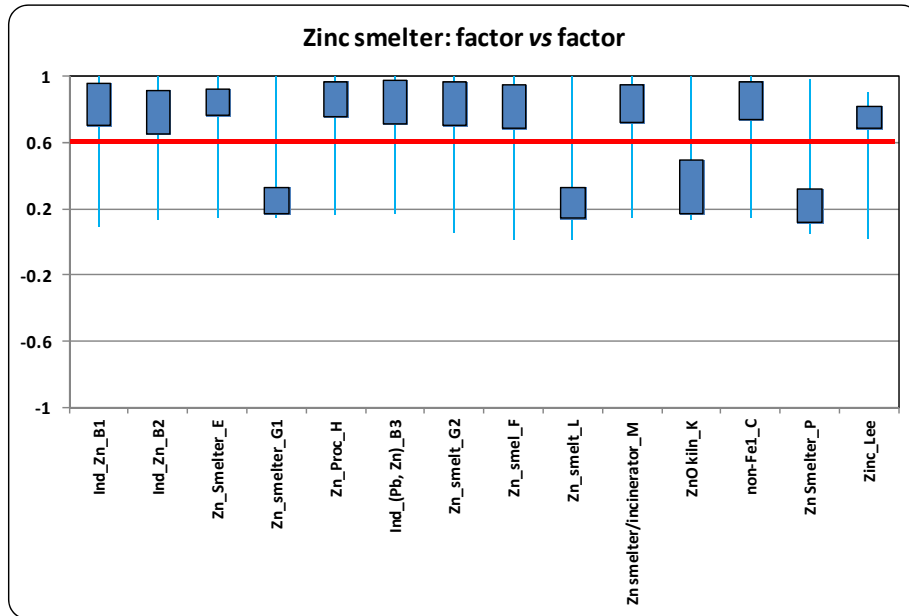


Figure 9.1.10.1: Correlation between Zinc smelter factor/source profiles using raw data.

Correlations with raw data show that factor profiles **Zn_smelter_G1**, **Zn_smelt_L** and **ZnO kiln_K** are poorly correlated with other factor/source profiles in the same category (Figure 9.1.10.1). Analysis performed with log-transformed data confirms that only **Zn_smelter_G1** and **Zn_smelt_L** are poorly correlated with other factor/source profiles (Figure 9.1.10.2)

With the exception of **Zn_smelt_L** (zinc smelter) and **ZnO kiln_K**, all factor/source profiles are correlated with the reference source profile **Zn_Smelter_P** (Figures 9.1.10.3 and 9.1.10.4).

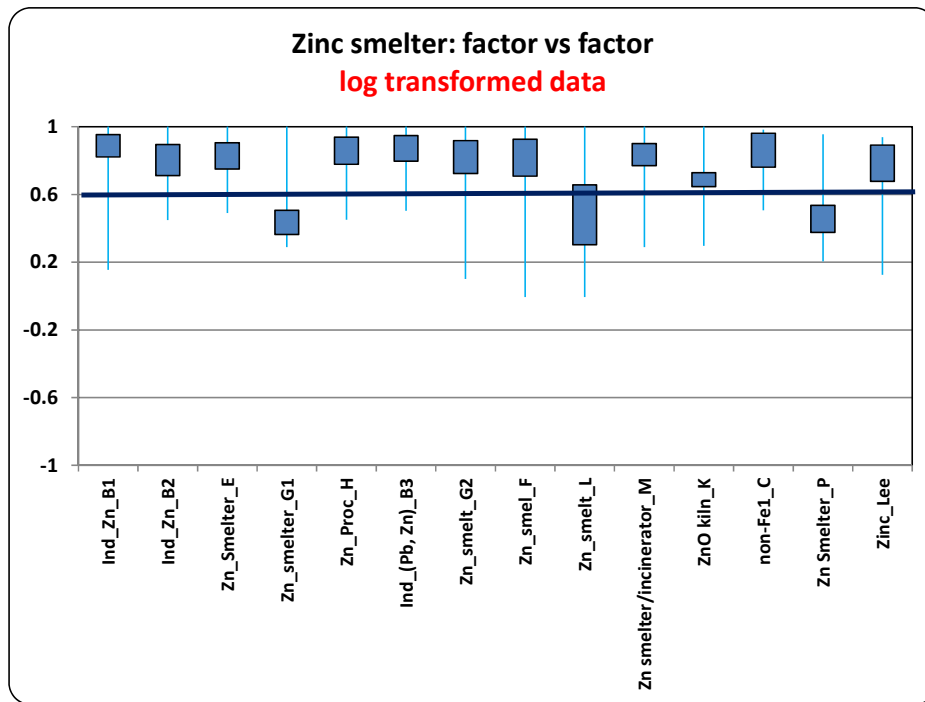


Figure 9.1.10.2: Correlation between Zinc smelter factor/source profiles using log-transformed data.

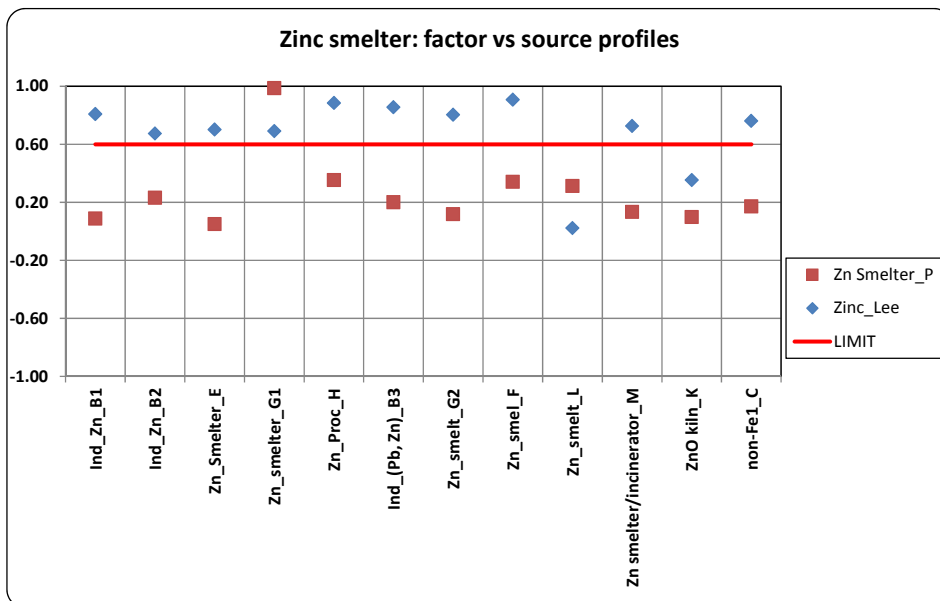


Figure 9.1.10.3: Correlation between Zinc smelter factor/source profiles and reference source profiles using raw data.

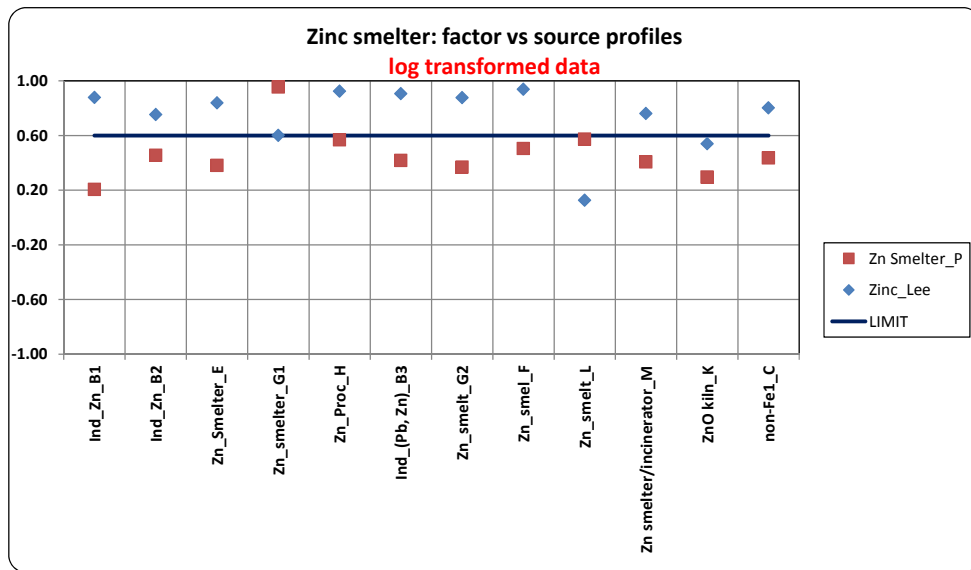


Figure 9.1.10.4: Correlation between Zinc smelter factor/source profiles and reference source profiles using log-transformed data.

9.1.11 Copper metallurgy

Copper metallurgy factor/source was identified by 11 participants. **Cu Metallurgy_P** and **Cu_Lee** were chosen as “reference source profiles”.

CuO kiln_K is the only factor profile that shows poor correlation with the other factor/sources in the same category. Correlation analyses with raw and log-transformed data shows a good agreement for the overall correlation between factor/source profiles (Figures 9.1.11.1 and 9.1.11.2).

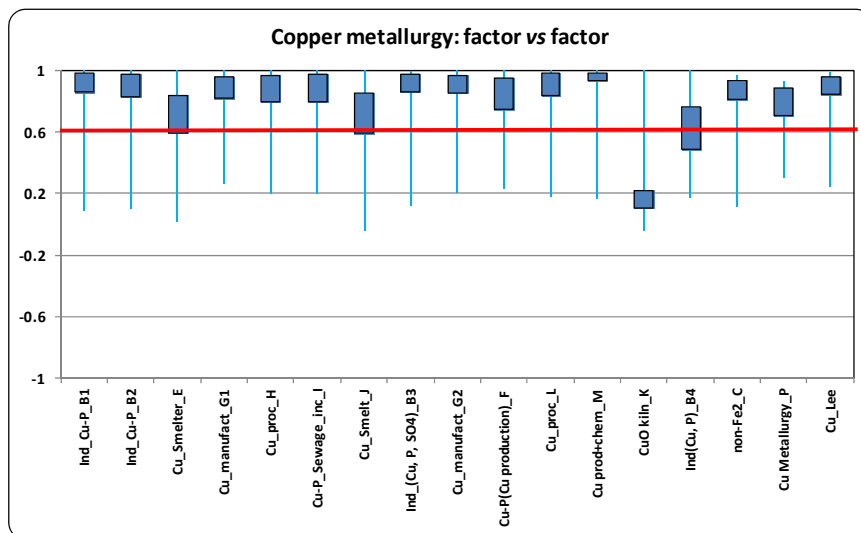


Figure 9.1.11.1: Correlation between Copper metallurgy factor/source profiles using raw data.

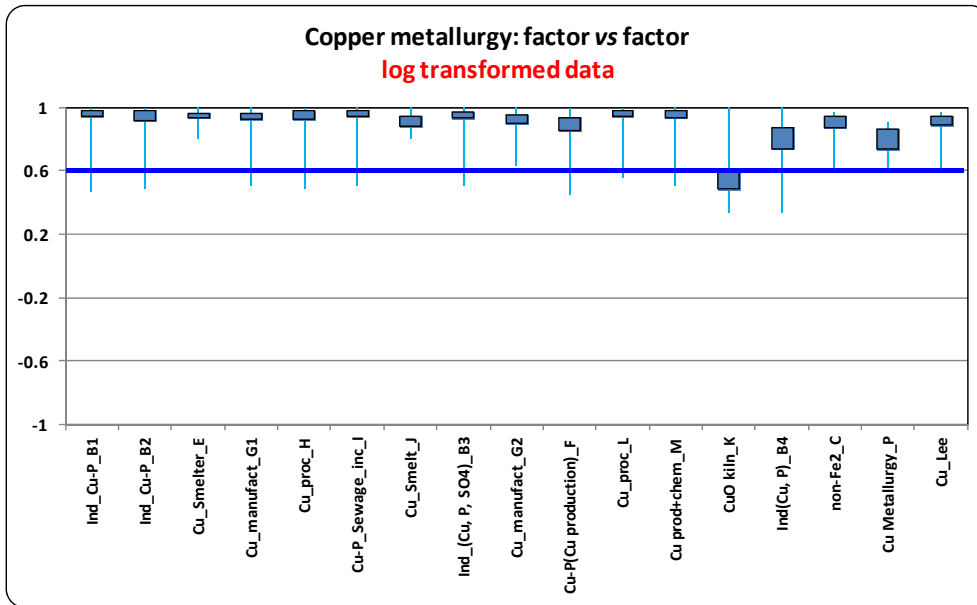


Figure 9.1.11.2: Correlation between Copper metallurgy factor/source profiles using log-transformed data.

Analysis of raw data shows that, with the exception of **CuO kiln_K**, all factor/source profiles are correlated with at least one reference source profile (Figure 9.1.11.3). Instead correlations performed with log-transformed data show that all factor/source profiles are in good correlation with reference source profiles (Figure 9.1.11.4).

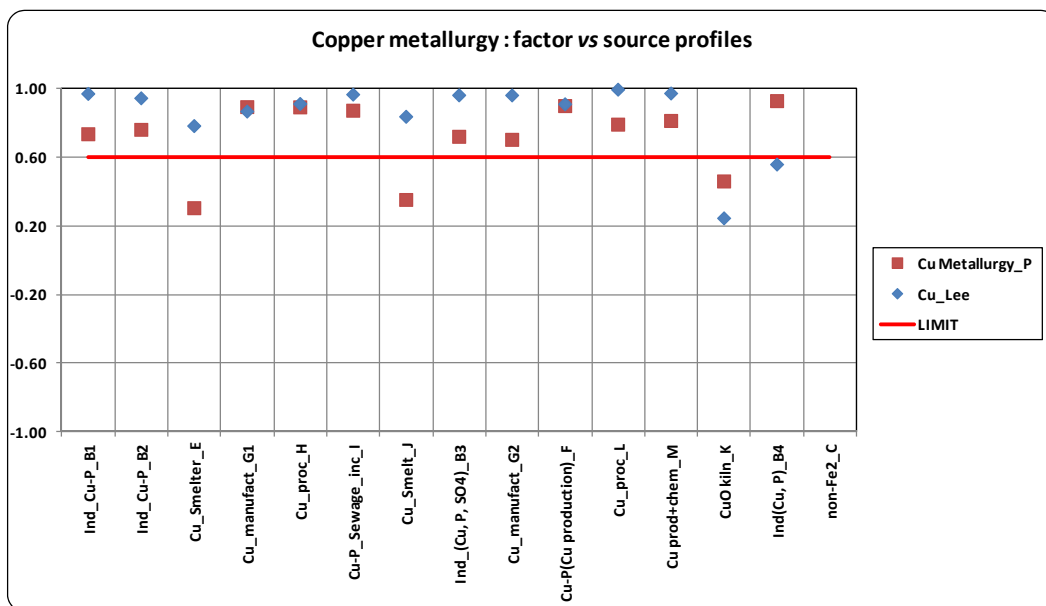


Figure 9.1.11.3: Correlation between Copper metallurgy factor/source profiles and reference source profiles using raw data.

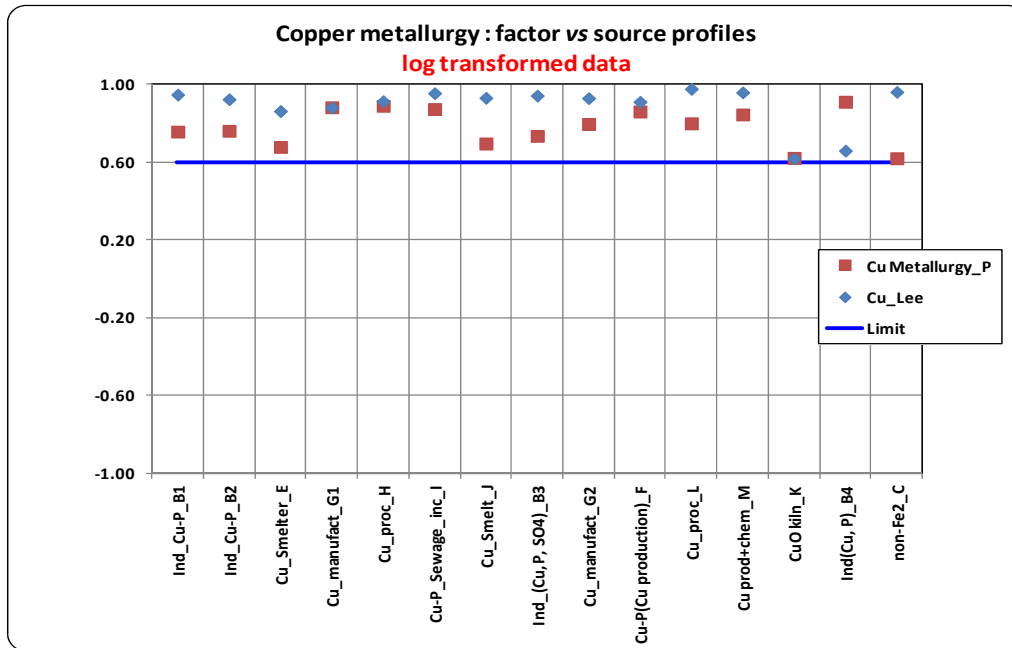


Figure 9.1.11.4: Correlation between Copper metallurgy factor/source profiles and reference source profiles using log-transformed data.

9.1.12 Lead metallurgy

Lead metallurgy factor/source was identified by 7 participants. **Pb Smelter_P**, **Pb_smelt_SPEC**, **Pb_product_comp_SPEC** (lead production composite), **Pb_process_comp_SPEC** (lead processing composite) and **Pb_Lee** were chosen as “reference source profiles”.

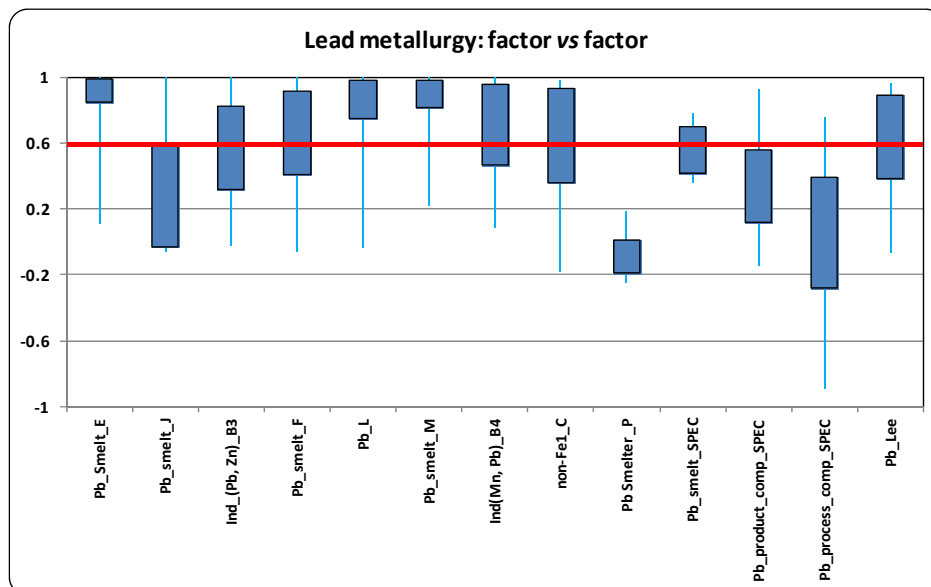


Figure 9.1.12.1: Correlation between Lead metallurgy factor/source profiles using raw data.

Correlation analysis with raw data showed that **Pb_smelt_J** and **Ind_(Pb, Zn)_B3** (Lead and Zinc from industry) were not correlated with other factor/source profiles of the same source

category identified by other participants (Figure 9.1.12.1). The same result was observed from analysis performed with log-transformed data (Figure 9.1.12.2).

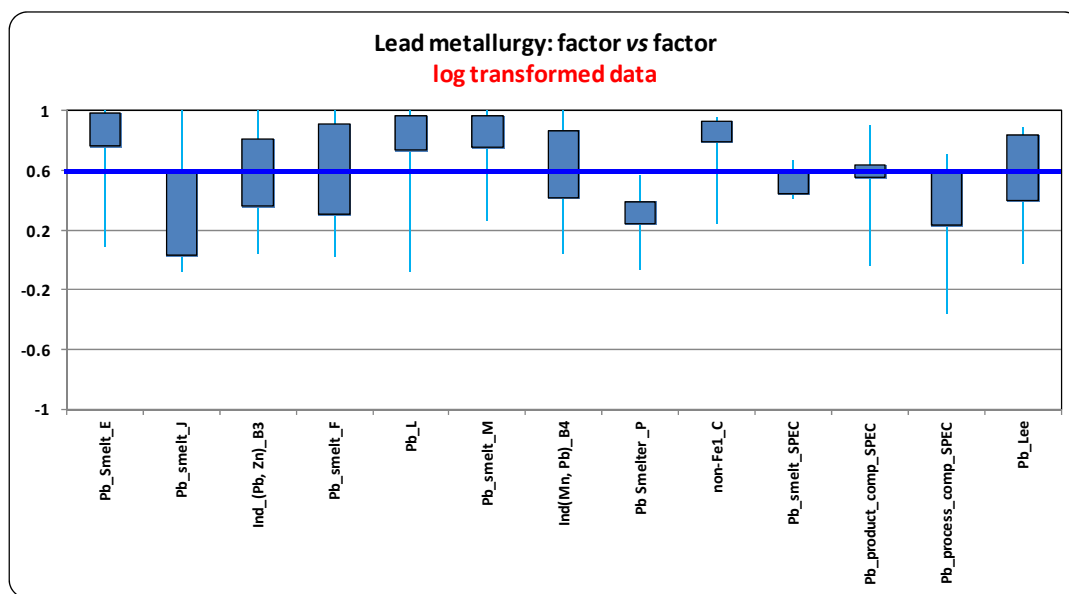


Figure 9.1.12.2: Correlation between Lead metallurgy factor/source profiles using log-transformed data.

In the correlation analysis of factor/source profiles with reference source profiles, it was decided to use only one source profile from the SPECIATE database (**Pb_smelt_SPEC**) because there was a high collinearity between the three available source profiles.

As shown in Figure 9.1.12.3, no factor/source profile is correlated with the reference source profile **Pb_Smelter_P**. However, from the overall evaluation of the correlation with raw and log-transformed data it is observed that all factor/source profiles are correlated to at least one reference profiles (Figure 9.1.12.3, Figure 9.1.12.4).

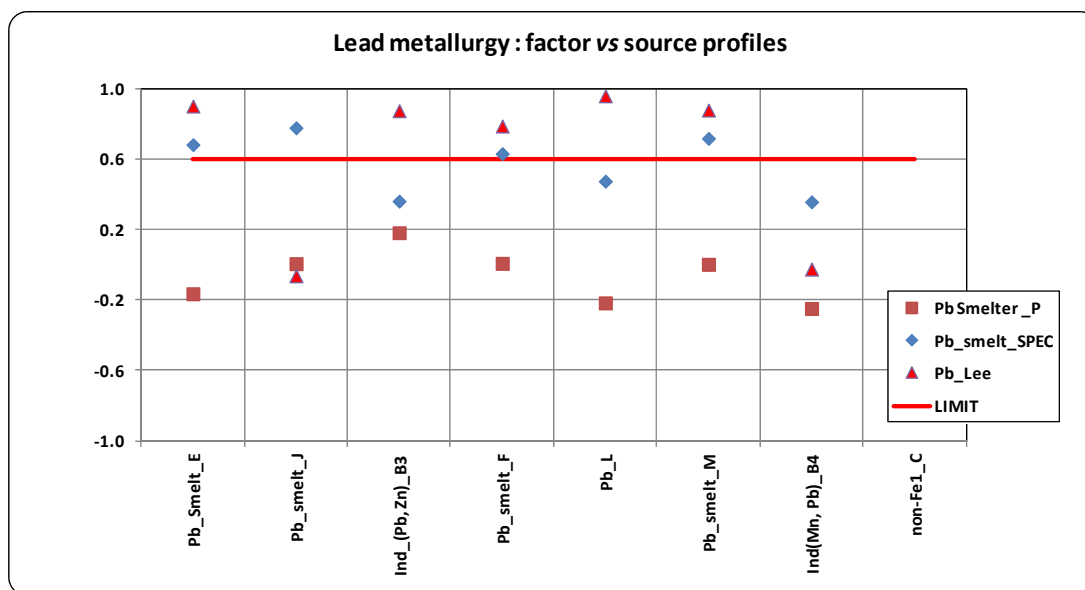


Figure 9.1.12.3: Correlation between relative factor/source profiles and reference source profiles of Lead metallurgy using raw data.

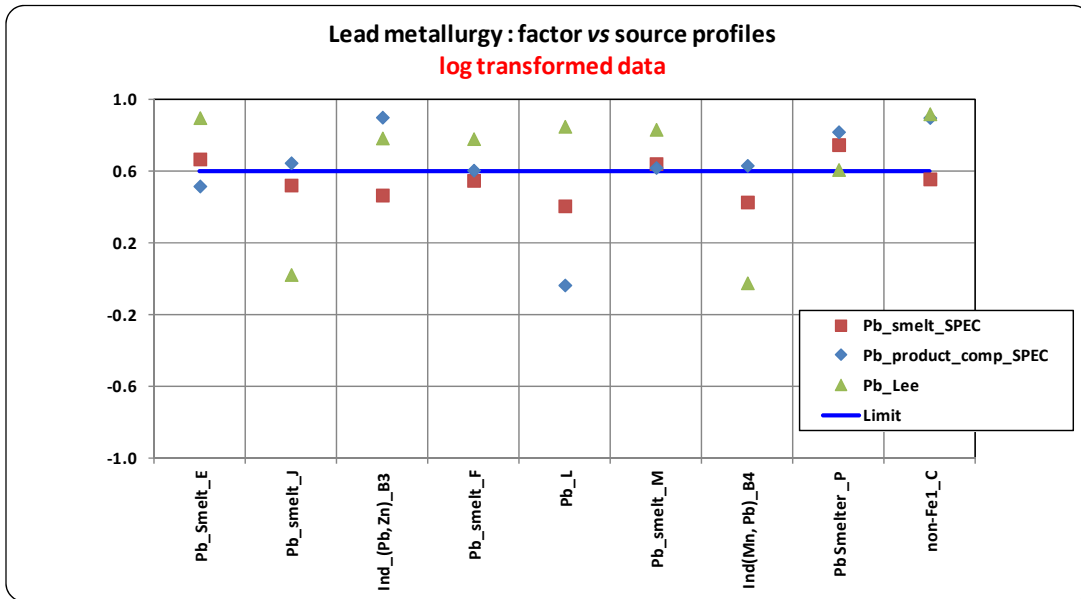


Figure 9.1.12.4: Correlation between Lead metallurgy factor/source profiles and reference source profiles using log-transformed data.

9.1.13 Steel processing

Steel processing factor/source was identified by 8 participants. **Iron_Lo**, **Steel_prod_SPEC** (steel production) and **Steel_Lee** were chosen as “reference source profiles”.

Correlation analysis performed with raw data shows that **Steel_Proc_J** (steel processing) is poorly correlated with other factor/source profiles of the same category (Figure 9.1.13.1). On the other hand, analysis with log-transformed data indicated that all factor/sources are correlated among each other (Figure 9.1.13.2).

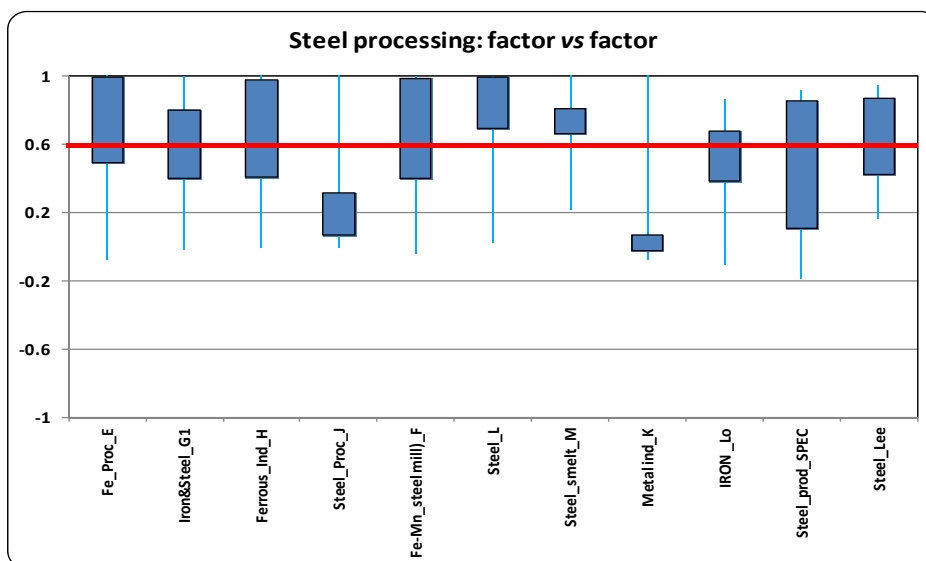


Figure 9.1.13.1: Correlation between Steel processing factor/source profiles using raw data.

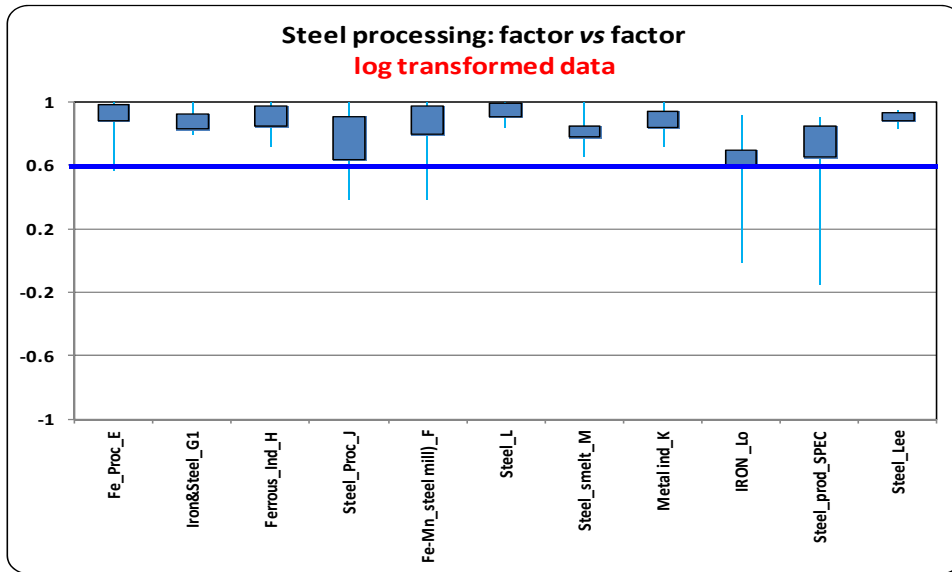


Figure 9.1.13.2: Correlation between Steel processing factor/source profiles using log-transformed data.

Analysis with raw data showed that, except **Steel_Proc_J**, all factor/source profiles are correlated with at least the one reference source profile (Figure 9.1.13.3). On the other hand, correlations performed with log-transformed data show that all factor/source profiles are correlated with at least one reference source profile (Figure 9.1.13.4).

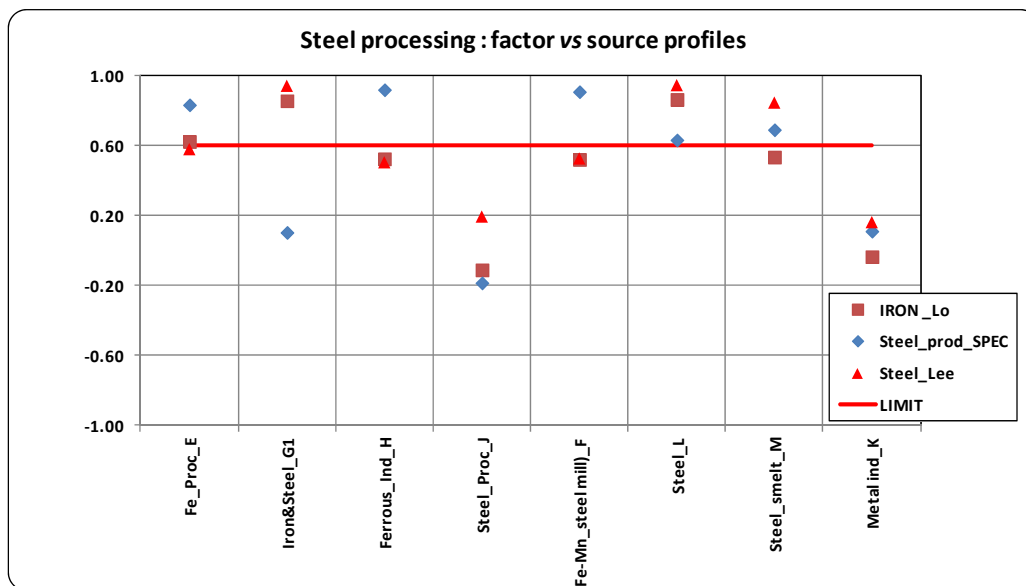


Figure 9.1.13.3: Correlation between Steel processing factor/source profiles and reference source profiles using raw data.

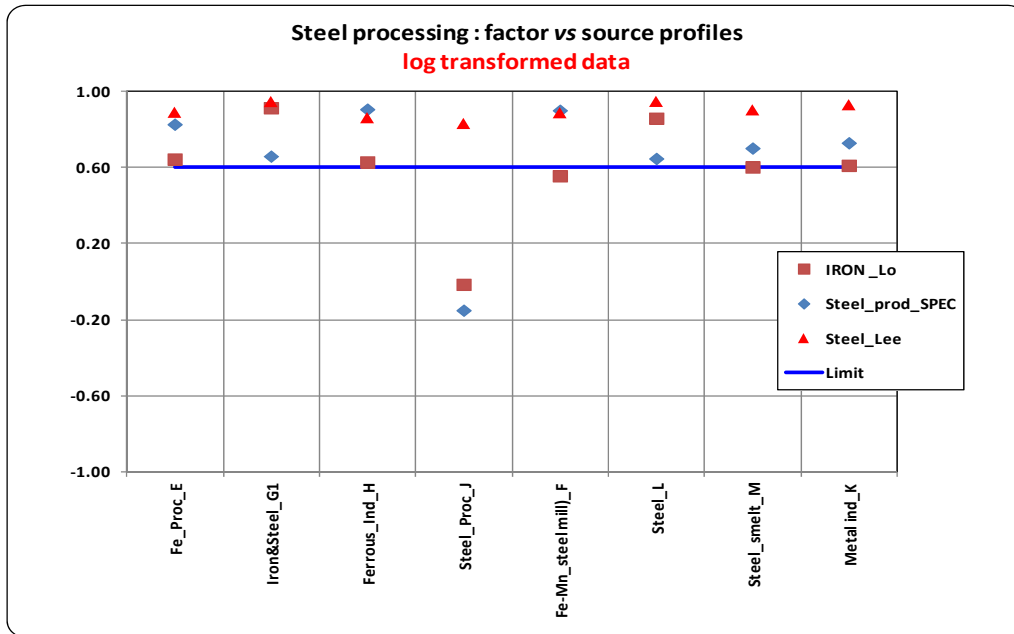


Figure 9.1.13.4: Correlation between Steel processing factor/source profiles and reference source profiles using log-transformed data.

9.1.14 Industry-combustion

Industry-combustion factor/source was identified by all participants. Since this is a heterogeneous source category many “reference source profiles” were selected: **Fuel_Lo**, **Coal_Lo**, **Cement_Comp_SPEC**, **Cement_SPEC**, **Oil_Power_SPEC** (Oil combustion from power plant) and **C-rich sulphate_Lee** (carbon rich sulphate).

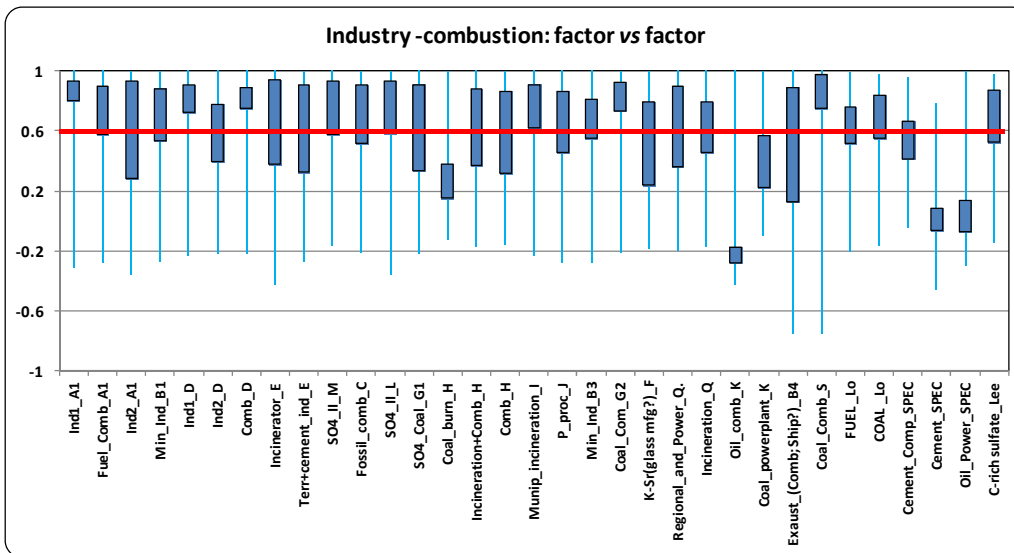


Figure 9.1.14.1: Correlation between Industry-combustion factor/source profiles using raw data.

Correlation performed between raw data of factor/source profiles assigned to **Industry-combustion** show that factor/sources **Coal_burn_H**, **K-Sr(glass mfg?)_F**, **Oil_comb_K**, **Coal_powerplant_K**, **Exhaust_(Comb; Ship?)_B4** and **Coal_Comb_S** are not correlated with the majority of the factor/sources in this category (Figure 9.1.14.1). On the other hand,

correlation performed with log-transformed data shows that only **Oil_comb_K** and **Coal_powerplant_K** are not correlated with the other factor/source profiles.

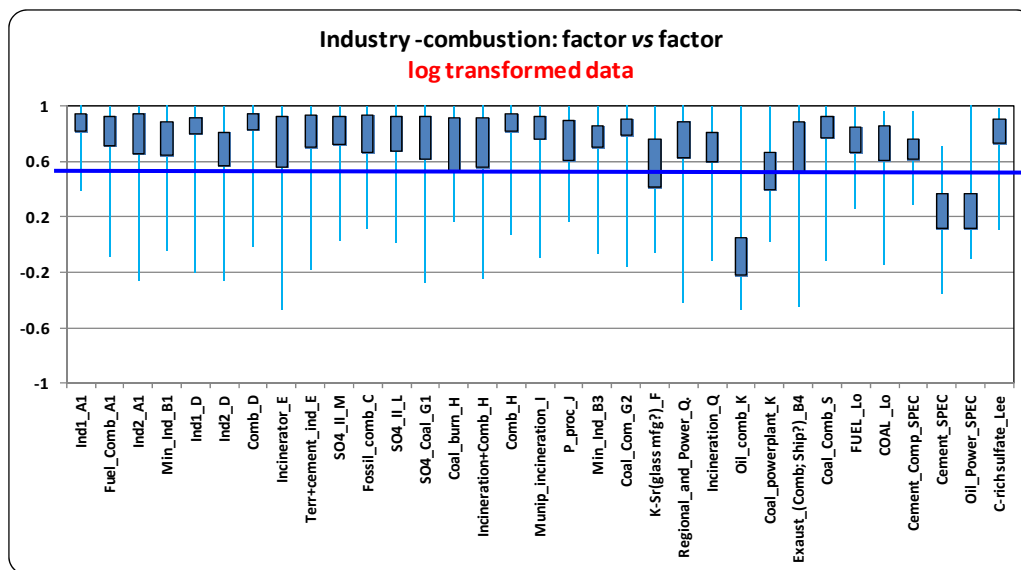


Figure 9.1.14.2: Correlation between Industry-combustion factor/source profiles using logarithmic data.

To cope with heterogeneity of this source category, a range of reference source profiles from different industrial and combustion sources were used to test the profiles reported by participants. Many factor/source profiles are correlated with the reference source profiles **FUEL_Lo**, **COAL_Lo** and with **C-rich sulphate_Lee**.

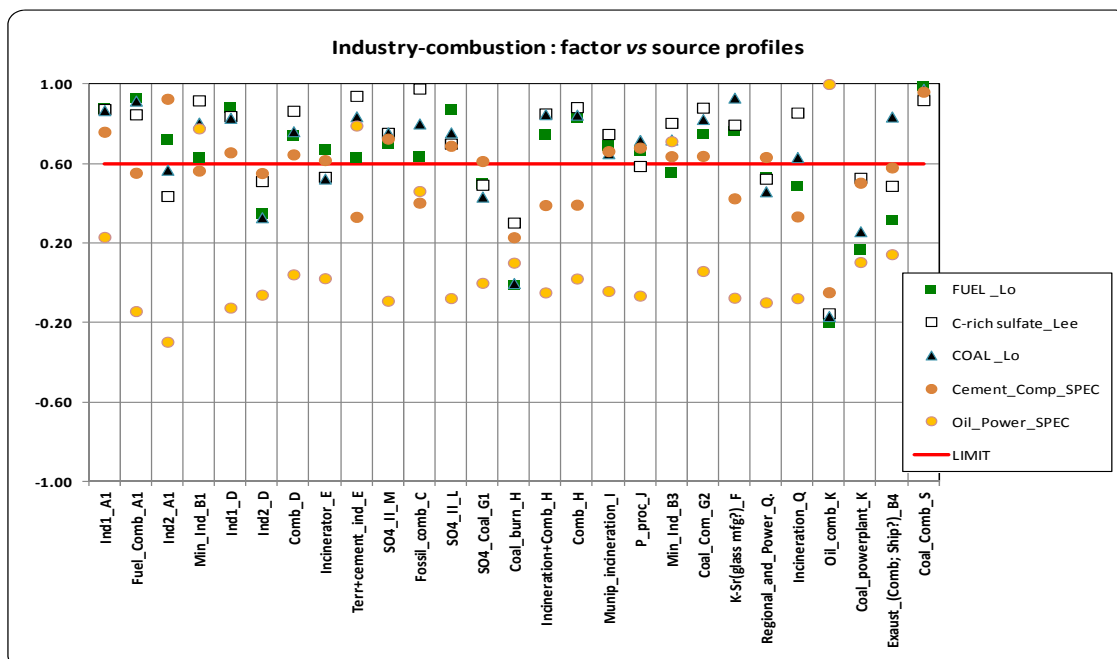


Figure 9.1.14.3: Correlation between Industry-combustion factor/source profiles and reference source profiles using raw data.

As shown in Figure 9.1.14.3, **Coal_burn_H** (coal burning) and **ind2_D** show poor correlations with all reference source profiles. Although **Oil_Comb_K** factor profile is poorly correlated with

the majority of the reference source profiles it is highly correlated with **Oil_Power_SPEC** (oil combustion from power plant). Correlations with log-transformed data confirm that all factor/source profiles are correlated with more than one reference source profile. However, also in this analysis, the reference source profile **Oil_Power_SPEC** is poorly correlated with most of the factor/source profiles (Figure 9.1.14.4).

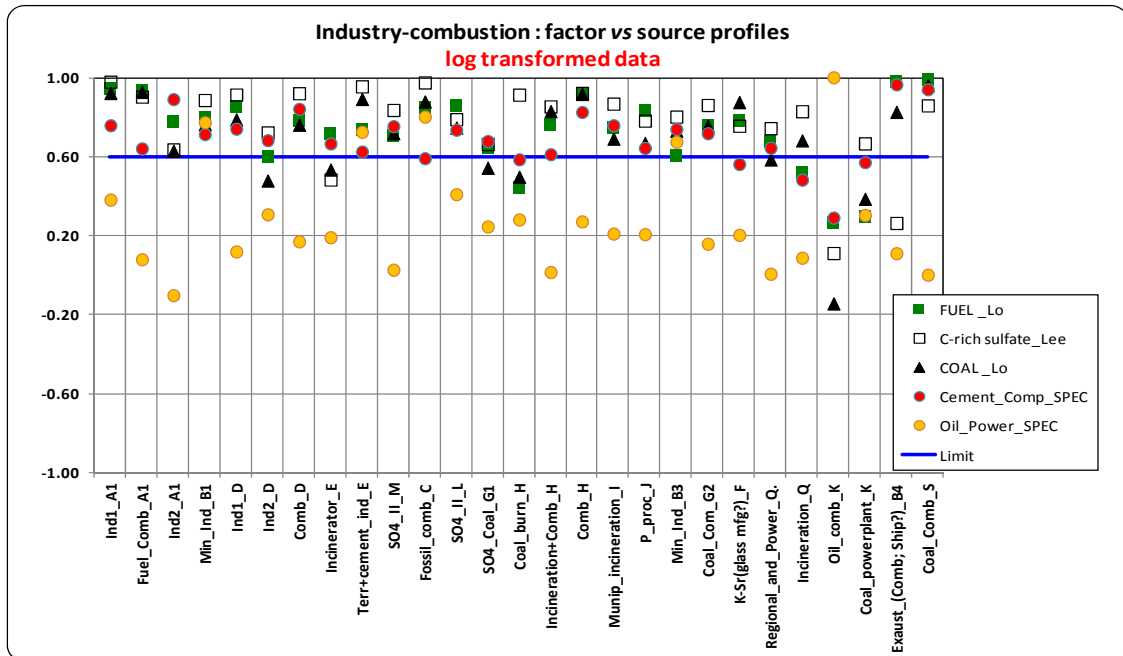


Figure 9.1.14.4: Correlation between Industry-combustion factor/source profiles and reference source profiles using log-transformed data.

9.1.15 Ship emission

Eight factor/source showing affinities with Ship emissions were identified by 6 participants. **MARVES1_NP** (marine vessel), **Fuel_Lo** and **C-rich sulfate_Lee** (carbon rich sulphate) were chosen as “reference source profiles”.

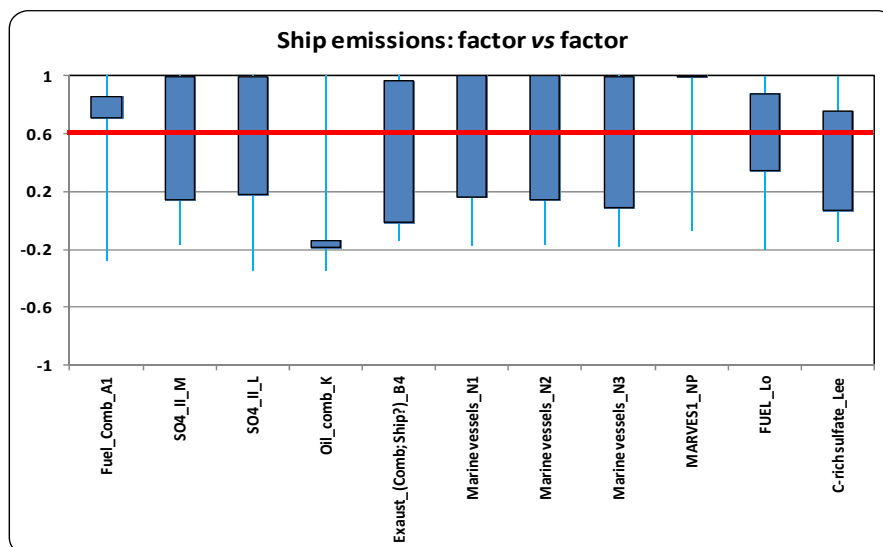


Figure 9.1.15.1: Correlation between Ship emissions factor/source profiles using raw data.

Analysis carried out with raw data show poor correlations among all factor/source profiles (Figure 9.1.15.1). This suggests that some of the profiles do not belong to this category. On the other hand, in the analysis carried out with log-transformed data, only **Oil_Comb_K** show poor correlation with the other factor/source profiles of the same category (Figure 9.1.15.2).

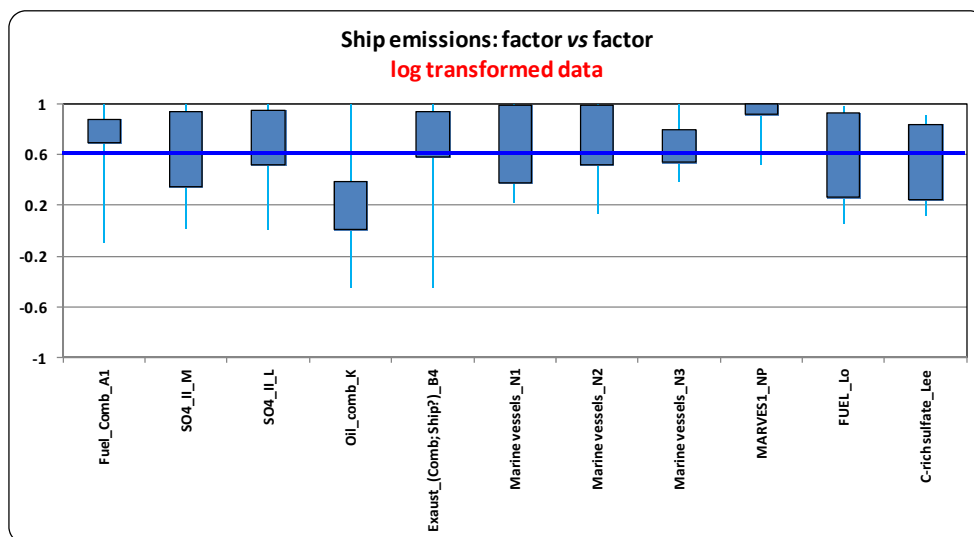


Figure 9.1.15.2: Correlation between Ship emissions factor/source profiles using log-transformed data.

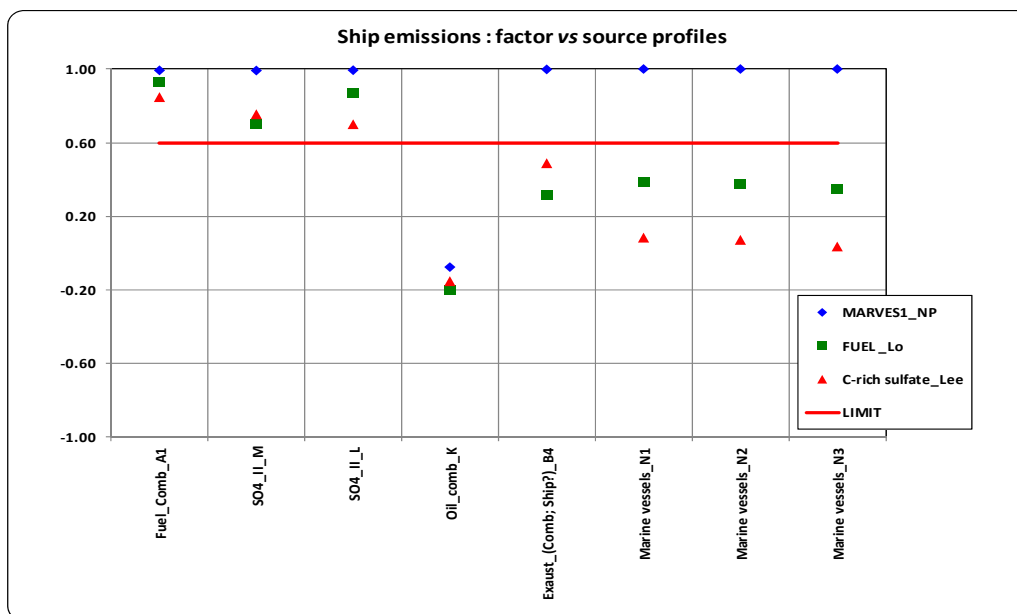


Figure 9.1.15.3: Correlation between Ship emission factor/source profiles and reference source profiles using raw data.

Only four factor/source profiles show good correlation with the reference source profile **MARVES1_NP** and poor correlation with the others reference source profiles.

The other factor/source profiles are either correlated with all the reference source profiles or with none of them (e.g. **Oil_comb_K**) (Figure 9.1.15.3). A similar picture emerges from the analysis using log-transformed data (Figure 9.1.15.4).

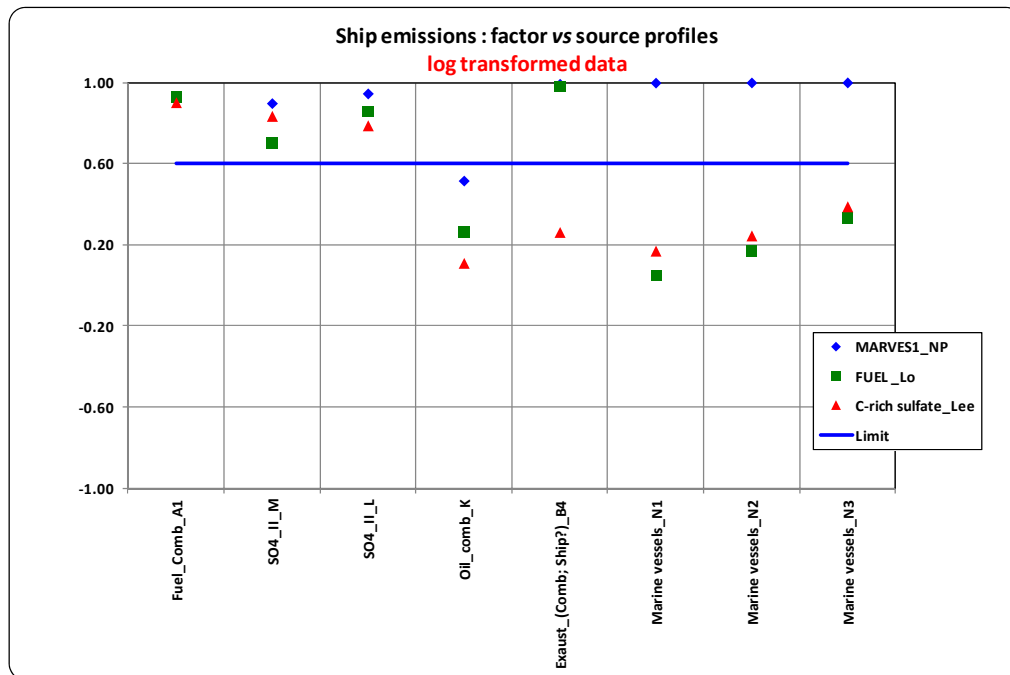


Figure 9.1.15.4: Correlation between Ship emission factor/source profiles and reference source profiles using log-transformed data.

9.2 Preliminary test II: Weighted difference analysis of factor/source profiles

One of the most important features of receptor models is the possibility to estimate the uncertainty of the output profiles. In this exercise participants reported the uncertainties for each species composing factor/source profiles. This information is used in the weighted difference index to weight the difference between two factor/source profiles with their uncertainties. The weighted difference (WD) is defined as the average differences between factor profiles weighted on the sum of their uncertainties (Karagulian & Belis, 2012). As for the Pearson correlation, WD was calculated for all possible pairs of factor profiles.

9.2.1 Biomass Burning

Boxes & whiskers in figure 9.2.1.1 represent the minimum, maximum, 25th and 75th percentile of the summary results of the weighted differences. Weighted differences calculated for factors/sources in the Biomass Burning source category show that solutions obtained with the model EPA PMF 3.0 are those with the lowest WD indexes that fall within the area of acceptability (≤ 2).

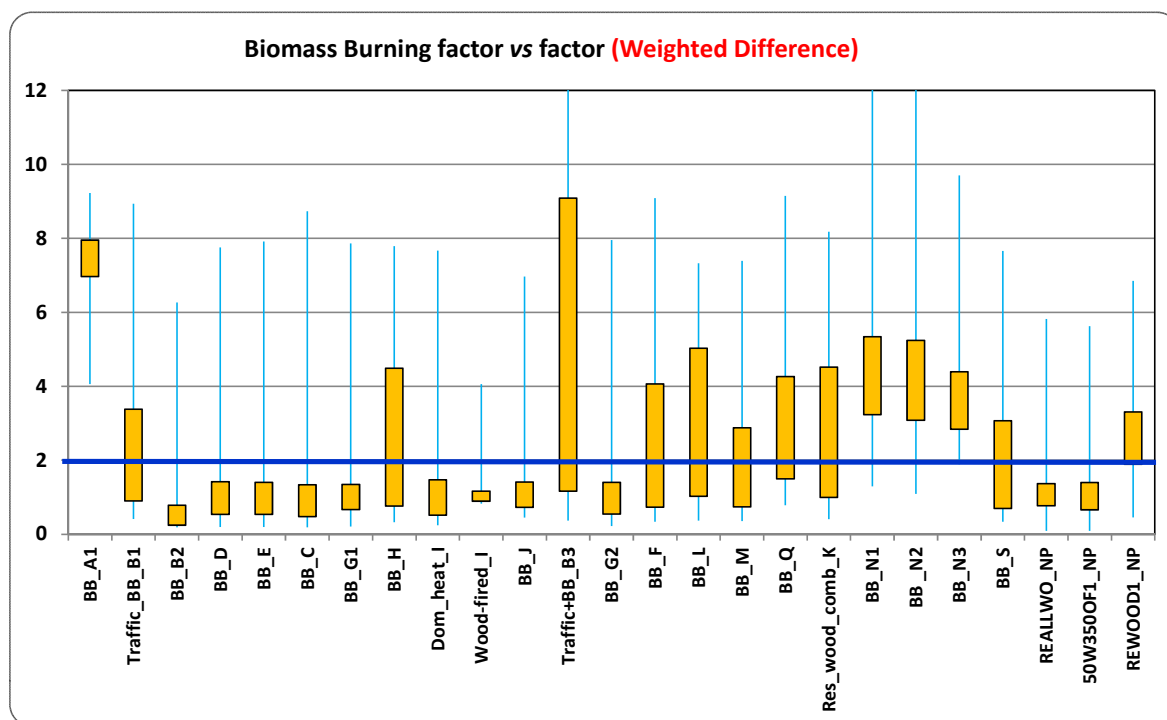


Figure 9.2.1.1: Weighted difference (WD) between factor/source profiles of Biomass Burning emissions.

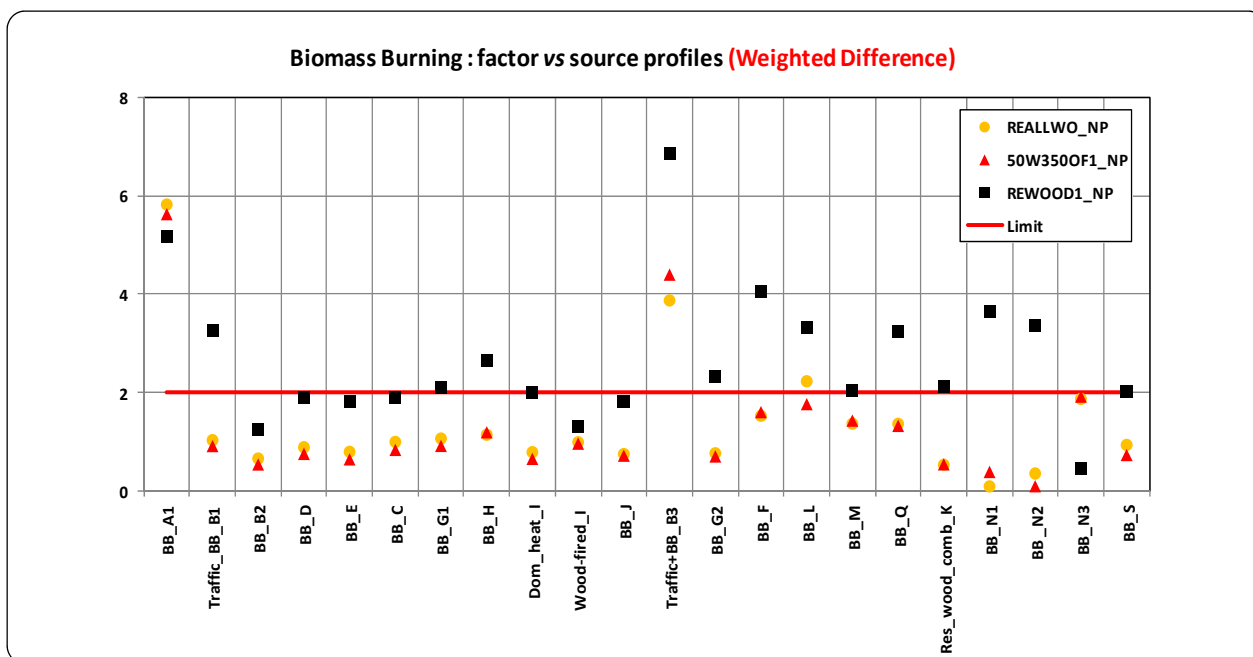


Figure 9.2.1.2: Weighted difference between factor/source profiles of Biomass Burning and reference source profiles.

WD calculated for **BB_A1** and **Traffic+BB+B3** are outside the acceptability area indicating that the distance between these two factors/sources and the reference source profiles is much higher than their uncertainties (Figure 9.2.1.2). These test results indicate that either the estimated uncertainties are too small or these factors/sources are not associated with the reference sources. **BB_A1** correlation analysis on raw data is negative (section 9.1). Under the light of the negative WD result we conclude that this factor does not belong to the Source category Biomass Burning. If we also consider that the Pearson obtained using log-transformed data (P_{log}) passed the test, this may indicate the influence of a single or few species with high mass contribution in the **BB_A1** profile. After an exam of the **BB_A1** profile emerged that the reject is due to the anomalous high contribution of only one species (nitrates). The other problematic profile **Traffic+BB+B3** passed the Pearson test on raw data (P_{raw}) and the P_{log} tests but fails the WD test. We conclude that the profile probably belongs to this category but the uncertainty of the profile is likely underestimated.

9.2.2 Gasoline

Almost half of the Gasoline factors/sources are not comparable among each other in the WD analysis. **Gasoline_L**, **Gasoline_M**, **Traf_gasoline_Q**, **PAHs_B3** and **Gasoline_P** are not within the limit of acceptability (Figure 9.2.2.1). In addition, WD calculated for **Gasoline_M**, **Traf_gasoline_Q** and **PAHs_B3** are also not comparable with the reference source profiles (Figure 9.2.2.2). Since the correlation analysis for all these profiles gives positive results (section 9.1) we conclude that the negative performance in the WD test is likely associated to the underestimation of their uncertainties.

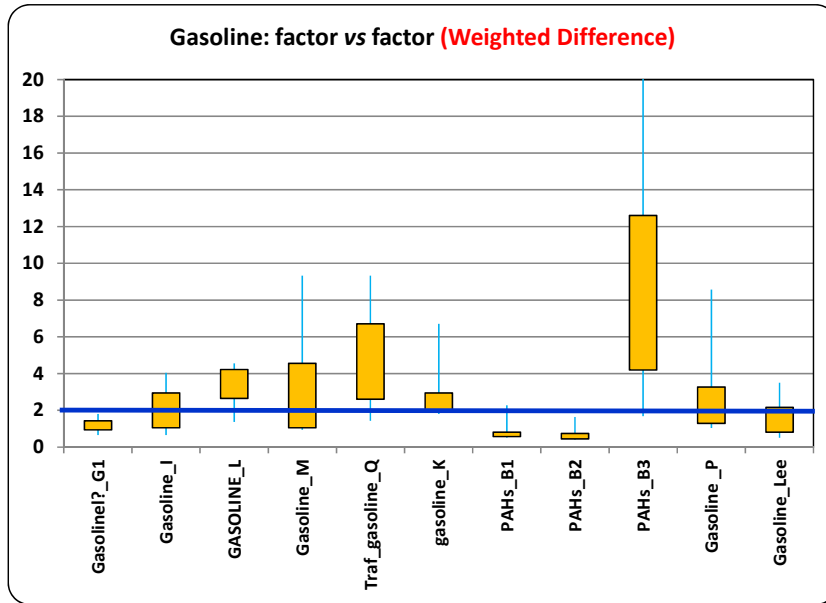


Figure 9.2.2.1: Weighted difference (WD) between factor/source profiles of Gasoline.

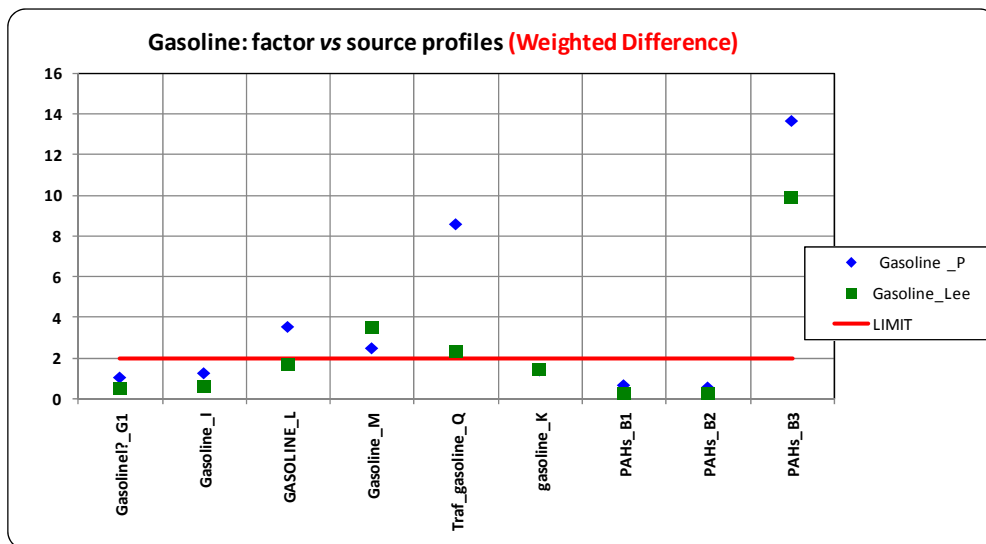


Figure 9.2.2.2: Weighted difference between factor/source profiles of Gasoline and reference source profiles.

9.2.3 Diesel

Diesel/Lightoil?_G2, diesel/ind_Ca_rich_F, DIESEL_L, Mn-rich/heavy_duty diesel_M, Traf_diesel_Q and diesel_K are beyond the limit of acceptability (Figure 9.2.3.1) and therefore they are not comparable with the other factor/sources in the WD analysis. The WD calculated for Mn-rich/heavy_duty diesel_M, and Traf_diesel_Q are not comparable with any WD of the reference source profiles (Figure 9.2.3.2). Considering that Mn-rich/heavy_duty diesel_M, and Traf_diesel_Q show positive results in the P_{raw} and P_{log} tests, these results indicate that the uncertainty was probably underestimated. On the other hand, Diesel_C that shows negative results in the P_{raw} and P_{log} tests but passes the WD test probably has an overestimated uncertainty.

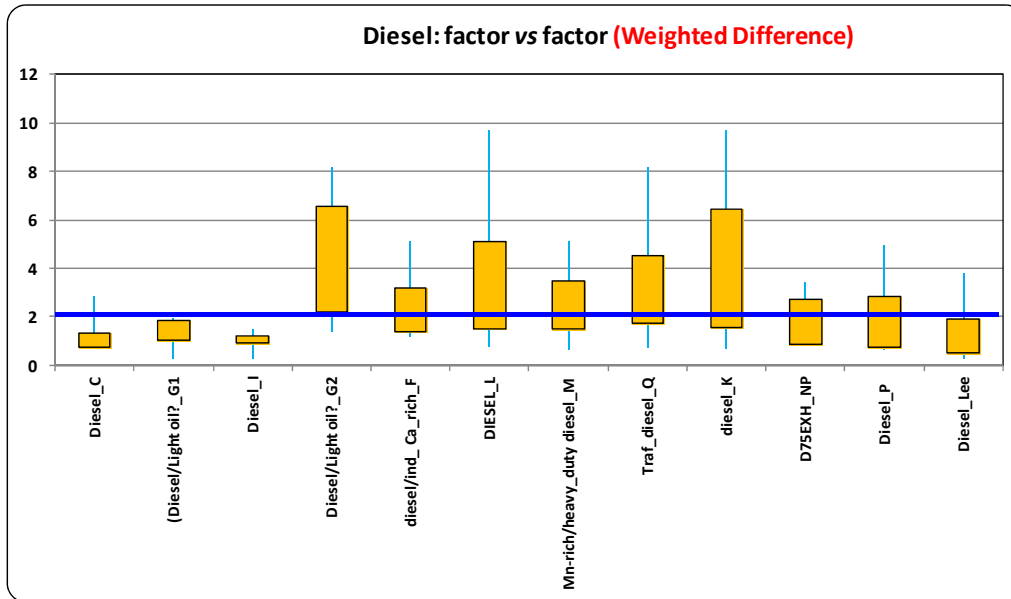


Figure 9.2.3.1: Weighted difference (WD) between factor/source profiles of Diesel.

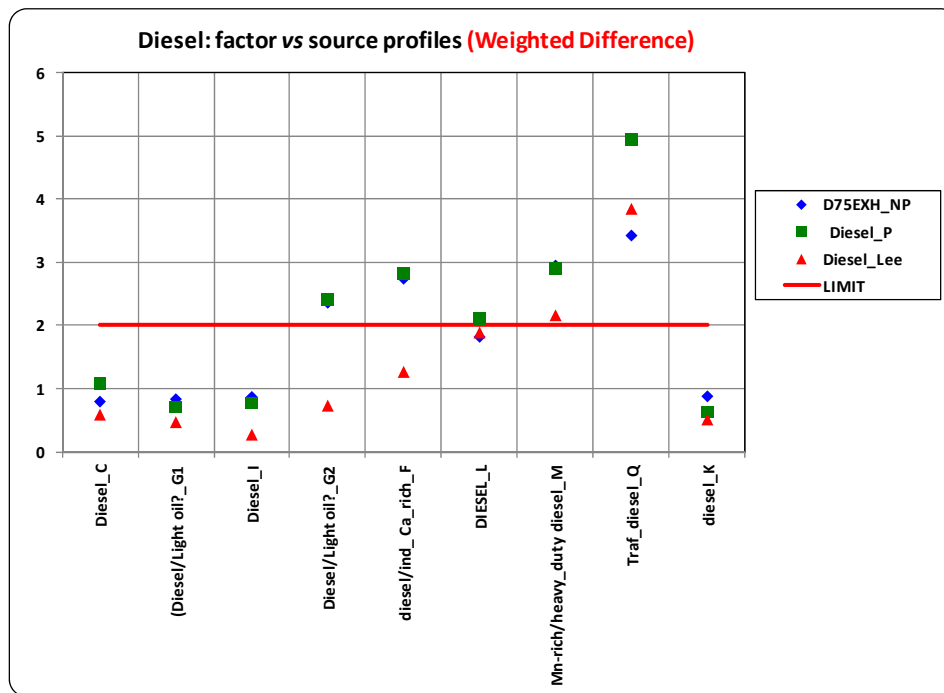


Figure 9.2.3.2: Weighted difference between factor/source profiles of Diesel and reference source profiles.

9.2.4 Brakes

One of the limitations of the analysis in this source category is the reduced number of profiles.

WD analysis shows that no Brakes factor/source profile was within the range of acceptability (Figure 9.2.4.1). Only the WD calculated for **Brake_I**, **Traff_brake_N3** and **RD_I** comply with the WD criteria calculated for the reference source profile (Figure 9.2.4.2).

RD/Brake1_A1, **RD/Brake2_A1** and **RD_Brake3_A1** failed or partially failed the P_{raw} and P_{log} tests, therefore, they may represent mixed factor/sources.

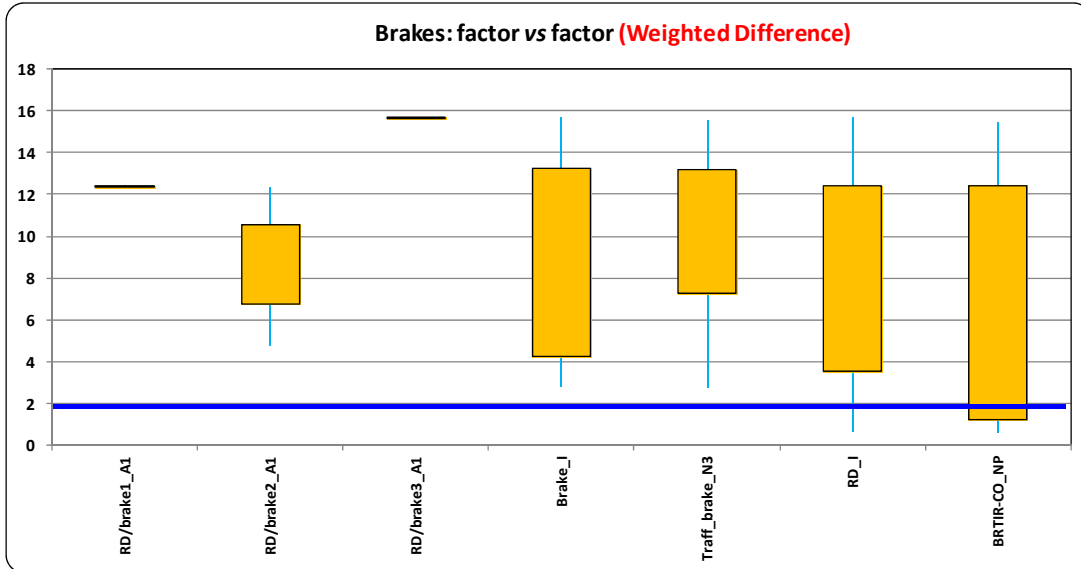


Figure 9.2.4.1: Weighted difference (WD) between factor/source profiles of Brakes.

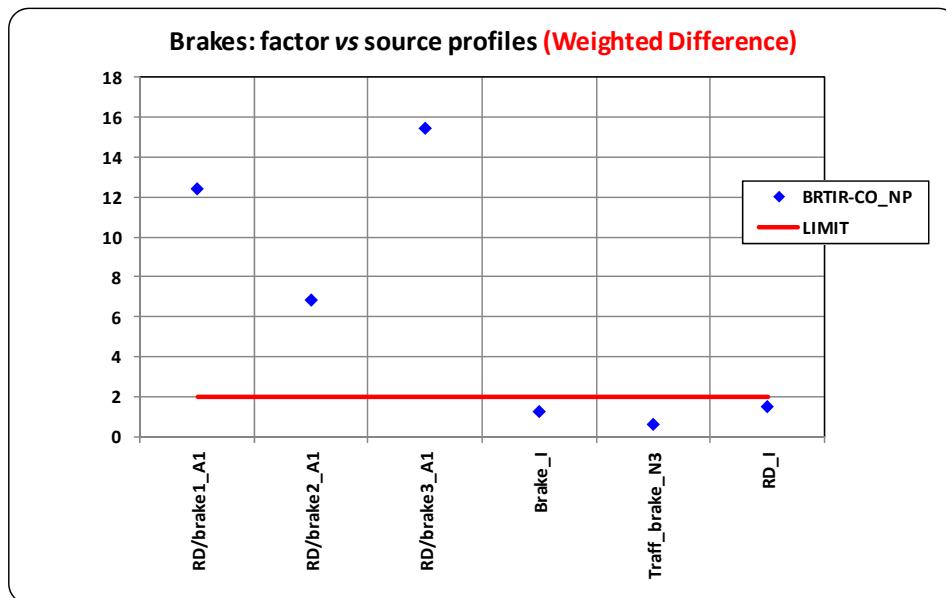


Figure 9.2.4.2: Weighted difference between factor/source profiles of Brakes and reference source profiles.

9.2.5 Traffic

Very few Traffic factor profiles fall within the limit of acceptability for the WD (**Road_Traf_B2**, **Traffic_D**, **Mobil_E** and **REVEHI_NP**) (Figure 9.2.5.1). The WD

calculated for **Veh_ex2_A1**, **Traffic+BB_B3** and **Traffic_exhaust_N3** with the reference source profiles do not comply with the test criteria (Figure 9.2.5.2). **Veh_ex2_A1** is likely to be excluded from this source category on the basis of the poor performance in the P_{raw} and P_{log} tests. **Traffic+BB_B3** and **Traffic_exhaust_N3** showed good performances in the P_{raw} and P_{log} tests therefore the poor results in WD tests are likely associated with the underestimation of the uncertainty.

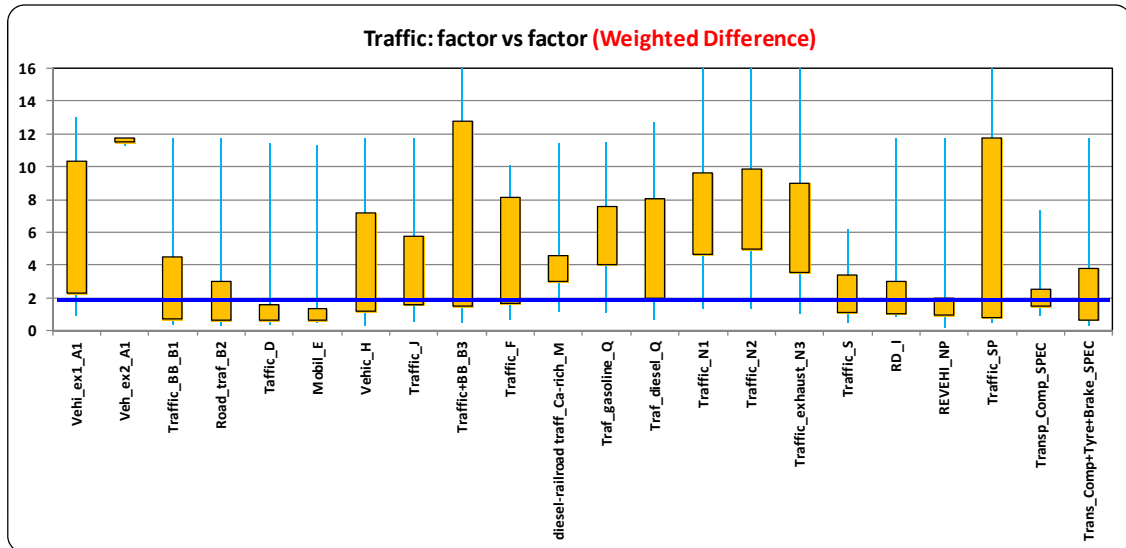


Figure 9.2.5.1: Weighted difference (WD) between factor/source profiles of Traffic.

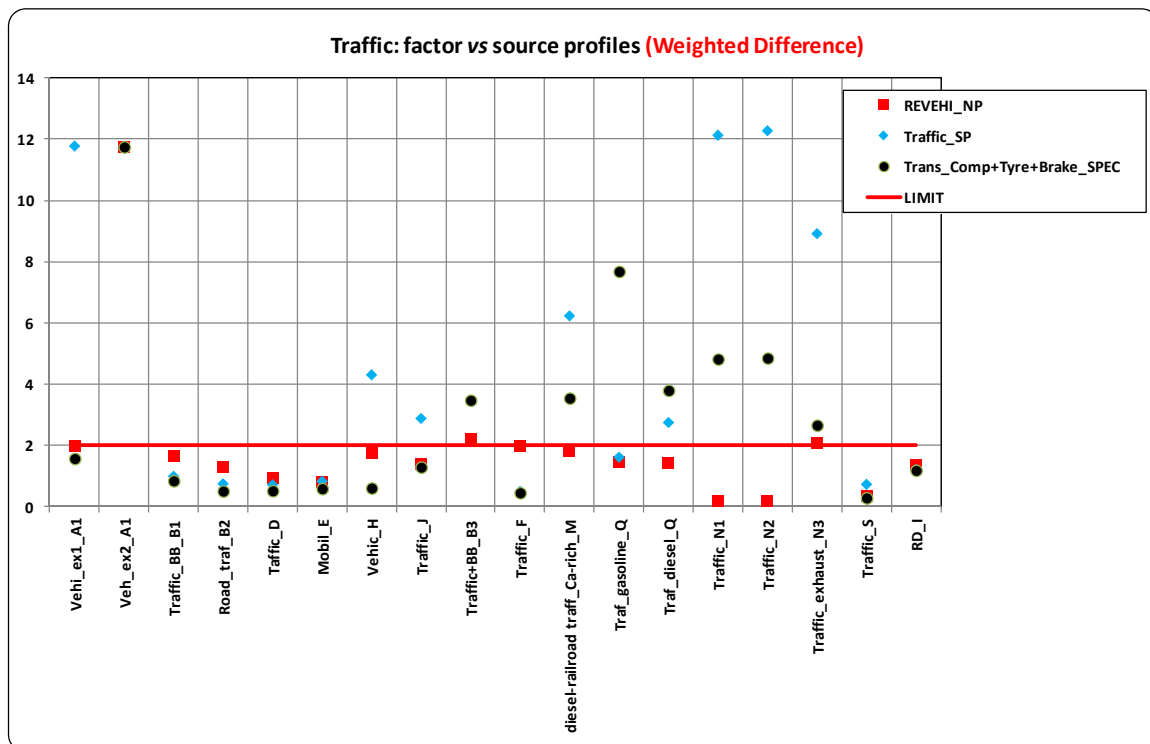


Figure 9.2.5.2: Weighted difference between factor/source profiles of Traffic and reference source profiles.

9.2.6 Dust – Re-Suspended Soil

Less than half of the WD calculated for the Dust factor profiles are within the limit of acceptability (Figure 9.2.6.1). On the other hand, with the exception of **MD_A1**, all the factor/source profiles are at least comparable with one of the reference source profile on the basis of the WD tests (Figure 9.2.6.2). **MD_A1** presents good performance in P_{raw} and P_{log} tests. Therefore, the poor results in the WD tests are attributable to the underestimation of the profile uncertainty.

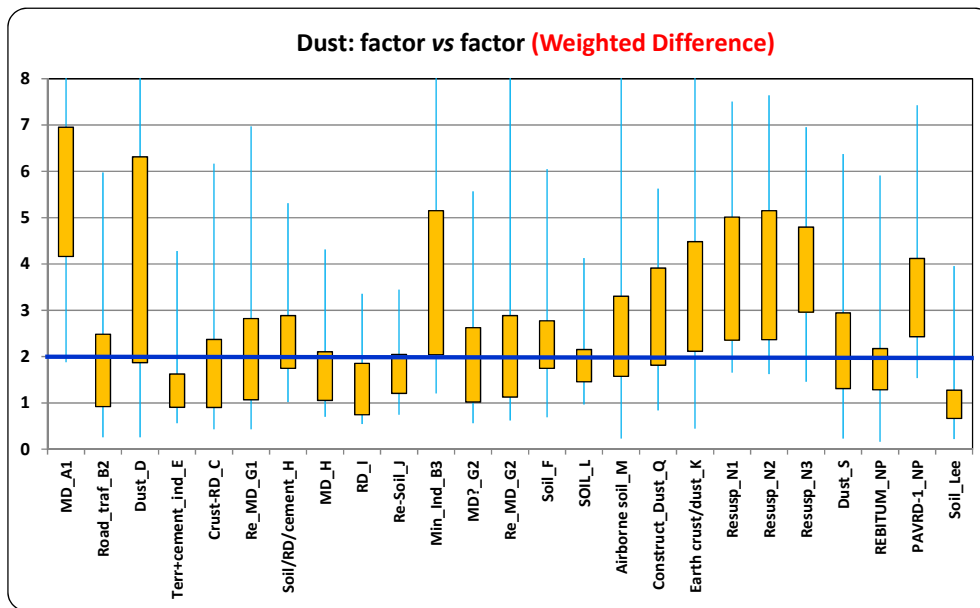


Figure 9.2.6.1: Weighted difference (WD) between factor/source profiles of Dust.

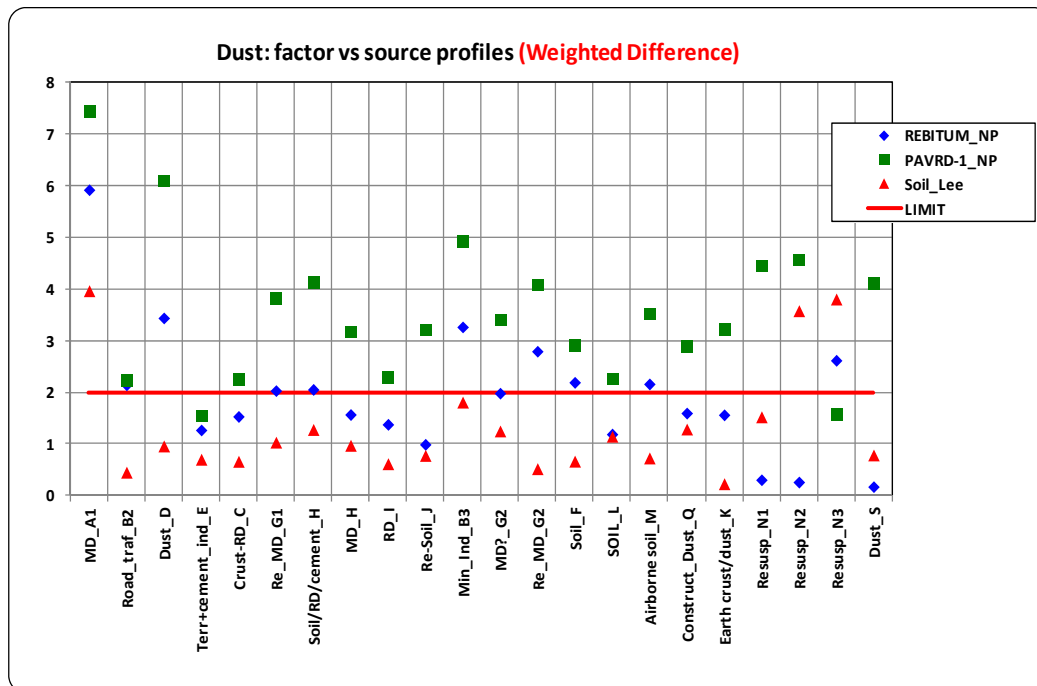


Figure 9.2.6.2: Weighted difference between factor/source profiles of Dust and reference source profiles.

9.2.7 Secondary aerosols

For the Secondary compounds factors, no relevant results could be obtained from the WD analysis due to limited availability of data. No reference source profiles are available for comparison with participants factor/source profiles. We only present the factor to factor WD test (Figure 9.2.7.1). Sec_A1 is the only factor that shows poor performance in the test, probably due to the underestimation of the profile uncertainty.

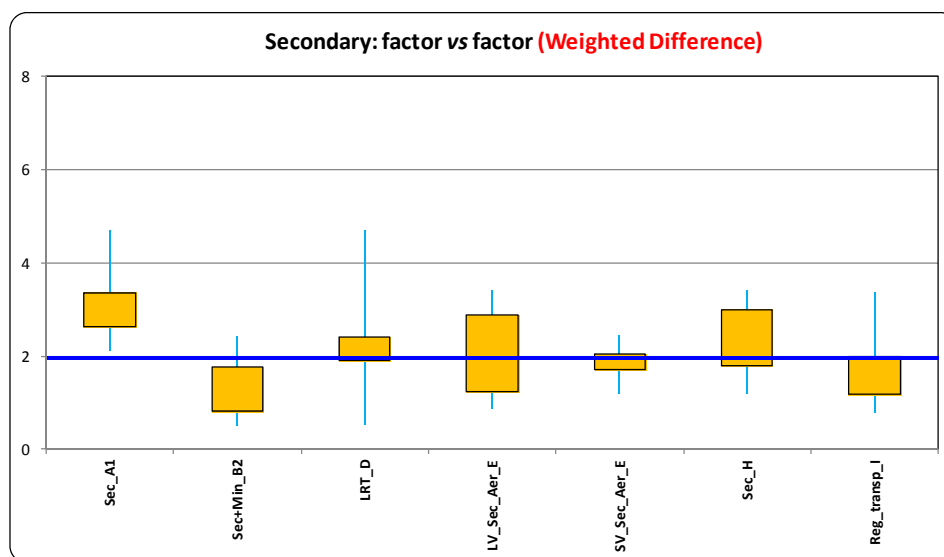


Figure 9.2.7.1: Weighted difference (WD) between factor/source profiles of Secondary compounds.

9.2.8 Sulphate

Almost half the WDs calculated for the Sulphate source category are beyond the limit of acceptability. **SO4_B3** is by far the profile with the highest WD index if compared with the other factor profiles. Also **SO4_Coal_G1**, **SO4_F**, **SO4_I_L** and **(NH4)2SO4_K** are little comparable with other participants' WD (Figure 9.2.8.1). In addition, the WD calculated for **SO4_Coal_G1** and **SO4_B3** are little comparable with the WD of the chosen reference source profile (Figure 9.2.8.2).

This is a particular kind of source profile due to the fact that the markers: sulphate and ammonium, are also the highest contributors to the PM mass. Therefore, despite the huge difference in concentration with respect to the other species they're not a source of noise for the factor/source chemical profile analysis. **SO4_B3** shows good performances in the P_{raw} and P_{log} tests. The high WD values observed in the tests are likely an indication of underestimated profile uncertainty.

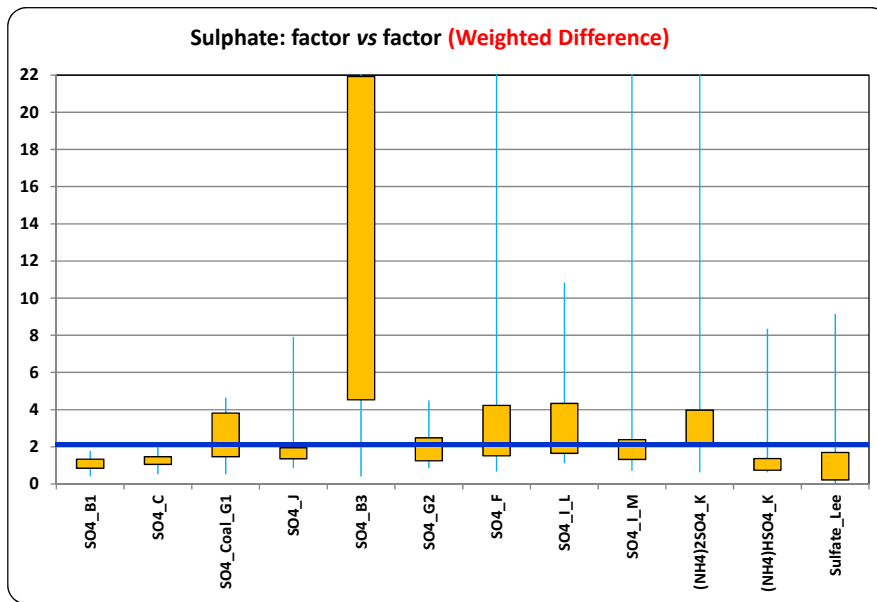


Figure 9.2.8.1: Weighted difference (WD) between factor/source profiles of Sulphate.

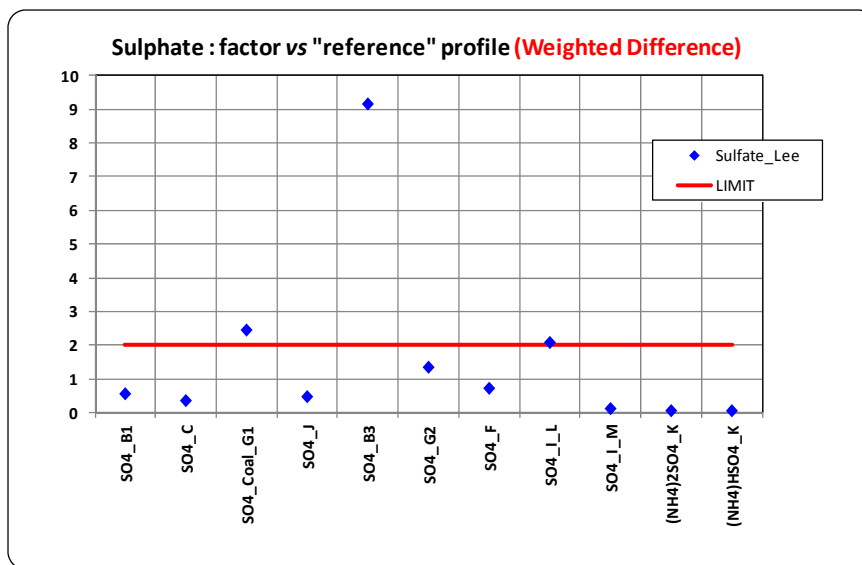


Figure 9.2.8.2: Weighted difference between factor/source profiles of Sulphate and reference source profiles.

9.2.9 Nitrate

Except for **NO3_F**, WDs calculated for nitrate factor/source profiles fall within the limit of acceptability (Figure 9.2.9.1). On the other hand, the same analysis shows that the WDs of factor profiles **NO3_F** and **NO3_L** are little when compared with the reference source profile (Figure 9.2.9.2). This kind of factor/source profiles is similar to those in the sulphate source category. They're characterized by a strong chemical fingerprint dominated by the markers. All nitrate

profiles show high performances in the P_{raw} and P_{log} tests. The bad performance of **NO3_F** and **NO3_L** are attributable to underestimated profile uncertainty.

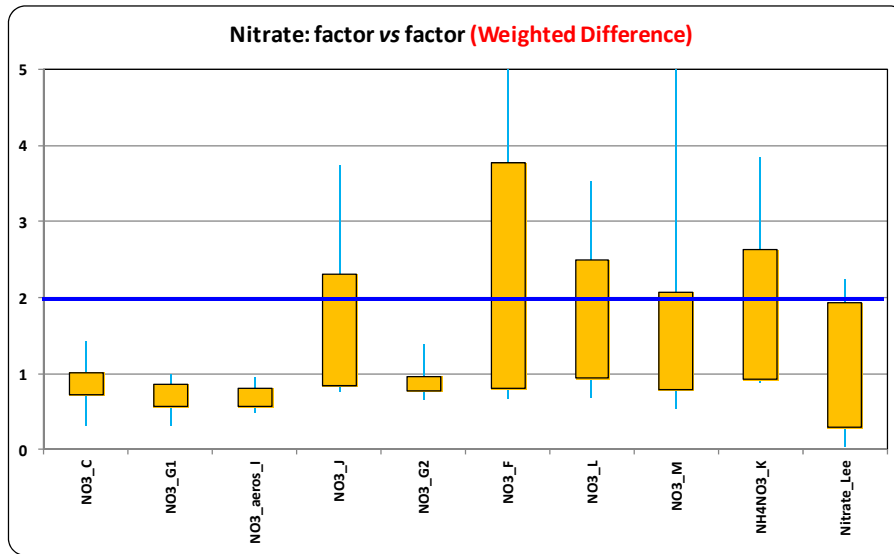


Figure 9.2.9.1: Weighted difference (WD) between factor/source profiles of Nitrate.

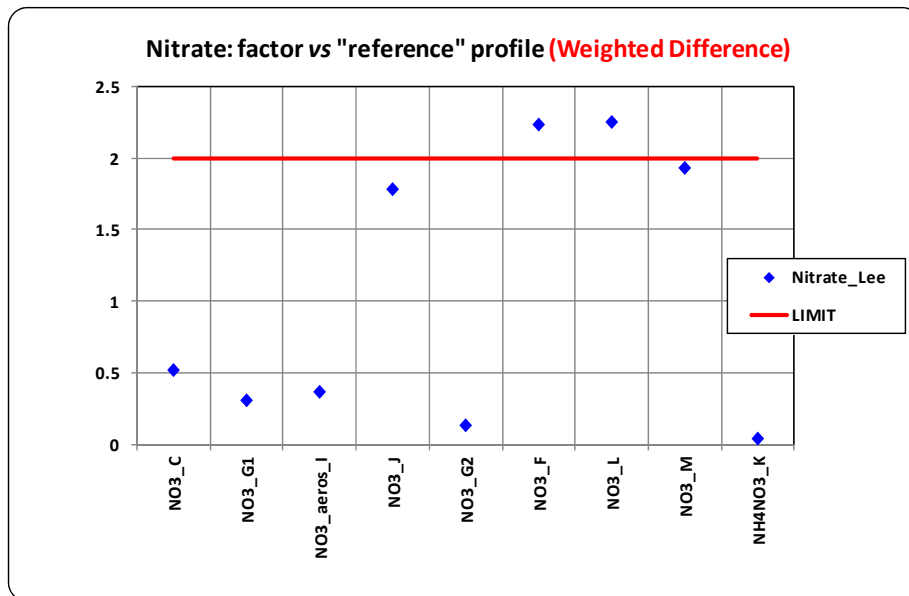


Figure 9.2.9.2: Weighted difference between factor/source profiles of Nitrate and reference source profiles.

9.2.10 Zinc Smelter

The majority of the participant Zinc smelter factor/source profiles fall within the limit of acceptability. The only exceptions is **ZnO kiln_K** (Figure 9.2.10.1). On the other hand, all the factor/source profiles show WD indexes with the Zinc smelter reference source profiles within the acceptability area for at least one of the reference sources (Figure 9.2.10.2).

ZnO kiln_K presents poor performances in the P_{raw} and P_{log} tests. On the other hand, it passes the WD test with the reference factor profile reported by Lee et al. (2006).

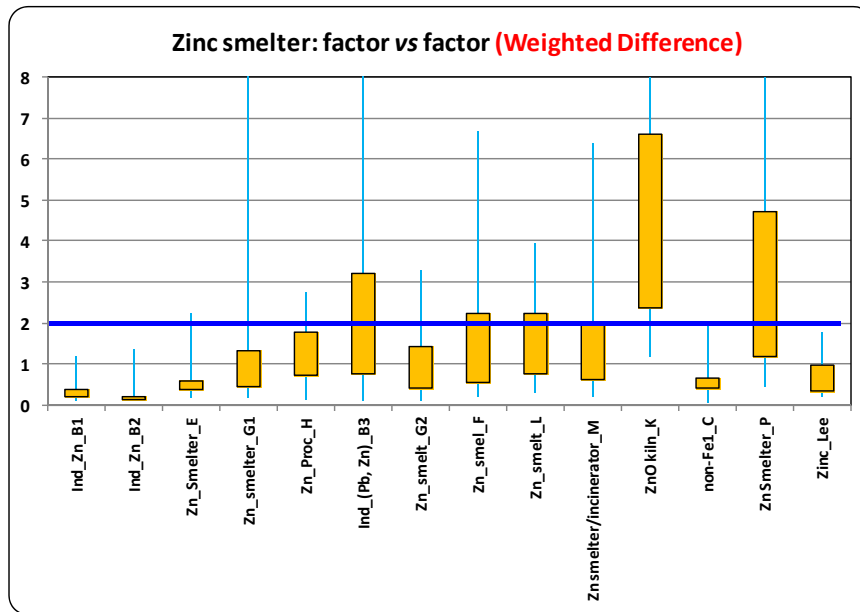


Figure 9.2.10.1: Weighted difference (WD) between factor/source profiles of Zinc smelter.

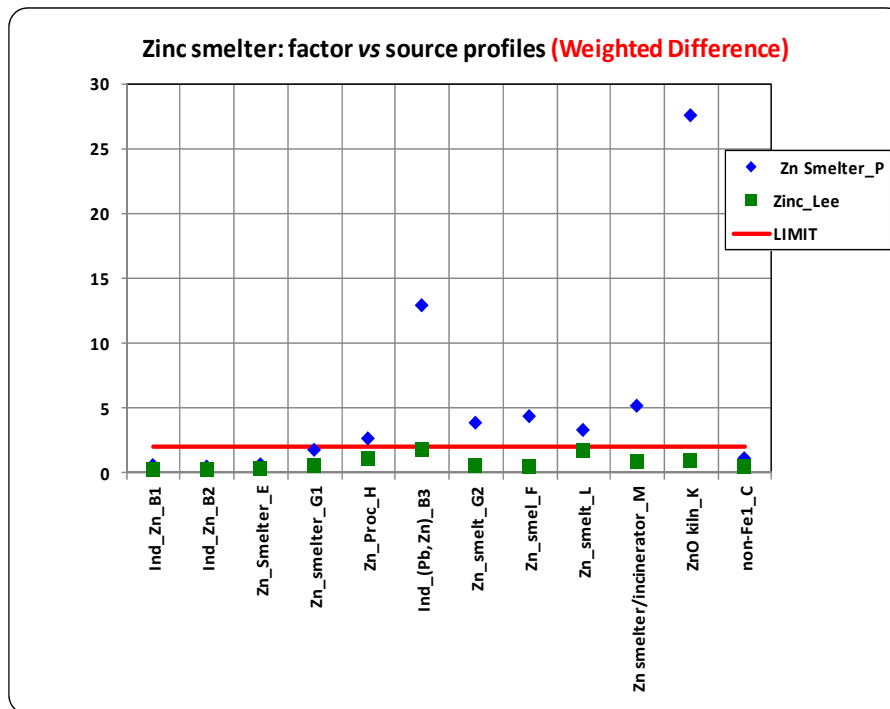


Figure 9.2.10.2: Weighted difference between factor/source profiles of Zinc smelter and reference source profiles.

9.2.11 Copper metallurgy

According to the WD test, most of the Copper metallurgy factor/sources reported by participants result comparable among each other. Only **CuO kiln_K** is beyond the limit of acceptability (Figure 9.2.11.1). On the other hand, **Ind_(Cu,P, SO₄)_B3** is the only

factor/source that does not comply with the WD test criteria for the reference source profiles (Figure 9.2.11.2). **Ind_(Cu,P, SO4)_B3** poor results are probably due to the underestimation of the profile uncertainty.

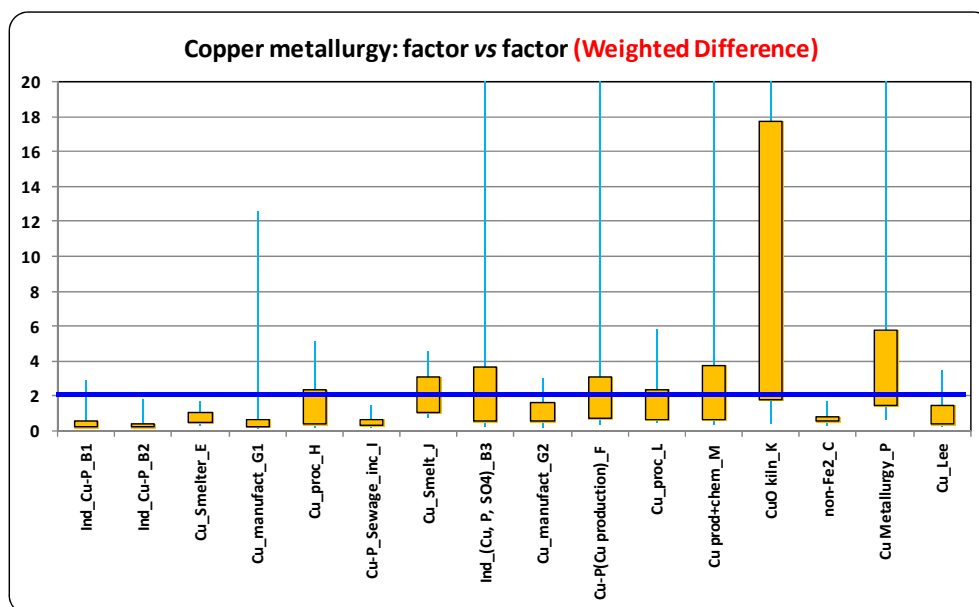


Figure 9.2.11.1: Weighted difference (WD) between factor/source profiles of Copper metallurgy.

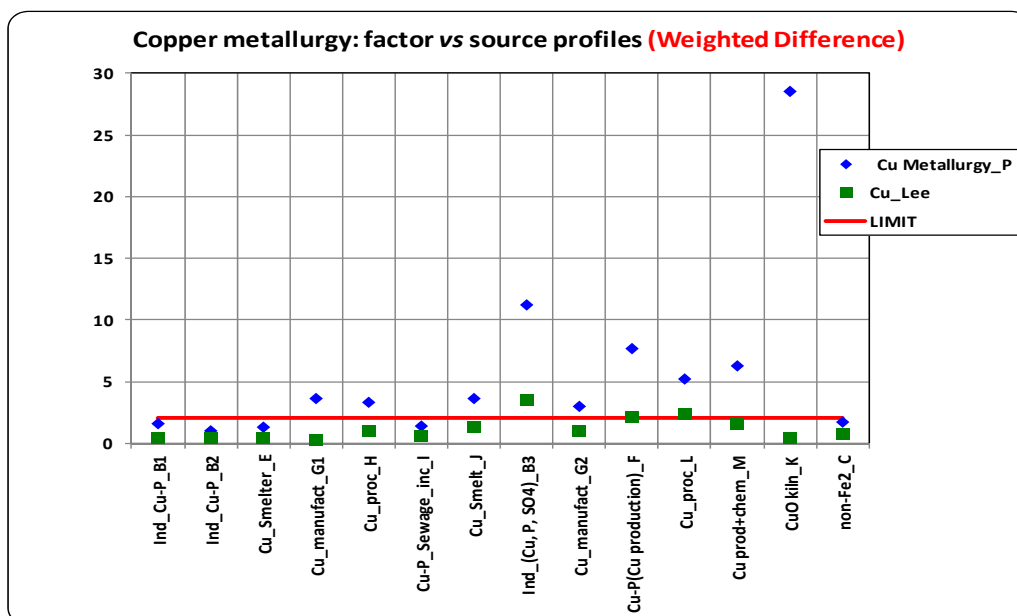


Figure 9.2.11.2: Weighted difference between factor/source profiles of Copper metallurgy and reference source profiles.

9.2.12 Lead metallurgy

Only one factor WD index is above the limit of acceptability: **ind(Pb, Zn)_B3**. Other factors such as, **Pb_smelter_F** and **Pb_L** are slightly above the limit of acceptability (Figure 9.2.12.1) On the other hand, all the WD indexes calculated for factors assigned to lead metallurgy comply with the WD criteria when compared with the reference source profiles (Figure 9.2.12.2). Due to

the reduced number of factors/sources, the tests comparing factors/sources with reference sources are to be considered more reliable than the factor vs. factor test. Therefore, **ind(Pb, Zn)_B3** is likely to be accepted as member of this source category taking into account the good performance in the factor vs reference source (fs) tests.

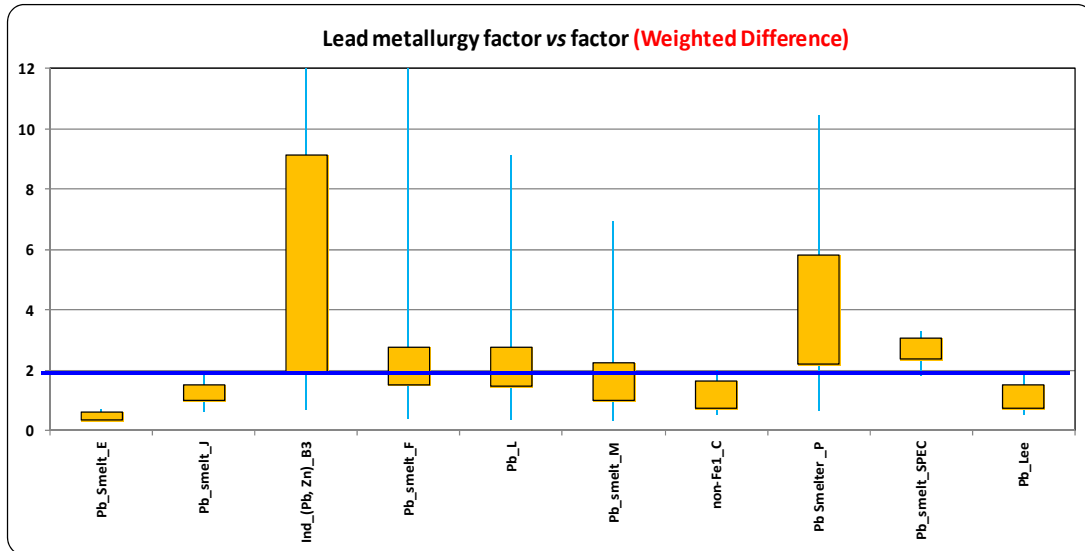


Figure 9.2.12.1: Weighted difference (WD) between factor/source profiles of Lead metallurgy.

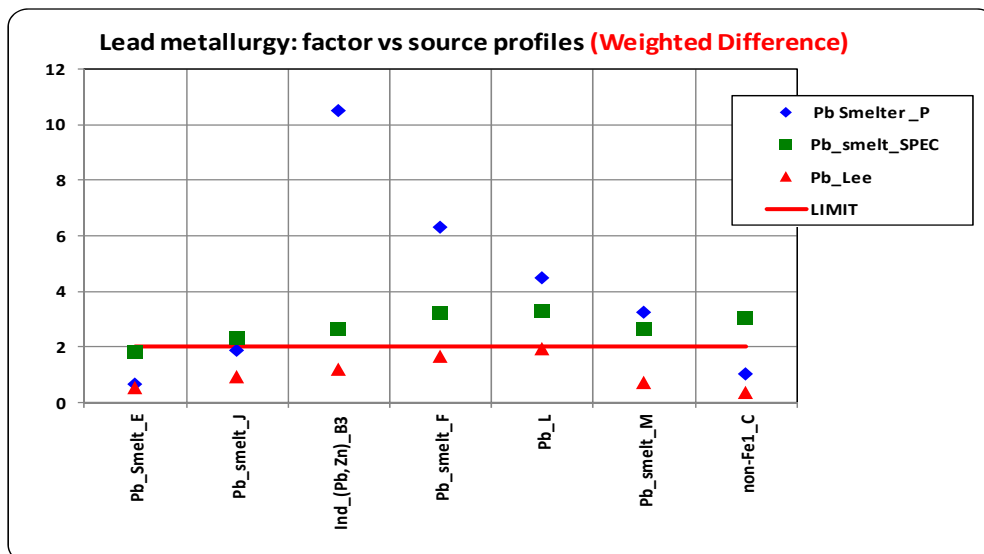


Figure 9.2.12.2: Weighted difference between factor/source profiles of Lead metallurgy and reference source profiles.

9.2.13 Steel processing

Apart from **Iron&Steel_G1** and **Steel_Proc_J**, most of the WD calculated for the factor profiles assigned by the participants to Steel processing are not within the limit of acceptability for this factor (Figure 9.2.13.1). On the other hand, all the WD of these factors comply with the

WD criteria for the reference source profiles for Steel processing (Figure 9.2.13.2). All the factor/sources show a relatively good performance in the correlations test, especially on log-transformed data. The positive results of the tests between factor/sources against reference sources provide additional evidence in favor of considering these profiles as members of the same source category.

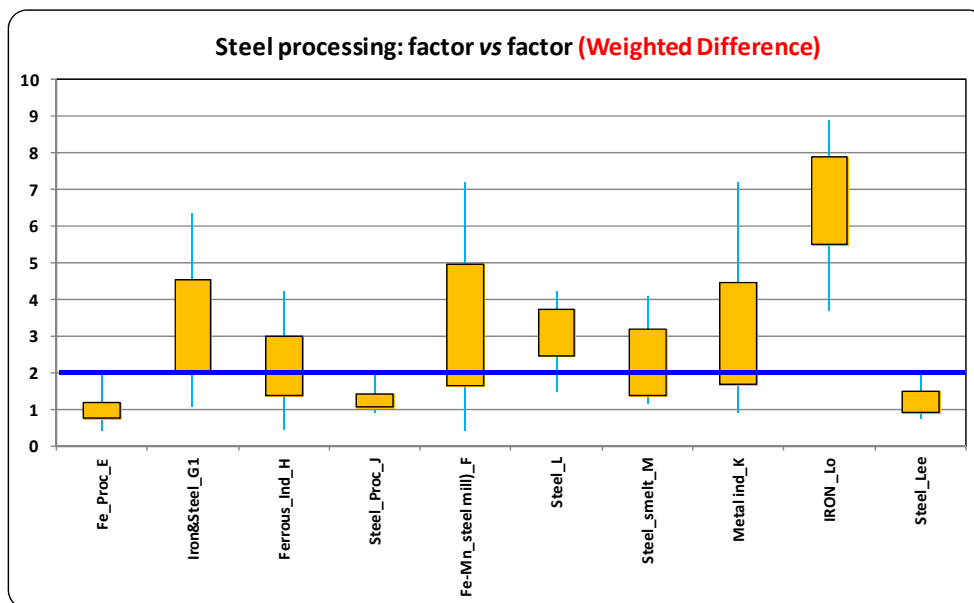


Figure 9.2.13.1: Weighted difference (WD) between factor/source profiles of Steel processing.

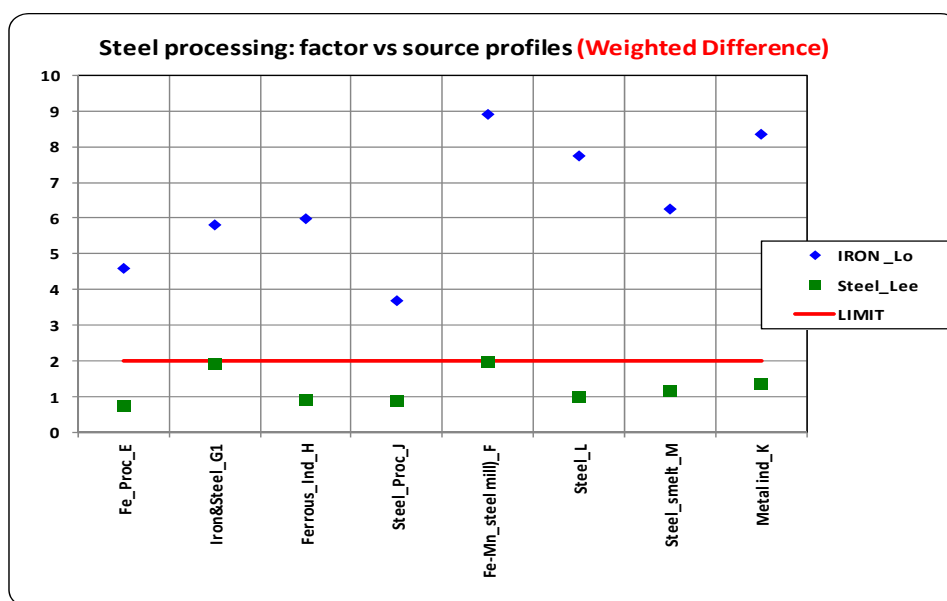


Figure 9.2.13.2: Weighted difference between factor/source profiles of Steel processing and reference source profiles.

9.2.14 Industry-combustion

The majority of the Industry-combustion factor/source profiles show WD indexes beyond the limit of acceptability. The profiles that pass the WD test correspond to solutions obtained with the model EPA PMF 3.0 (Figure 9.2.14.1). Excepting **Ind_A1**, **Fuel_Comb_A1**, **Min_Ind_B3**,

and **Coal_powerplant_K**, all WD for reference source profiles comply with the acceptability criteria (Figure 9.2.14.2). The factor vs reference source tests in this category include different types of reference source profiles, therefore their power to prove that factors belong to the same category is weaker than in other categories.

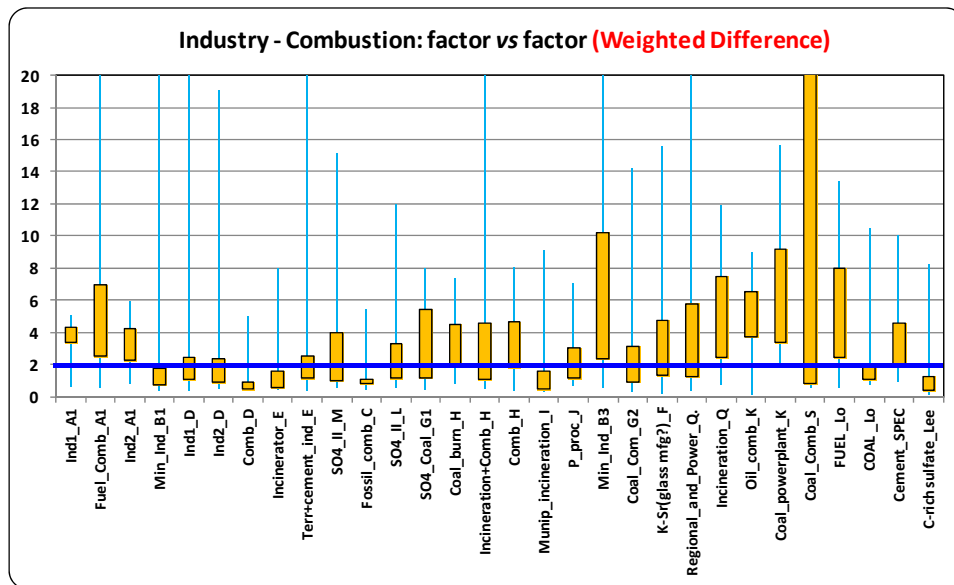


Figure 9.2.14.1: Weighted difference (WD) between factor/source profiles of Industry-combustion.

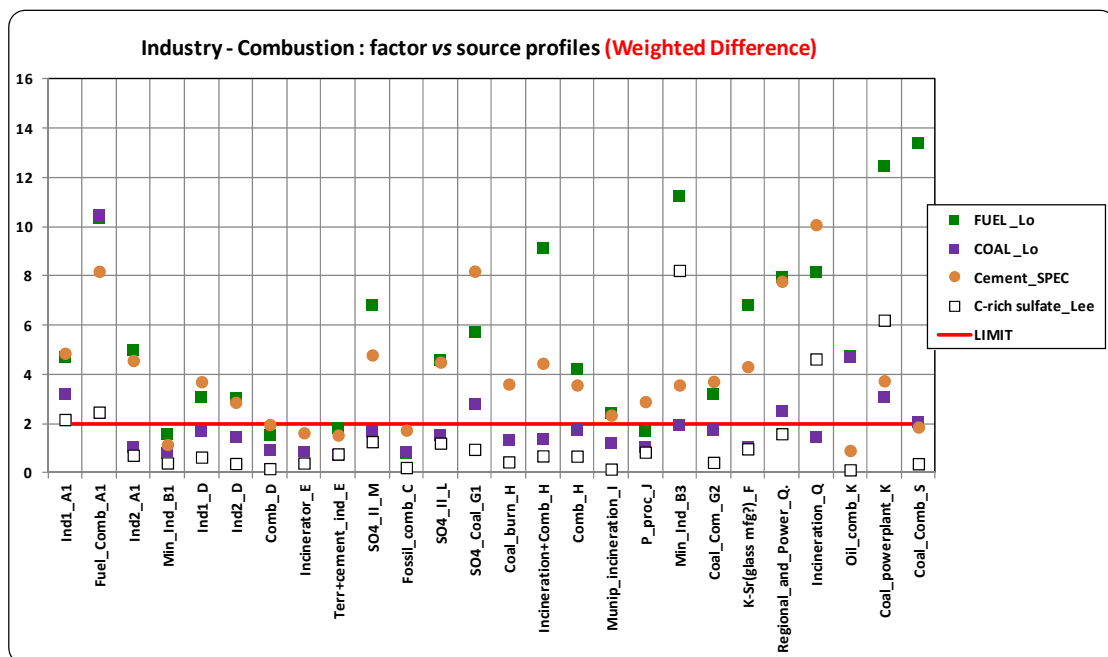


Figure 9.2.14.2: WD between factor profiles of Industry-combustion and reference source profiles.

Ind_A1, **Fuel_Comb_A1**, and **Min_Ind_B3** show good performances in the P_{raw} and P_{log} tests. Therefore, the poor performance with WD test is likely the result of uncertainty underestimation. On the contrary, **Coal_powerplant_K** show poor performance in all tests and is probably not a member of this source category.

9.2.15 Ship emissions

This is a small and heterogeneous category that includes some profiles that roughly may fit ship emissions despite the different name attributed by participants. None of the WD calculated for the Ship emission factor/source profiles fall within the limit of acceptability (Figure 9.2.15.1).

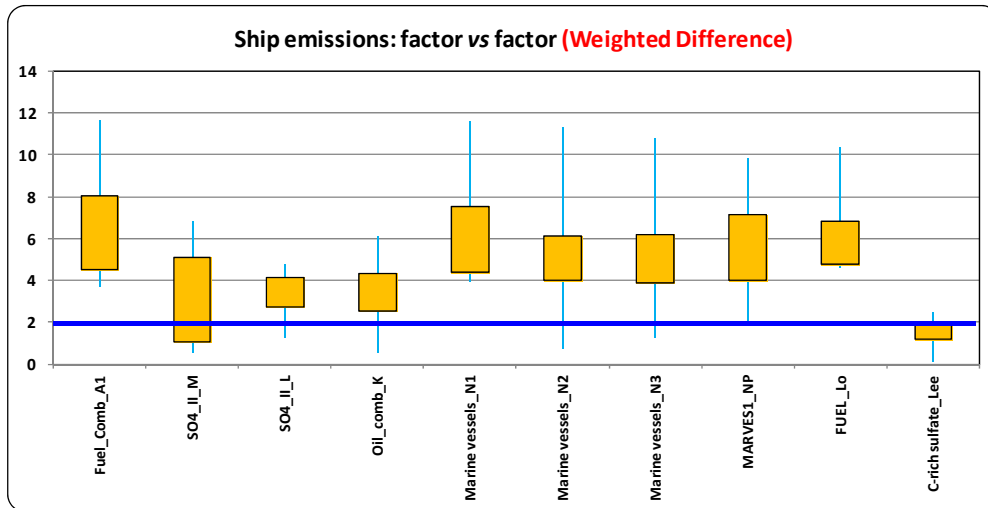


Figure 9.2.15.1: Weighted difference (WD) between factor/source profiles of Ship emissions.

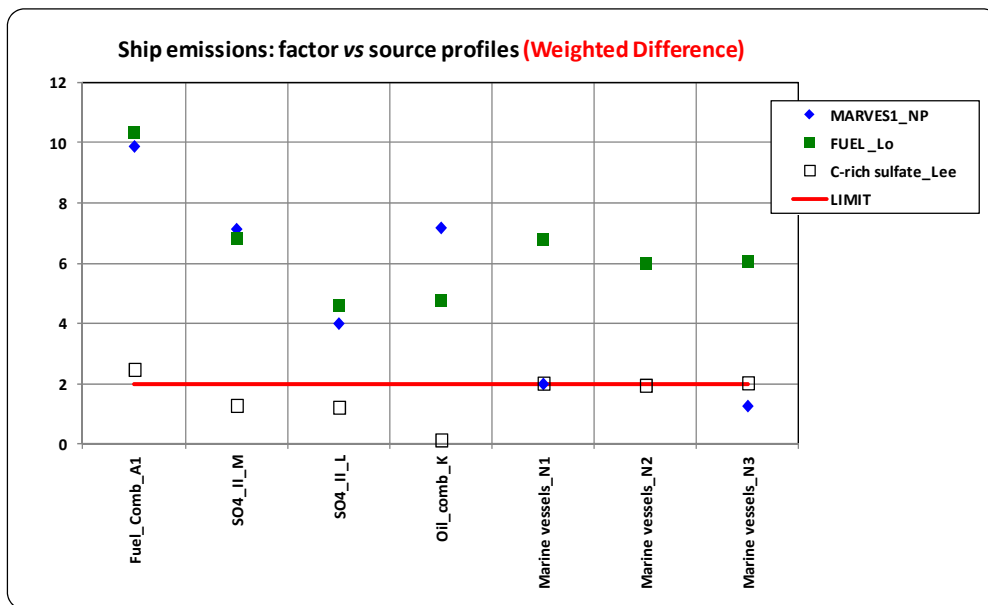


Figure 9.2.15.2: Weighted difference between factor/source profiles of Ship emissions and reference source profiles.

On the other hand, **SO4_II_M**, **SO4_II_L**, **Oil_comb_K** are comparable with Ca rich factor (Lee et al., 2006) while the **Marine vessels_ (N1, N2, and N3)** factor/sources fit the marine vessels reference source profile in addition to the Ca rich factor (Figure 9.2.15.2).

The test confirms that the category is quite heterogeneous and that the ship emission related profiles are not comparable with those not labeled as such by participants.

9.3 Preliminary test III: Correlation between factor/source contributions (time trends)

Participants reported source contributions corresponding to each factor/source profile in every sample, so called time trends. As for the source profile, correlation analysis was performed in order to check the comparability of the factor/source profiles on the basis of their contributions or **time trends**.

Unlike the fingerprints, no correlation with reference source profile was possible in this test.

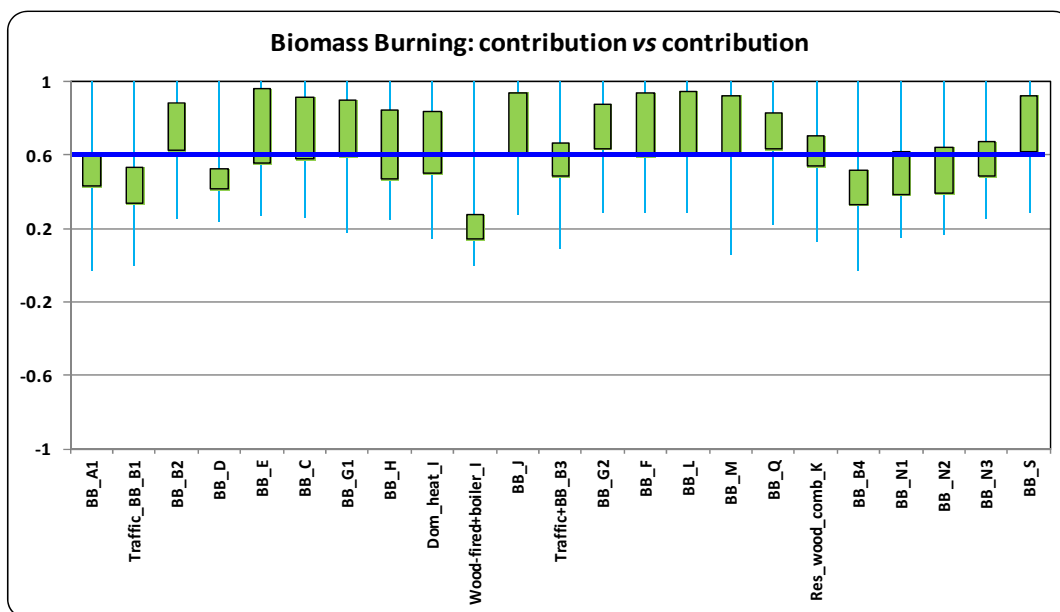


Figure 9.3.1: Correlation between Biomass Burning factor/source contributions expressed in mass concentration.

The majority of the factor contributions (time trends) calculated for the Biomass Burning factor are correlated among each other. On the other hand, **BB_A1, Traffic_BB_B1, BB_D, Wood-fired+boiler_I, Traffic+BB_B3, BB_B4, and BB_(N1, N2, and N3)** shows a correlation coefficient (R) below the established limit value (≥ 0.6) (Figure 9.3.1).

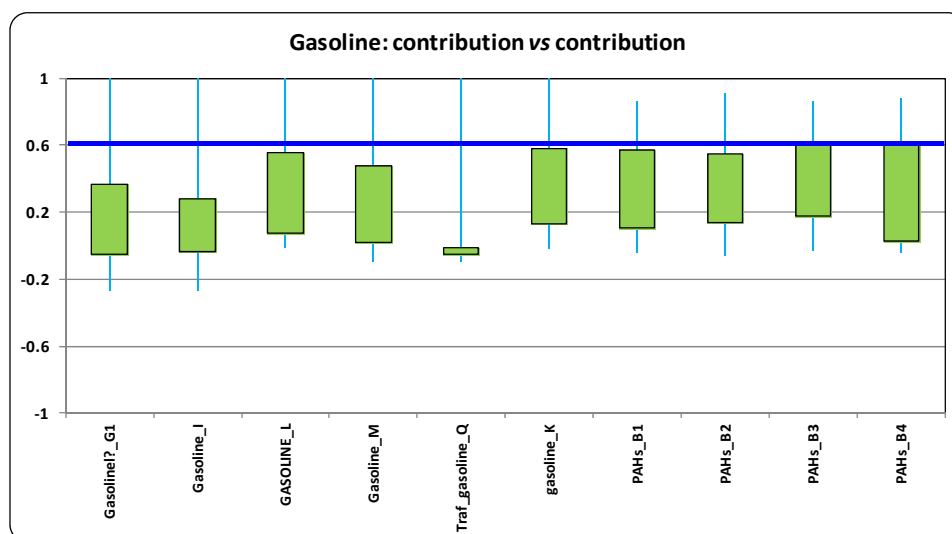


Figure 9.3.2: Correlation between Gasoline factor/source contributions expressed in mass concentration.

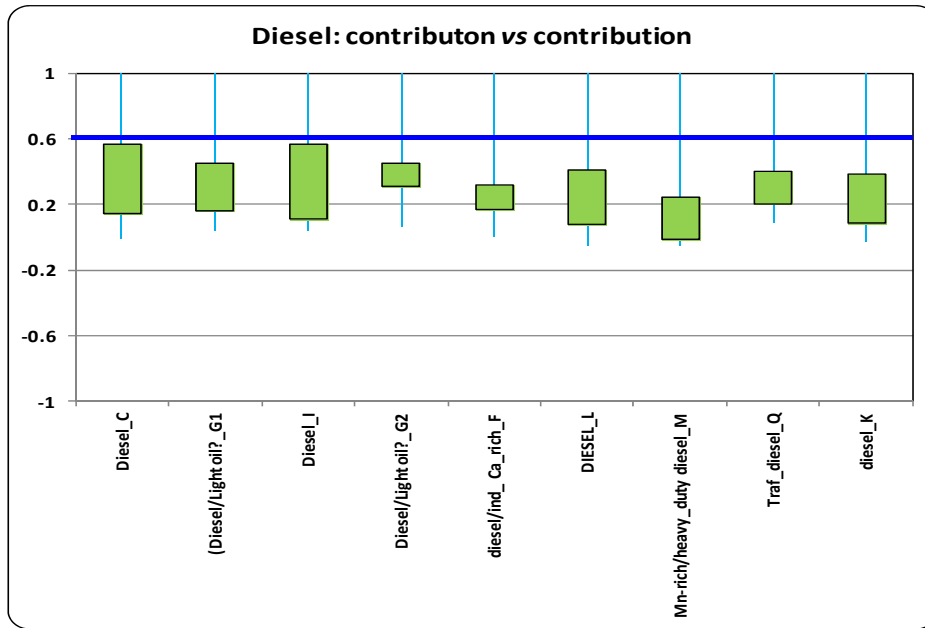


Figure 9.3.3: Correlation between Diesel factor/source contributions expressed in mass concentration.

Correlation between factor/source contributions calculated for the Gasoline, Diesel, Brakes and Traffic factors do not show any clear correlation between the factors/sources (Figures 9.3.2, 9.3.3, 9.3.4, and 9.3.5).

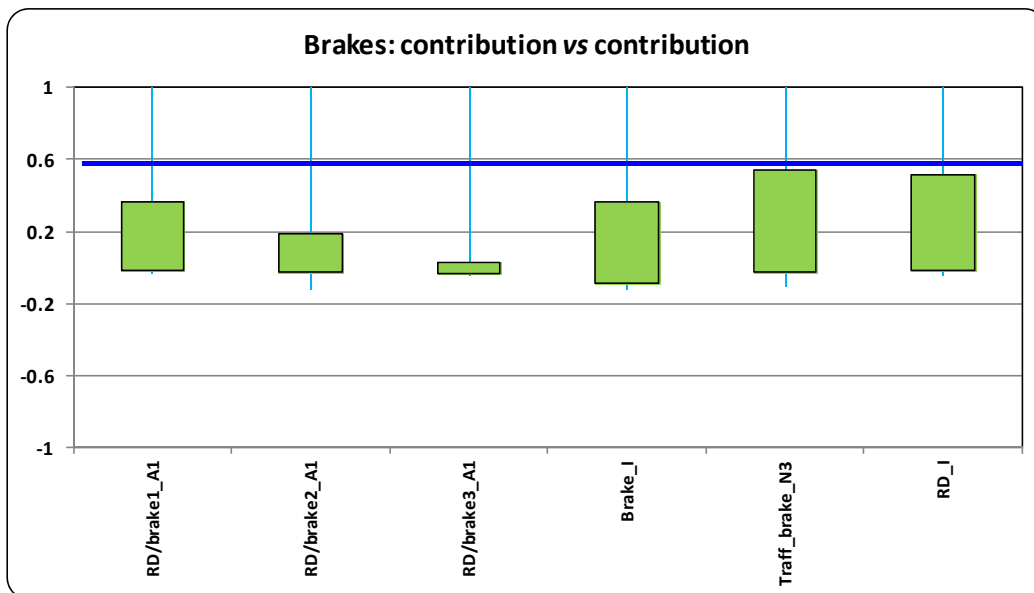


Figure 9.3.4: Correlation between Brakes factor/source contributions expressed in mass concentration.

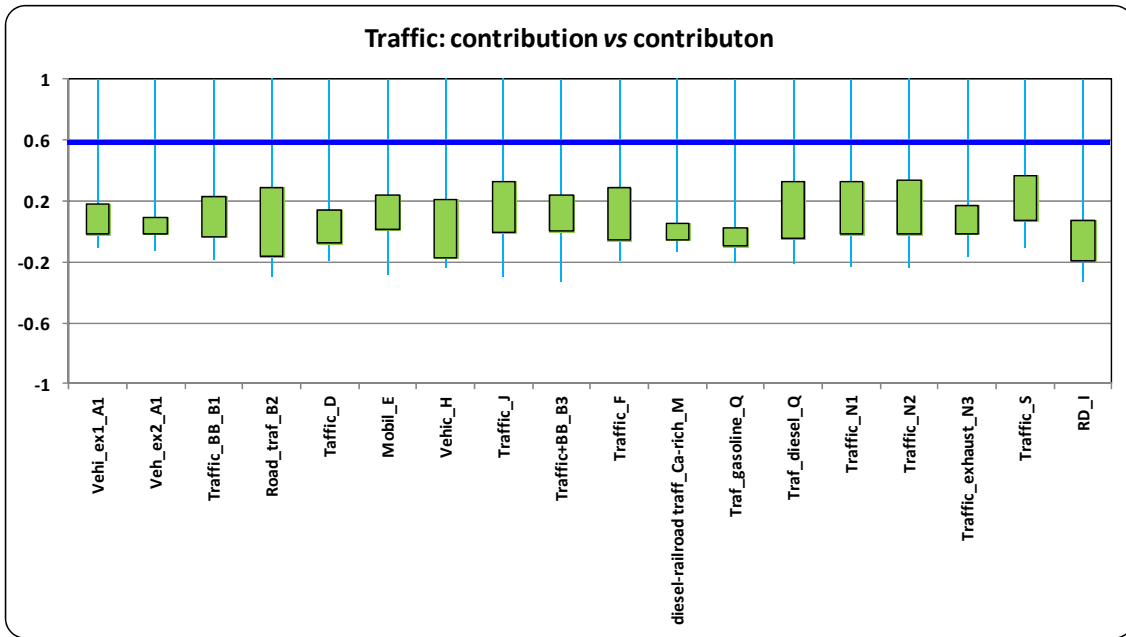


Figure 9.3.5: Correlation between Traffic factor/source contributions expressed in mass concentration.

The majority of the correlations of Dust, Re-suspended factor/source contributions are below the limit of acceptability. Few factor/source contributions such as, **MD_A1**, **Terr+cement_Ind_E**, **Soil_F**, **Soil_L**, **Mineral_B4**, **Resusp_N1**, **Resusp_N2** and **Dust_S** are slightly better correlated to all the others in the same category but their interquartile range cuts the line of acceptability (Figure 9.3.6).

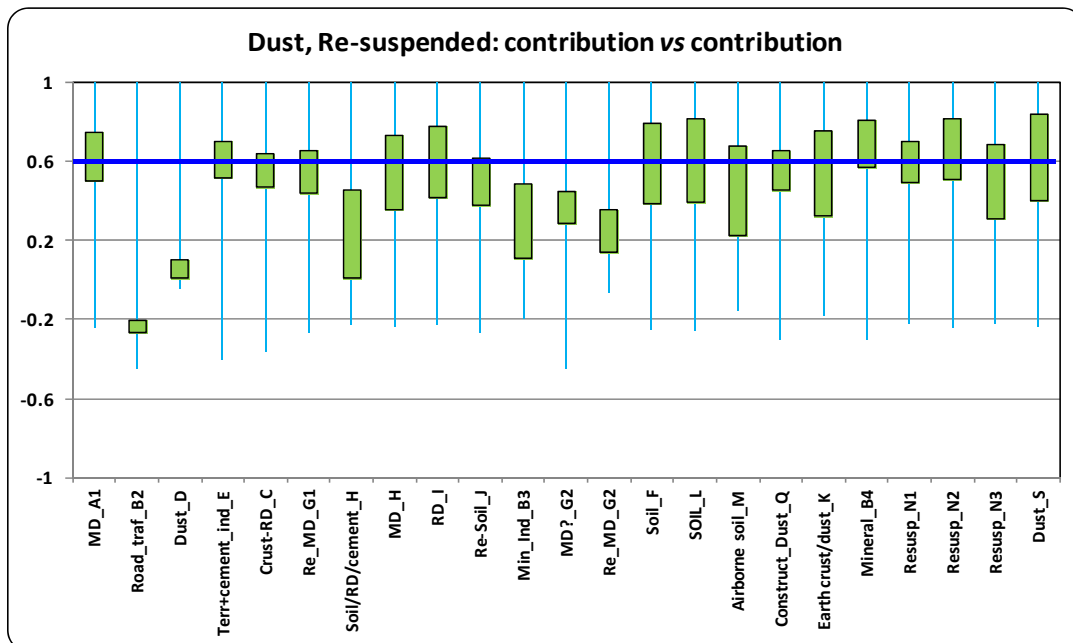


Figure 9.3.6: Correlation between Dust, Re-suspended factor/source contributions expressed in mass concentration.

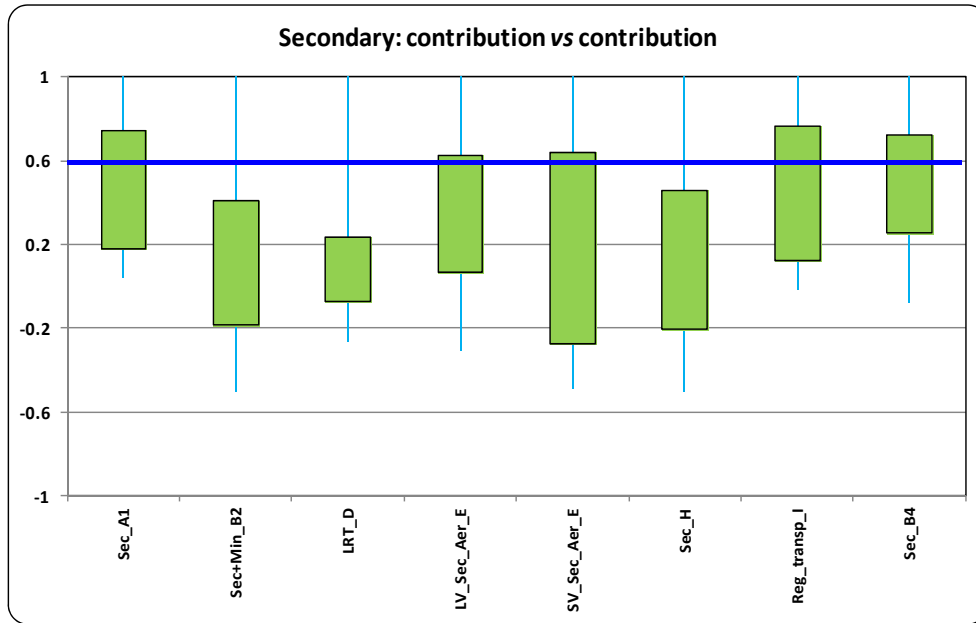


Figure 9.3.7: Correlation between Secondary factor/source contributions expressed in mass concentration..

Correlations between all factor contributions observed for the Secondary aerosol factor are below the limit of acceptability (Figure 9.3.7). On the other hand, Sulphate and above all, Nitrate factor contributions show very high correlations (Figure 9.3.8, Figure 9.3.9). Only few factors/sources such as **SO4_B1**, **SO4_C**, **SO4_B3** and **(NH4)HSO4_K** show correlations below the limit of acceptability (Figure 9.3.8). The similarity of the sulphate and nitrate factor/sources is attributed to the strong signal of the marker species for these profiles; which are also the main contributors to the PM mass.

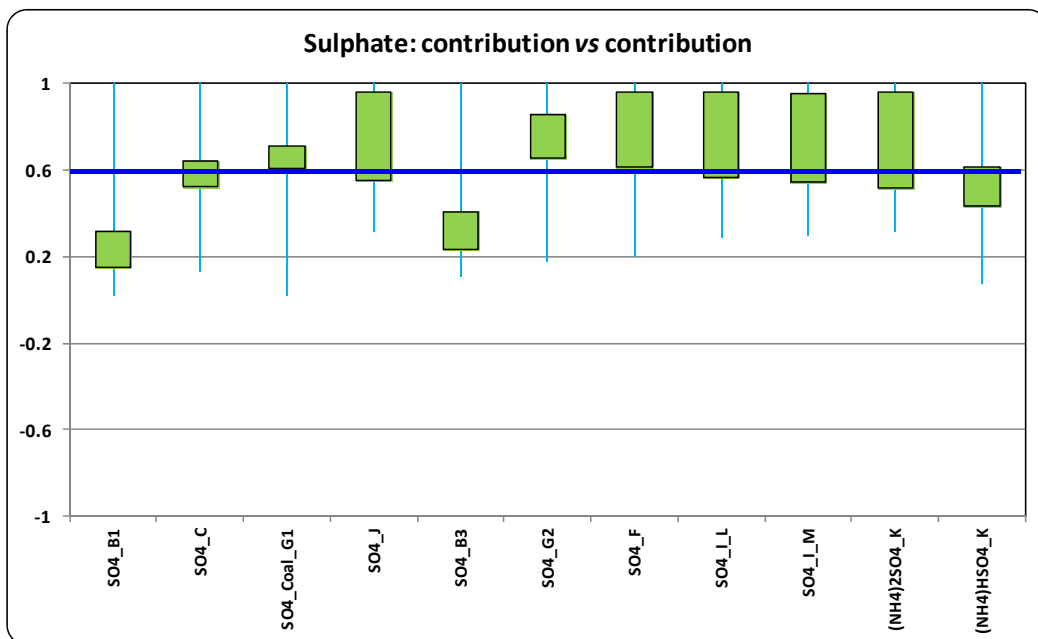


Figure 9.3.8: Correlation between Sulphate factor/source contributions expressed in mass concentration.

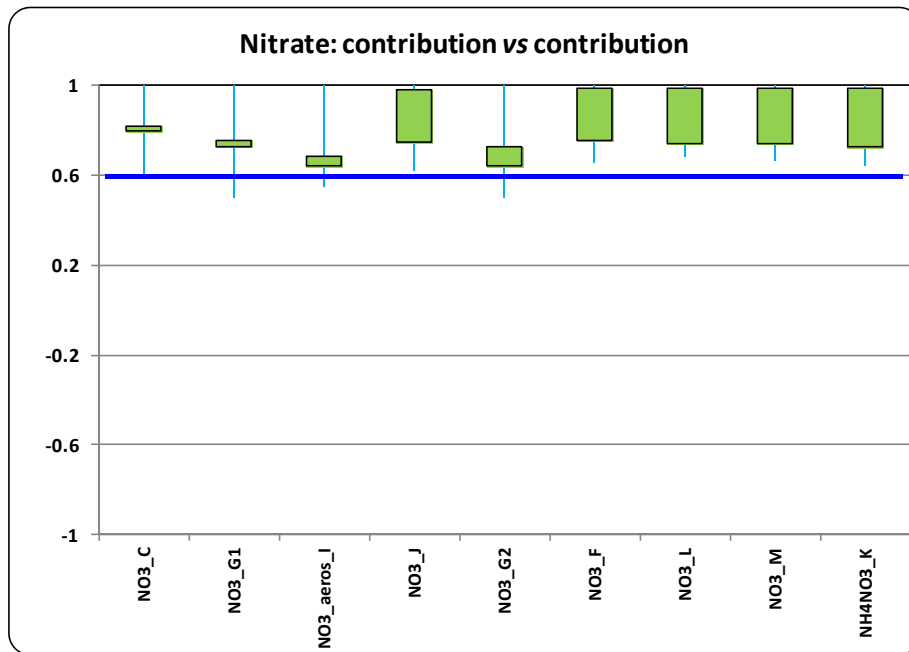


Figure 9.3.9: Correlation between Nitrate factor/source contributions expressed in mass concentration.

Correlations among the factor/source time trends of Zinc factor smelter source category show that **Ind_Zn_B1**, **Zn_Smelter_E**, **Zn_smelter_G1** and **Zn_smelt_G2** are not comparable with the other factor contributions of the same category (Figure 9.3.10). However, 8 over 12 factor/source contributions are within the limit of acceptability.

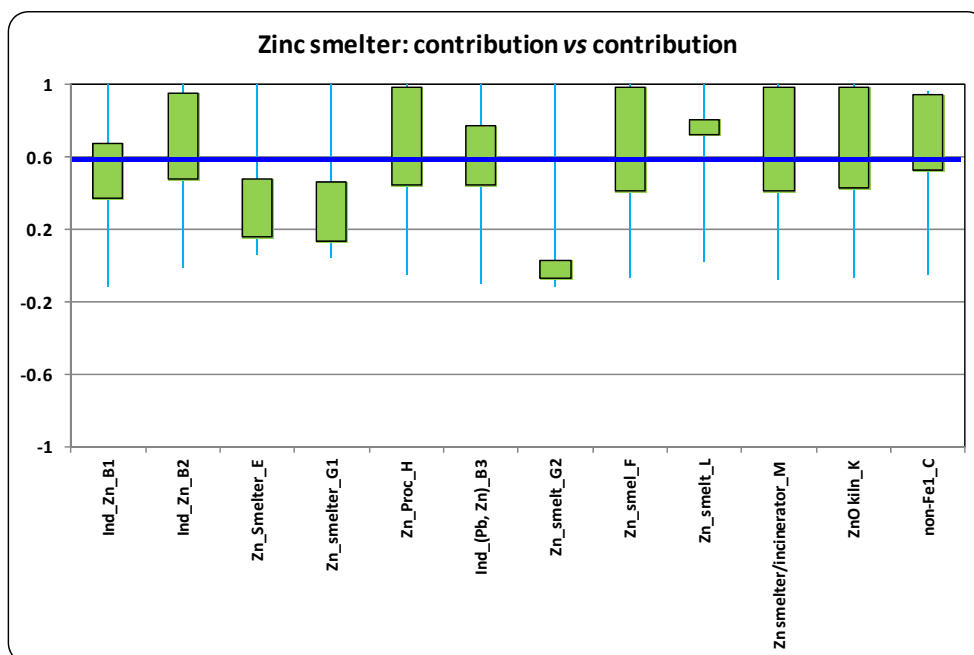


Figure 9.3.10: Correlation between Zinc smelter factor/source contributions expressed in mass concentration.

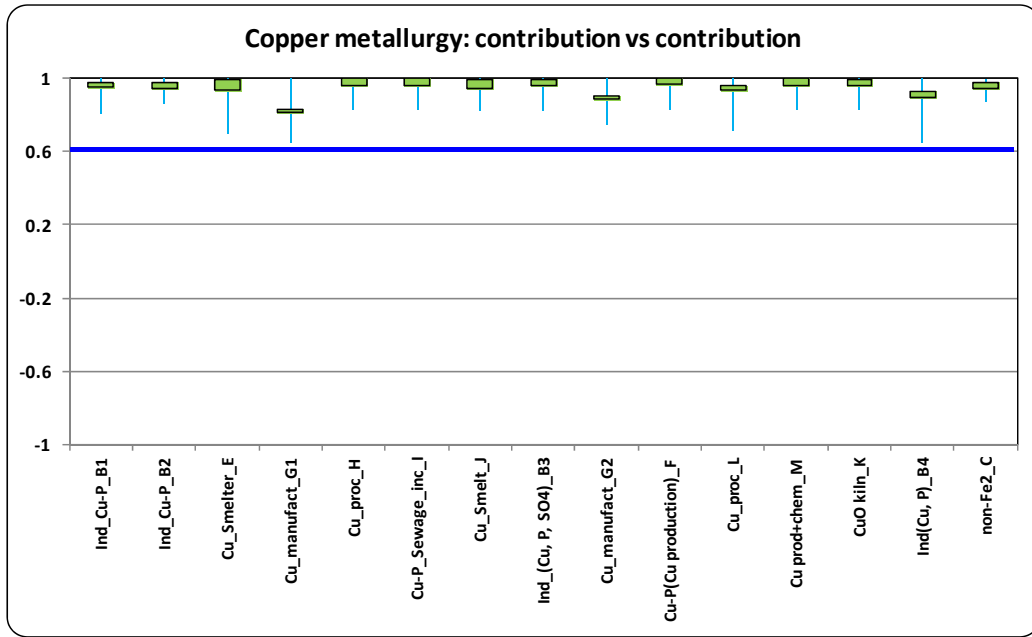


Figure 9.3.11: Correlation between Copper metallurgy factor/source contributions expressed in mass concentration.

All Copper metallurgy factor contributions present very similar time trends leading to highly correlated profiles (Figure 9.3.11).

Few factor contributions (**Ind_(Pb,Zn)_B3**, **Ind(Mn,Pb)_B4** and **non-Fe1_C**) assigned to Lead metallurgy were not correlated with other factor contribution of the same category (Figure 9.3.12).

The similarity of the time trends is probably associated with the intermittent nature of these sources that gives a distinct temporal pattern.

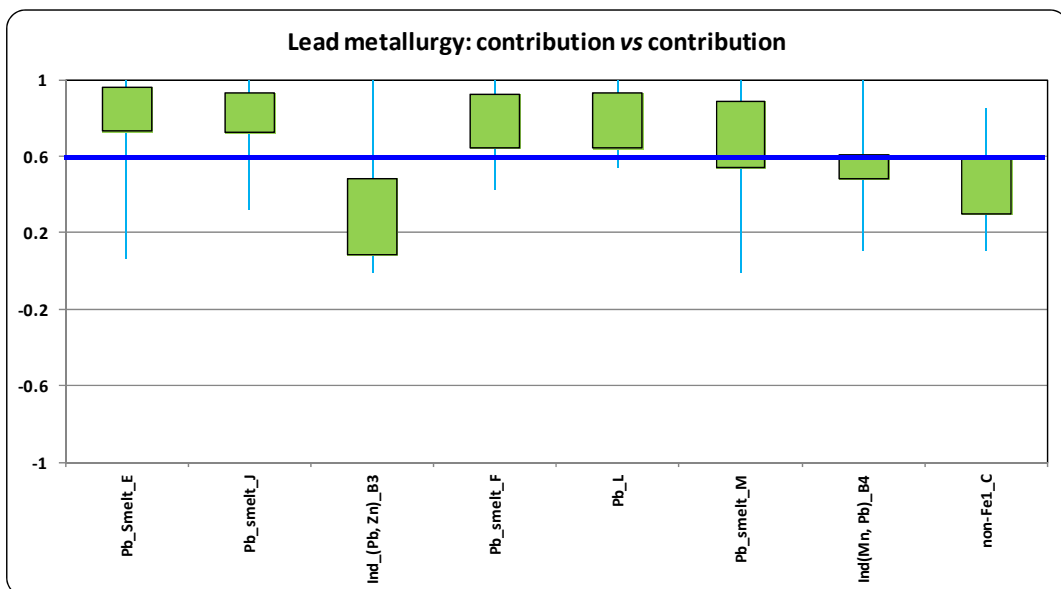


Figure 9.3.12: Correlation between Lead metallurgy factor/source contributions expressed in mass concentration.

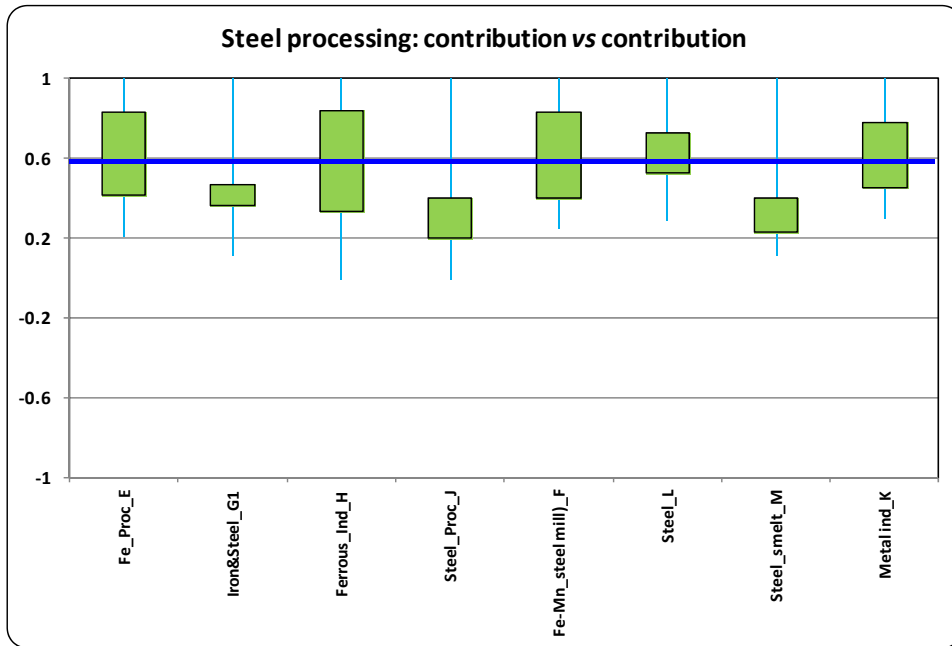


Figure 9.3.13: Correlation between Steel processing factor/source contributions expressed in mass concentration.

Factor/source contributions **Iron&Steel_G1**, **Steel_Proc_J** and **Steel_smelt_M** are not correlated with other factor/source contributions of the category Steel processing (Figure 9.3.13). On the other hand, no correlation is observed for all factor contributions for the Industry-combustion factor (Figure 9.3.14). Same for the Ship emissions factor contributions (Figure 9.3.15).

The lack of correlation in the last two source categories confirm the heterogeneity already identified in the previous tests (Section 9.1 and 9.2).

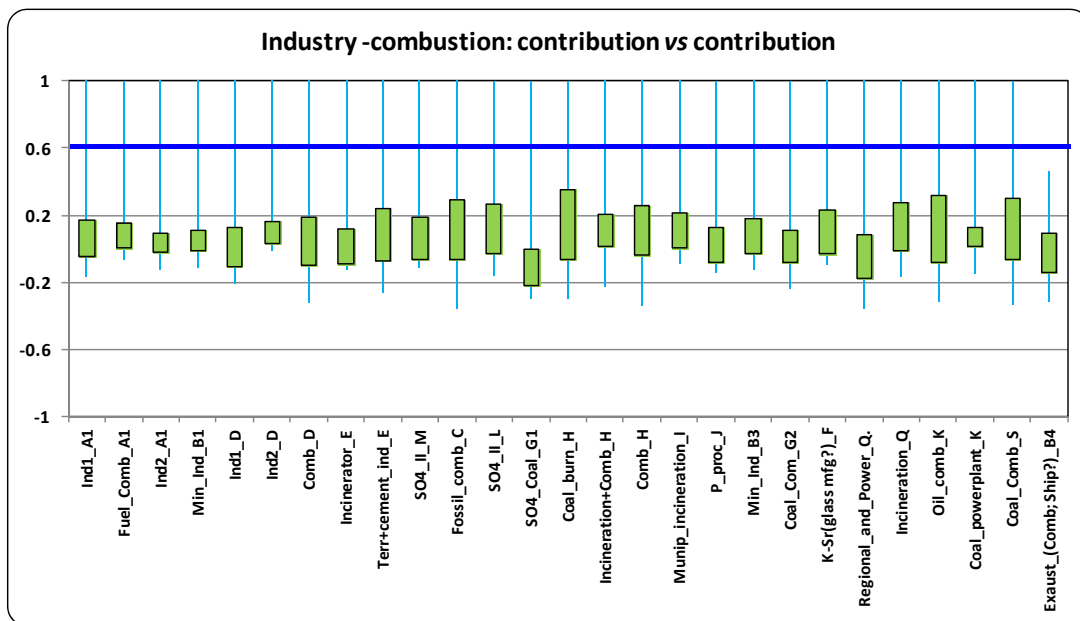


Figure 9.3.14: Correlation between Industry-combustion factor/source contributions expressed in mass concentration.

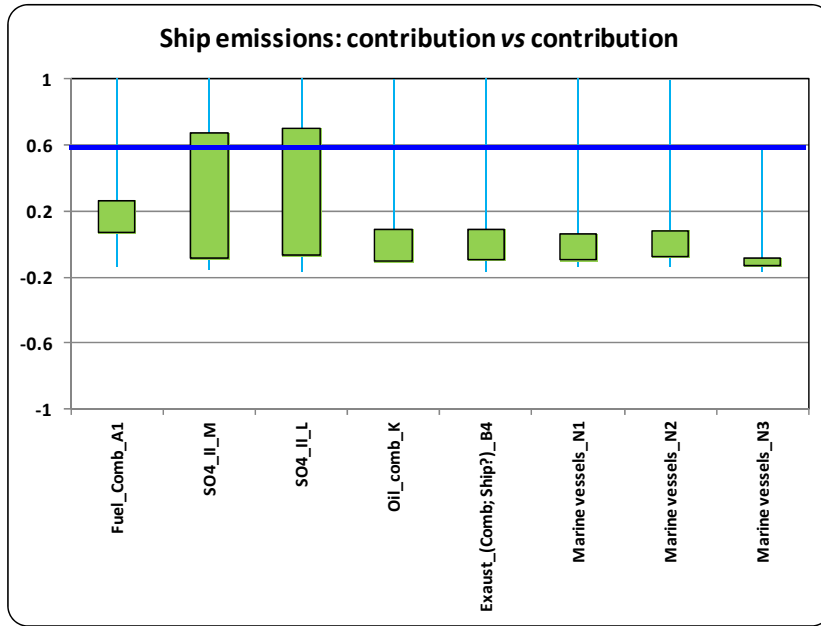


Figure 9.3.15: Correlation between Ship emissions factor/source contributions expressed in mass concentration.

10. Results. Test for Source Contribution Estimations (SCE)

10.1 Test performance evaluation using the z-score index

As discussed in Chapter 6, the z-score is the performance index computed by comparing the Source Contribution Estimation (in ng/m^3) of all the factor/source profiles attributed to the same source category against a reference value.

In order to avoid distortions due to attribution of factor/source profiles to source categories the z-scores reported in this section are those calculated using only factor/source profiles which met the criteria of acceptability in the preliminary tests (Chapter 9).

In the following graphs the area of acceptability ($|Z| < 2$) is the one bounded by yellow lines and the area of warning ($2 < |Z| \leq 3$) is the one between the yellow and the blue lines. Scores in the area beyond the blue lines ($|Z| > 3$) indicate an unsatisfactory performance. In other words, the quantification of the source contributions is too far from the reference.

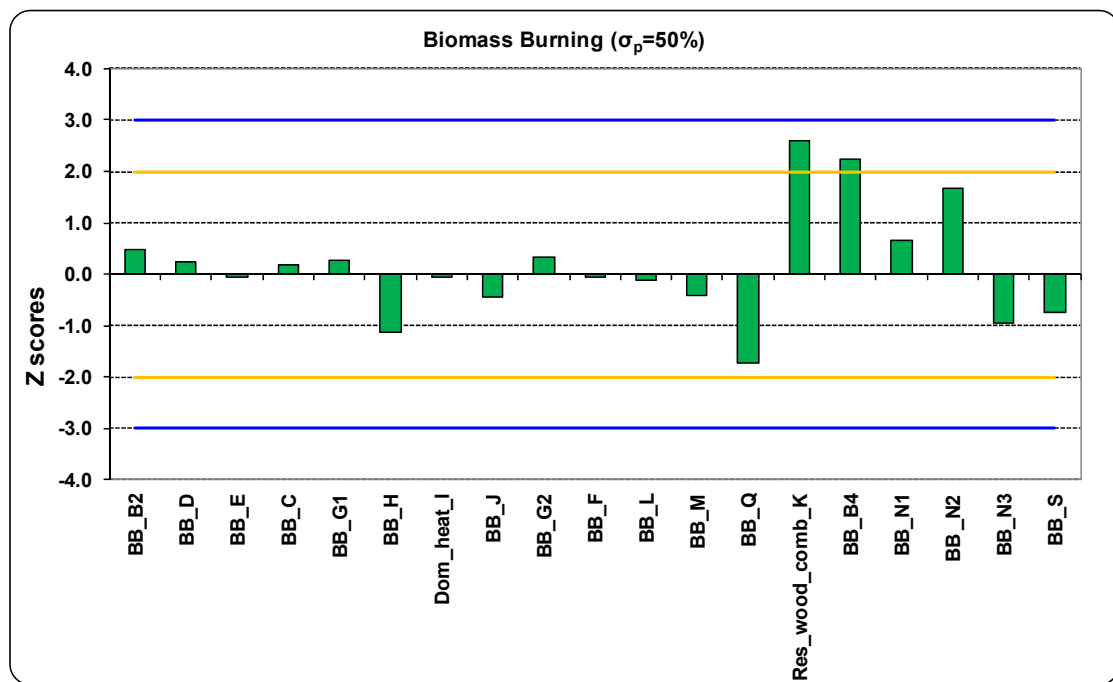


Figure 10.1.1: Z-scores of the factor/source profiles in the Biomass Burning source category.

The test for Biomass Burning shows that the Source Contribution Estimation (SCE) assigned to the factor profiles **Res_wood_comb_K** and **BB_B4** are beyond the limit of acceptability and fall in the “warning” area (Figure 10.1.1).

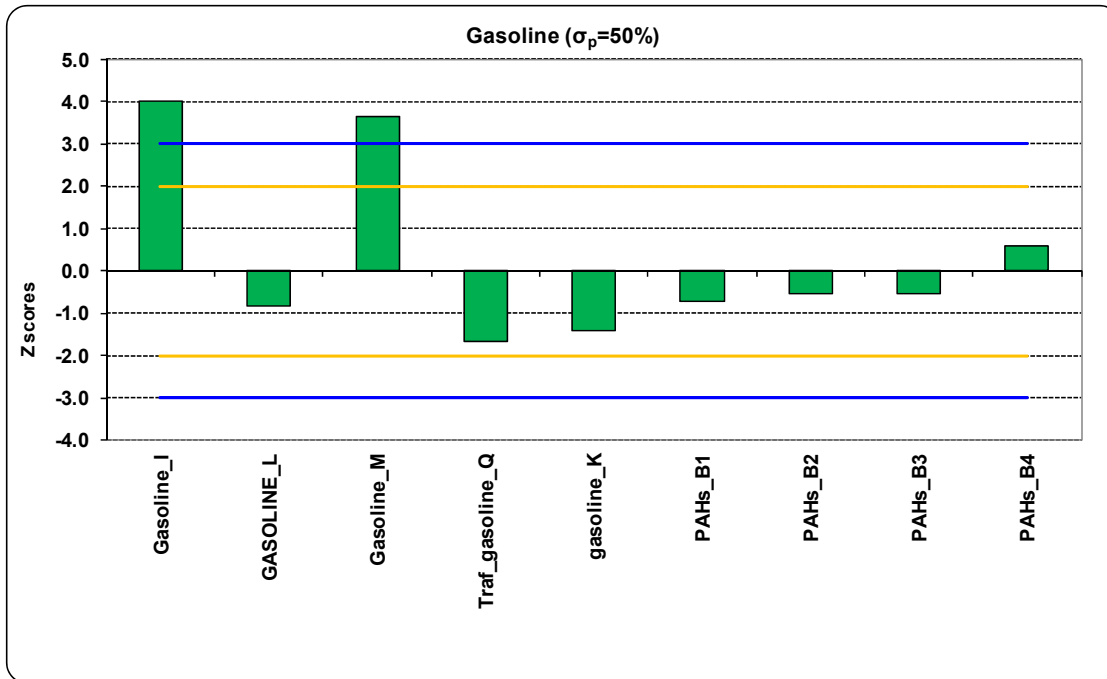


Figure 10.1.2: Z-scores of the factor/source profiles in the Gasoline source category.

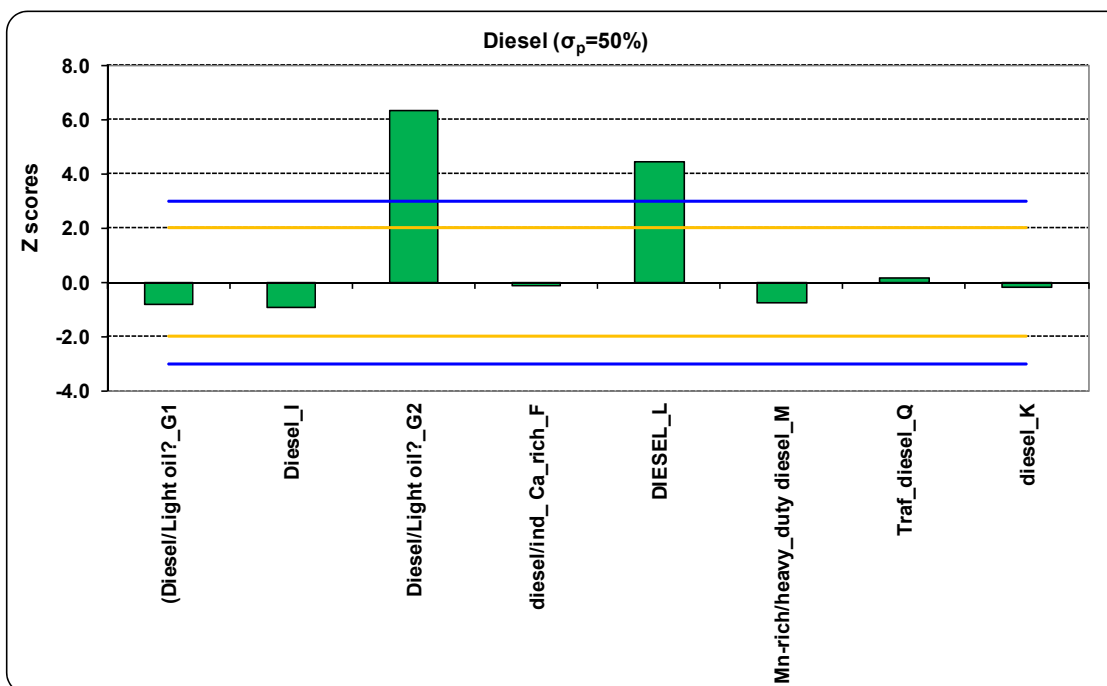


Figure 10.1.3: Z-scores of the factor/source profiles in the Diesel source category.

SCE of **Gasoline_I** and **Gasoline_M** stray from the criteria of acceptability considerably and are thus, marked as unsatisfactory (Figure 10.1.2). Similarly, SCE of **Diesel/Light oil?_G2** and **DIESEL_L** for the Diesel source category are unsatisfactory (Figure 10.1.3).

In both cases the unsatisfactory results are due to overestimation of the source contribution.

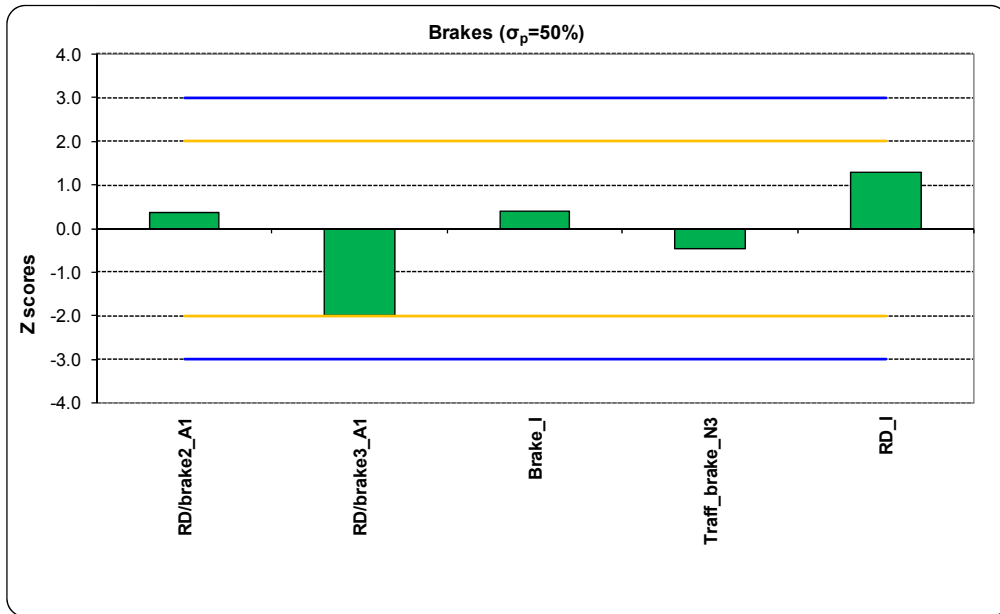


Figure 10.1.4: Z-scores of the factor/source profiles in the Brakes source category.

All the SCE for the (few) Brakes source category are within the limit of acceptability (Figure 10.1.4). Traffic source category shows only two questionable factor profiles: **Traffic_BB_B1** and **Vehi_H** (Figure 10.1.5).

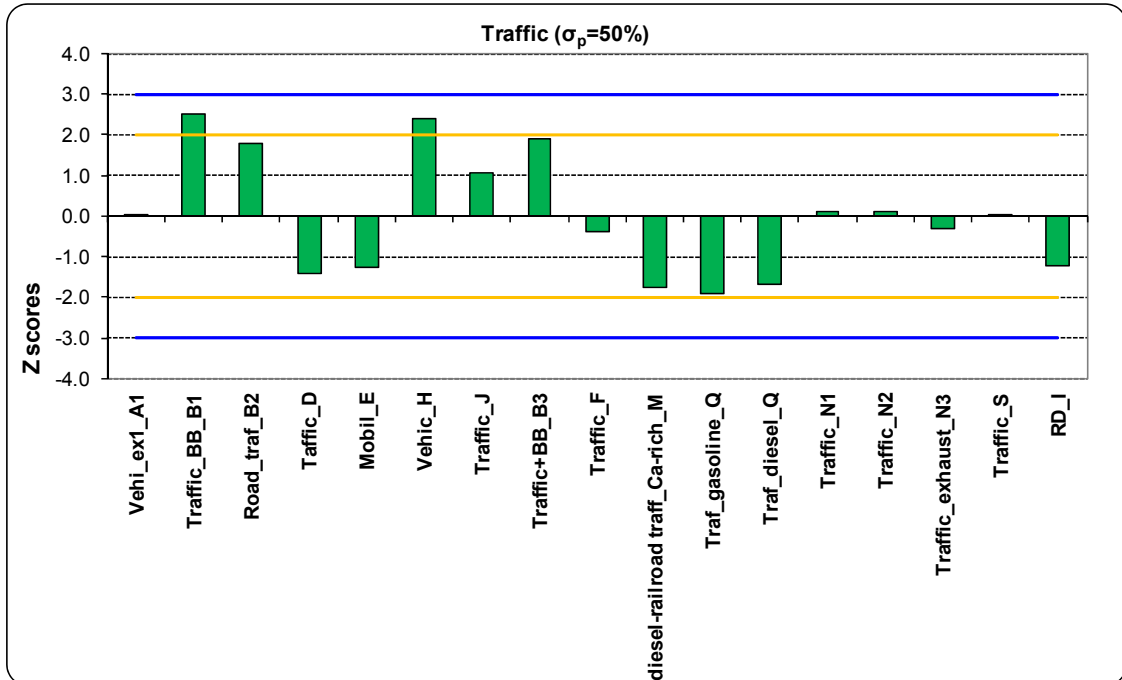


Figure 10.1.5: Z-scores of the factor/source profiles in the Traffic source category..

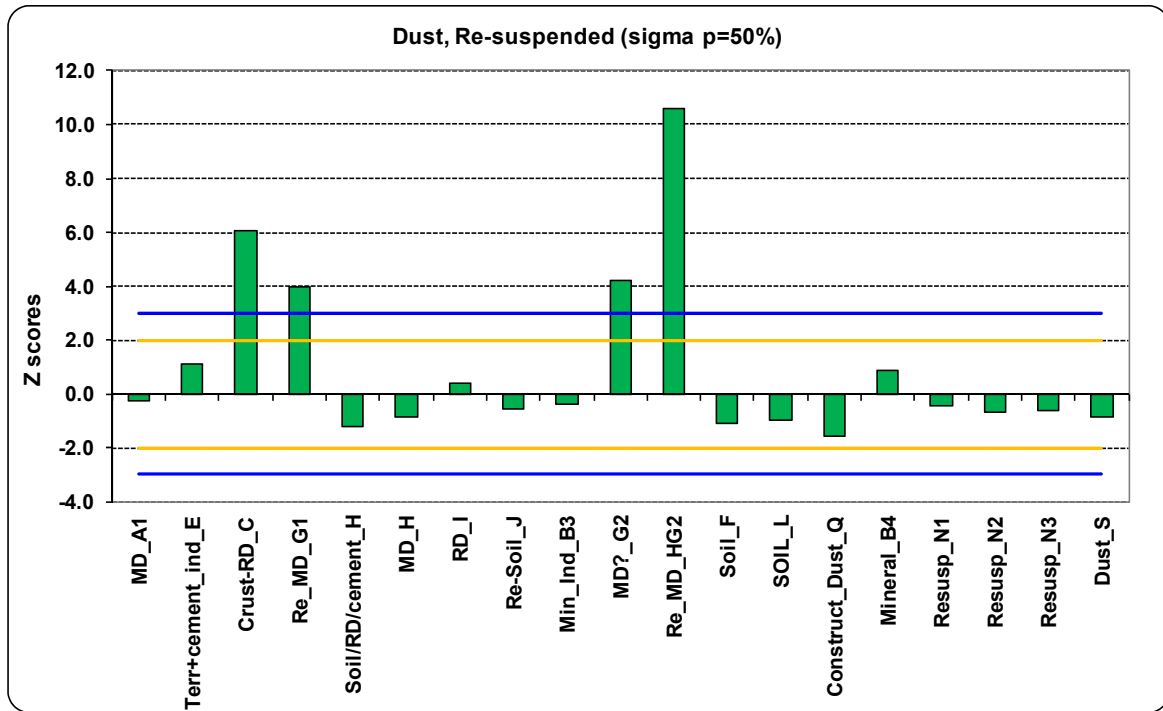


Figure 10.1.6: Z-scores of the factor/source profiles in the Dust/Re-suspended soil source category.

The test performed for Dust, Re-suspended soil source category shows that the SCE of **Crustal-RD_C**, **Re_MD_G1**, **MD?_G2** and **Re_MD_G2** are clearly unsatisfactory. All the remaining factor/sources are within the limit of acceptability (Figure 10.1.6).

The source categories Secondary (Figure 10.1.7), Sulphate (Figure 10.1.8), and Nitrate (Figure 10.1.9) show all the factor/sources within the limit of acceptability.

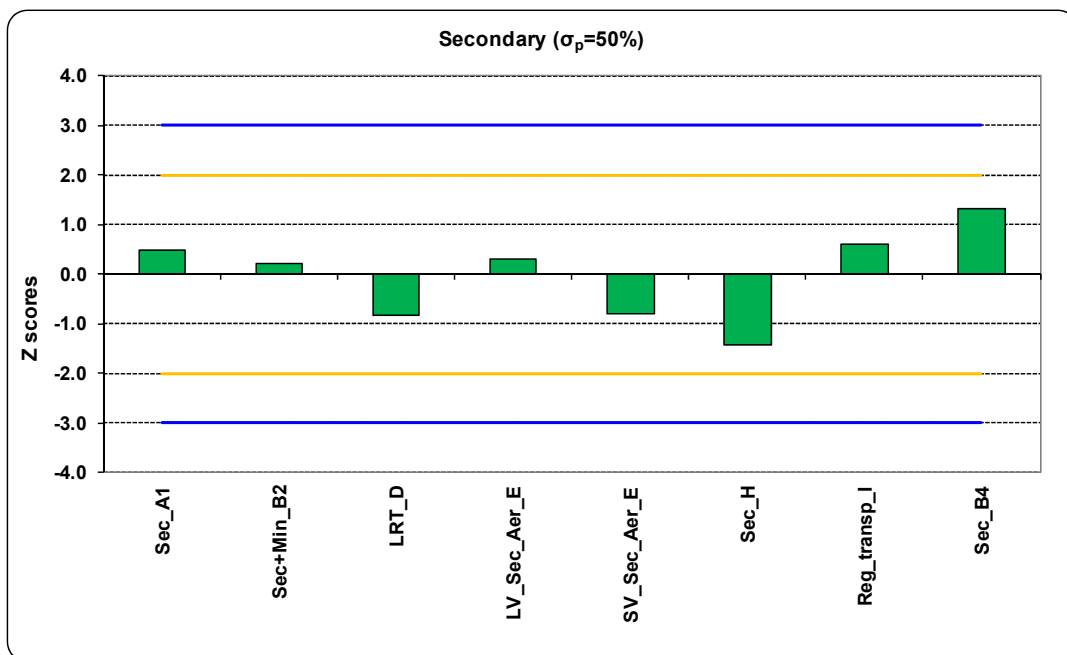


Figure 10.1.7: Z-scores of the factor/source profiles in the Secondary source category.

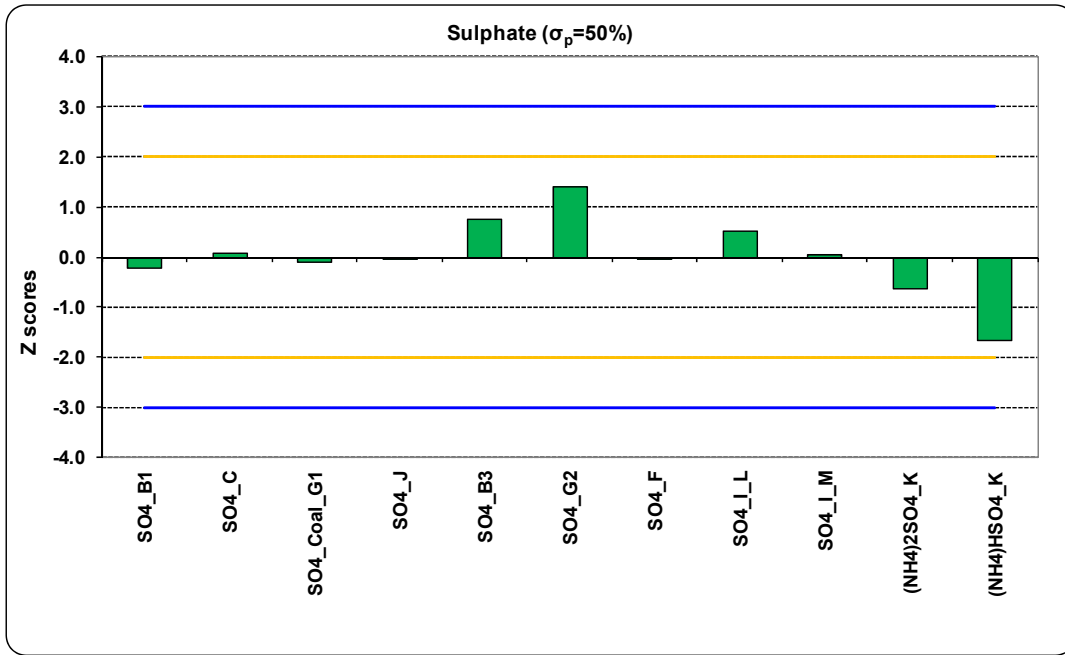


Figure 10.1.8: Z-scores of the factor/source profiles in the Sulphate source category.

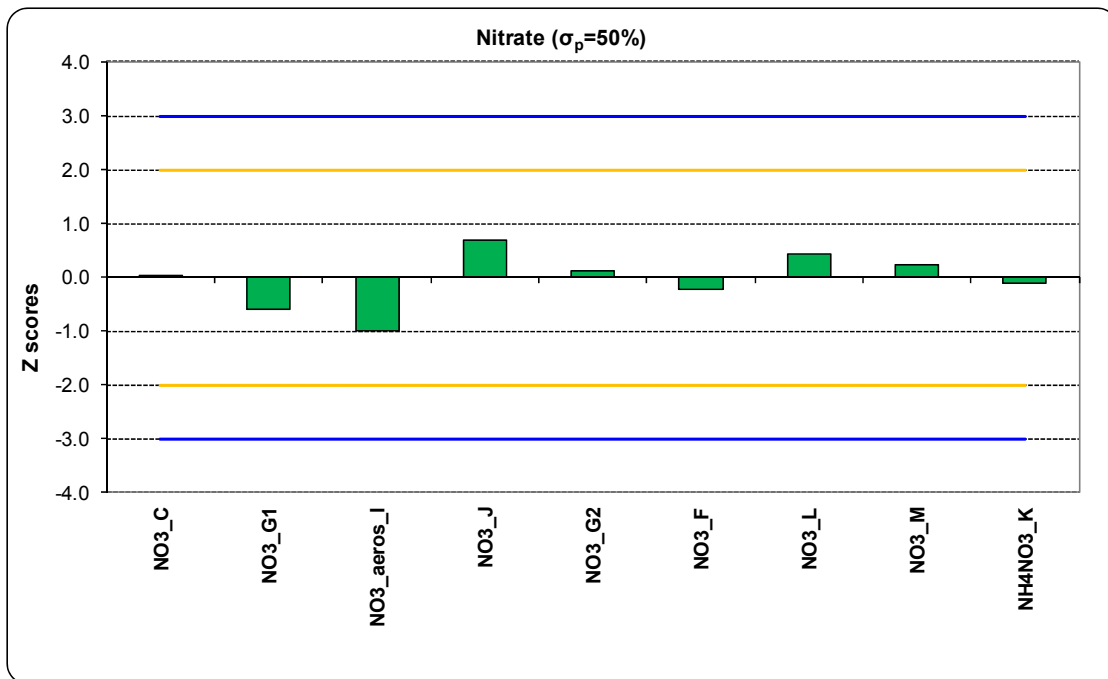


Figure 10.1.9: Z-scores of the factor/source profiles in the Nitrate source category.

Zinc smelter source category contains only the factor: **Zn_smelt_G2** marked as unsatisfactory (Figure 10.1.10).

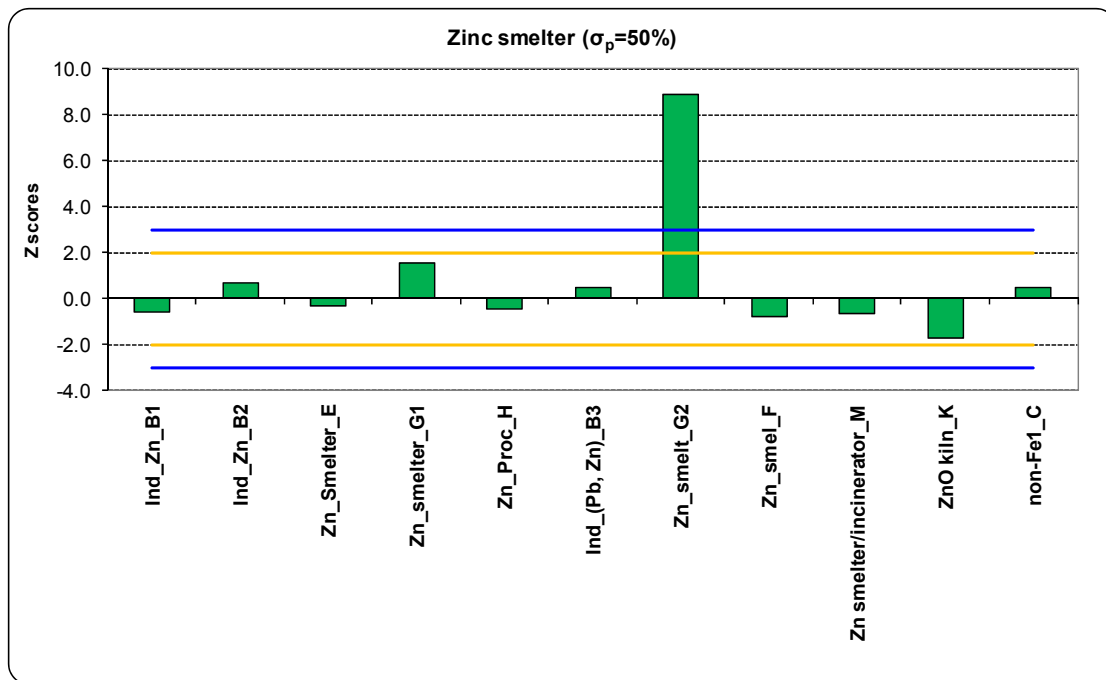


Figure 10.1.10: Z-scores of the factor/source profiles in the Zinc smelter source category.

SCEs for Lead metallurgy source category are all within the acceptability area (Figure 10.1.11). With the exception of **Cu_manufact_G2**, similar behavior is observed for the Copper metallurgy (Figure 10.1.12) and Steel processing SCEs (Figure 10.1.13).

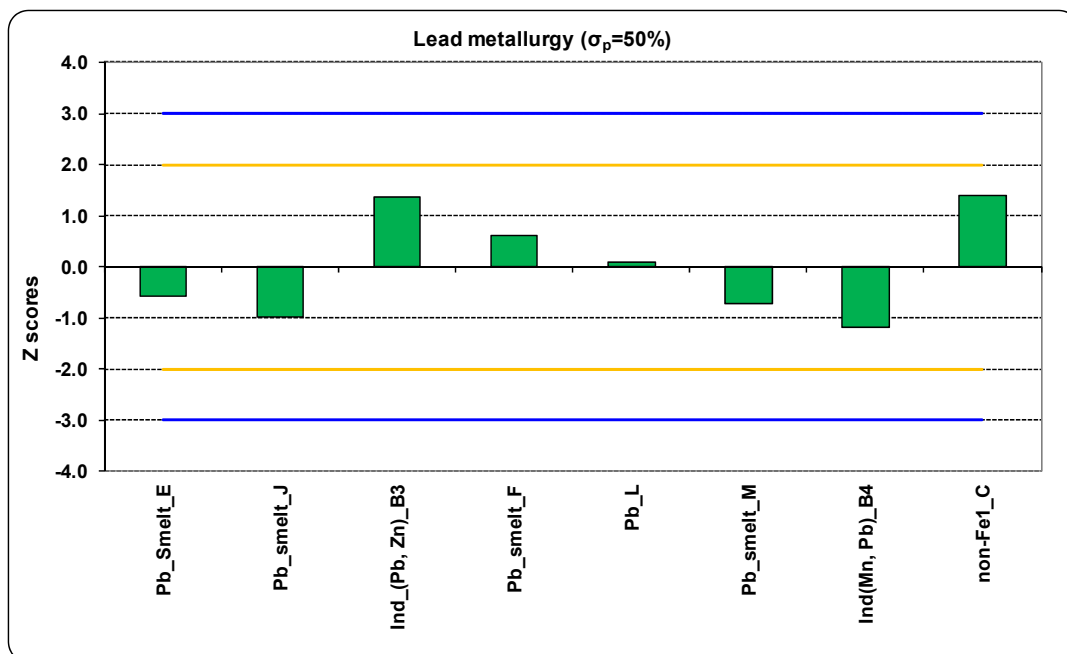


Figure 10.1.11: Z-scores of the factor/source profiles in the Lead metallurgy source category.

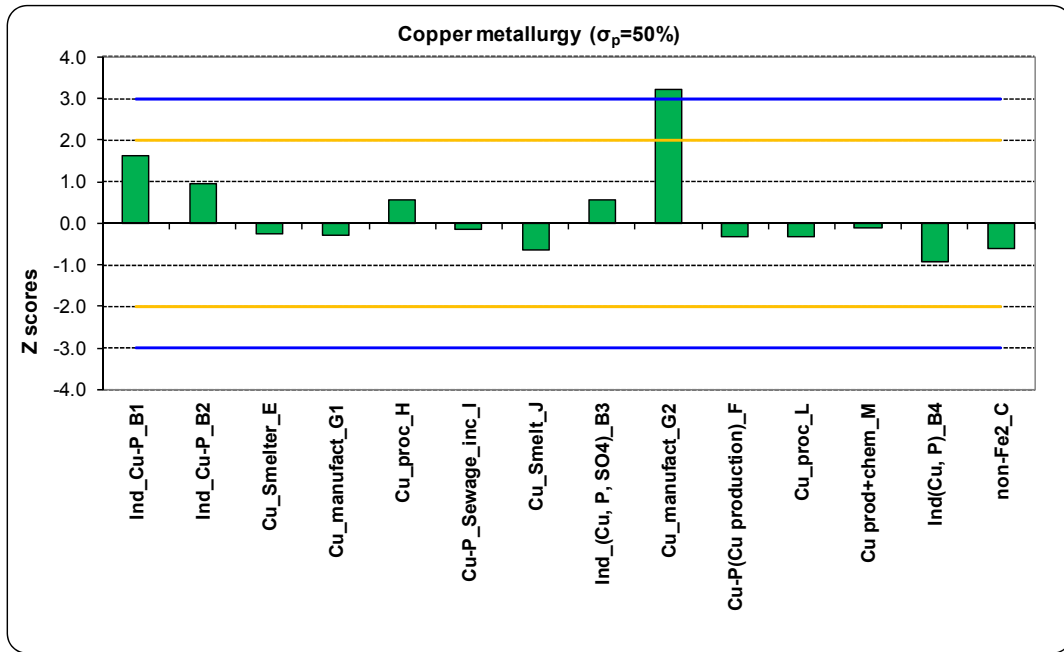


Figure 10.1.12: Z-scores of the factor/source profiles in the Copper metallurgy source category.

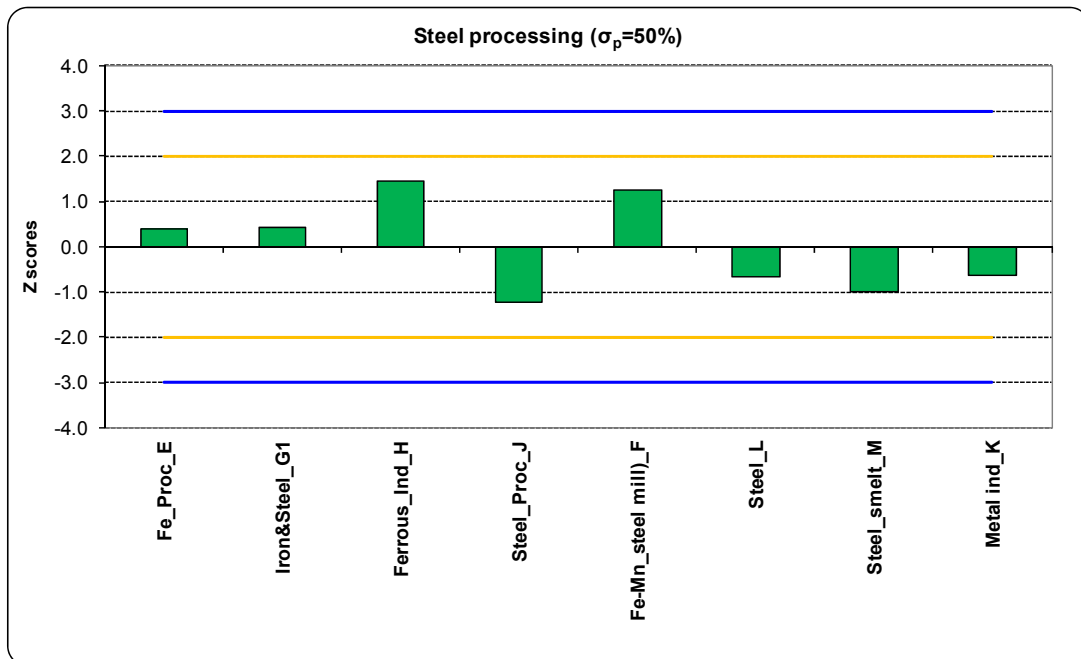


Figure 10.1.13: Z-scores of the factor/source profiles in the Steel processing source category.

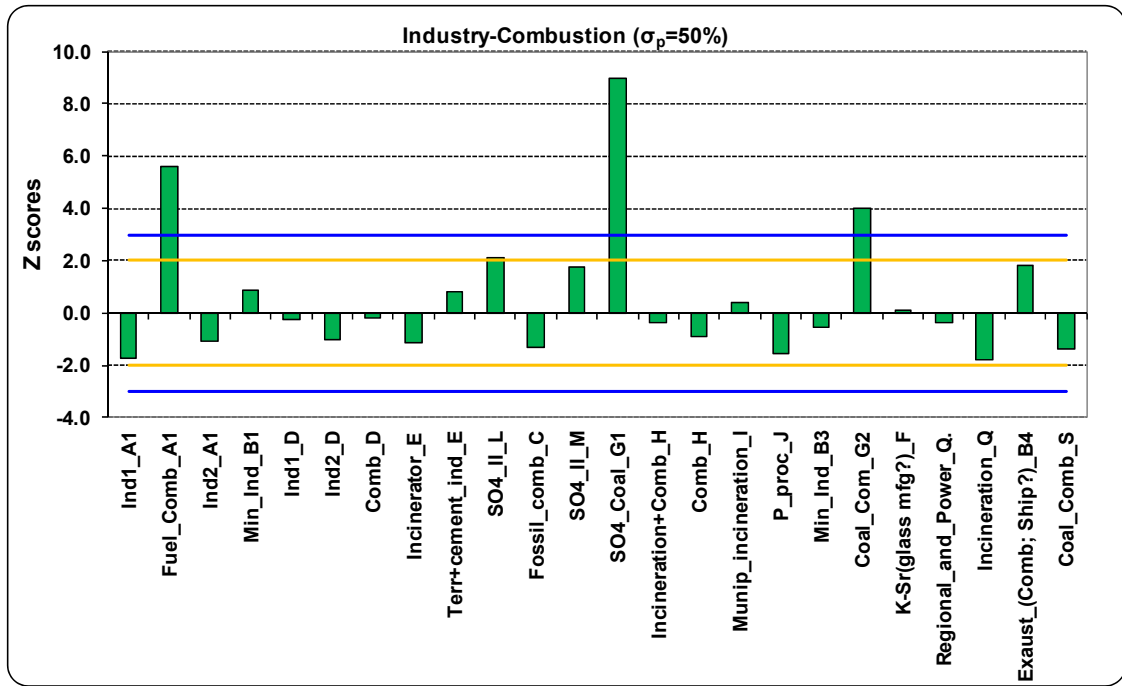


Figure 10.1.14: Z-scores of the factor/source profiles in the Industry-Combustion source category.

The test for factors/sources in the Industry-Combustion source category shows that **Fuel_Comb_A1**, **SO4_Coal_G1** and **Coal_Ind_G2** are marked as unsatisfactory due to the overestimation of the source contribution (Figure 10.1.14).

The results of the preliminary tests on the factor/sources of the Ship emission source category indicated that many of them were not eligible for this source category. Due to the limited number of profiles in this source category no test on the SCE was performed.

10.2 Summary statistics of z-scores by participant and by model

In this section are summarized all the z-scores obtained in the evaluation of the source contribution estimations (SCE) of all factor/source profiles (See Chapter 6). In the summary graphs the results are grouped either by solution or by model.

In order to assess the influence of the preliminary tests, that were used to establish whether a given factor/source profile belongs to a source category, the results are present in two ways: a) including all the reported profiles, and b) including only the profiles that passed the preliminary tests.

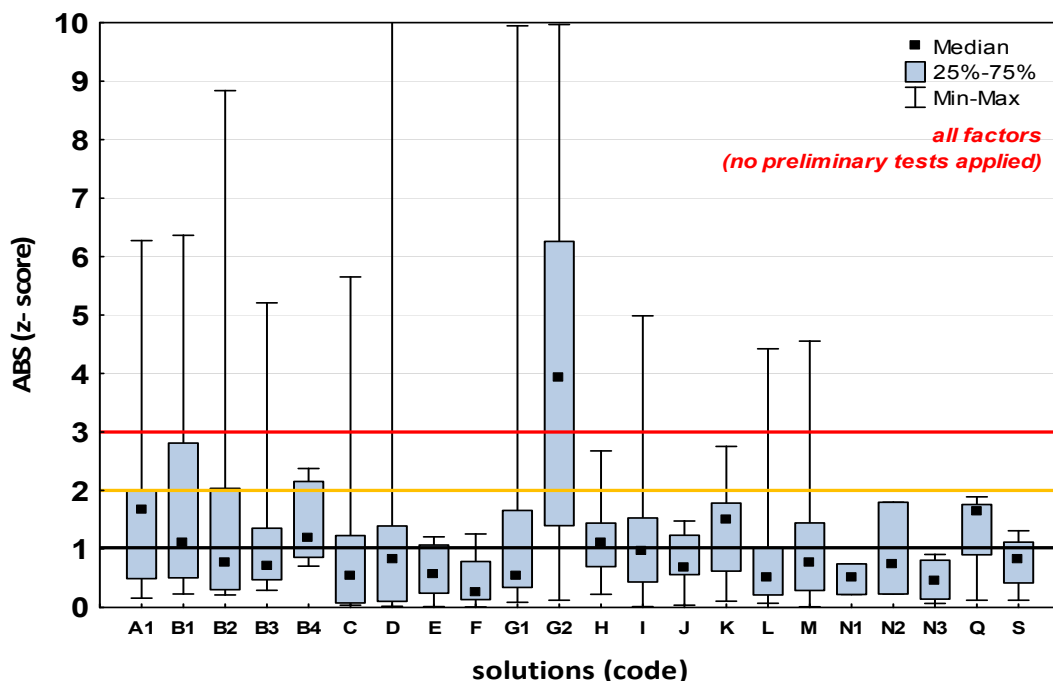


Figure 10.2.1. Boxplot summary of all performance tests calculated for all factor/source profiles and grouped by solution. ABS (z-scores) = absolute z-scores.

Figure 10.2.1 displays a boxplot with the absolute z-scores (without sign) grouped by participants' solutions (22) labeled with codes (Section 7). This analysis considers all the profiles reported by participants. The majority of the solutions (15) present z-scores median values falling in the optimum zone (<1). The whole interquartile range remains within the optimum zone in five solutions: E, F, L, N1 and N3. A total of 21 solutions show the median values in the area of acceptability (<2) while the median value of solution G2 fall in the area of rejection (Figure 10.2.1).

The interpretation of the boxplot of the absolute z-scores grouped by model should be made with caution due to the different number of solutions for every model. There is a considerable number of solutions for the PMF variants while the other models include a limited number of them. Figure 10.2.2 shows optimal median z-scores for **EPA PMF 3.0**, **PMF2** and **CMB**. Median z-scores fall in the area of acceptability for all models.

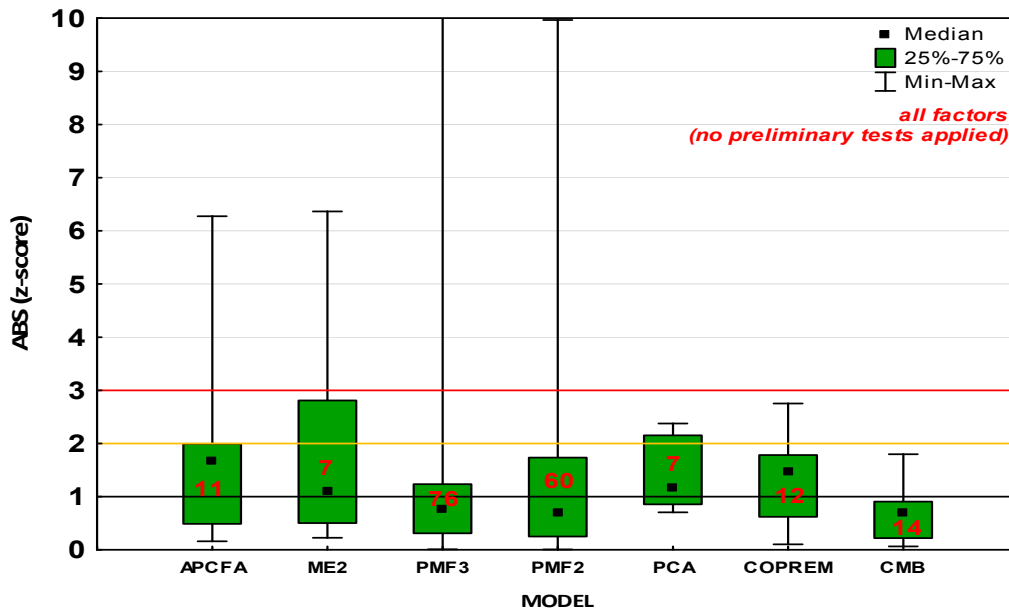


Figure 10.2.2: Boxplot summary of all proficiency tests, grouped by model, calculated for all the factors/sources reported by participants (number of tested factors/sources in red).

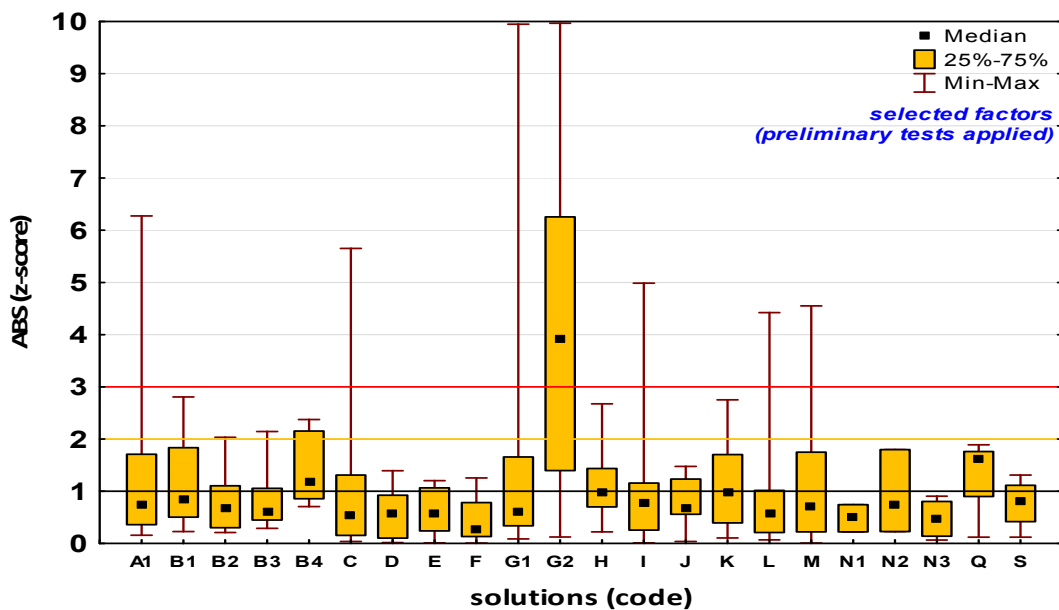


Figure 10.2.3. Boxplot summary of all performance tests, grouped by solution, calculated only for factor/source profiles that passed the preliminary tests.

Figure 10.2.3 displays a boxplot with the absolute z-scores, grouped by participants' solutions, of the profiles that have passed the preliminary tests.

The general picture is comparable to the one observed in figure 10.2.1. Nevertheless, a more detailed analysis reveals that solutions A1, B1, B2, and B3 improves their performance due to the elimination of extreme values and the shrinking of the interquartile range. For B1 and B2 this determines the interquartile range to be fully within the acceptability area. In these cases the identification and exclusion of mixed or misclassified profiles was effective to prevent distortion in the analysis.

Figure 10.2.4 presents the z-scores of profiles that passed the preliminary tests grouped by model. As for the solutions improvements are observed with respect to the unselected factor plot. In this plot, models APCS, ME2 and COPREM fall in the optimum area (<1) and interquartile ranges within the acceptability area (<2). PCA is the only model with z-scores median not falling in the optimum area (<1) and part of the interquartile range in the warning area. The interpretation of the boxplot of the absolute z-scores grouped by model should be made with caution due to the different number of solutions for every model.

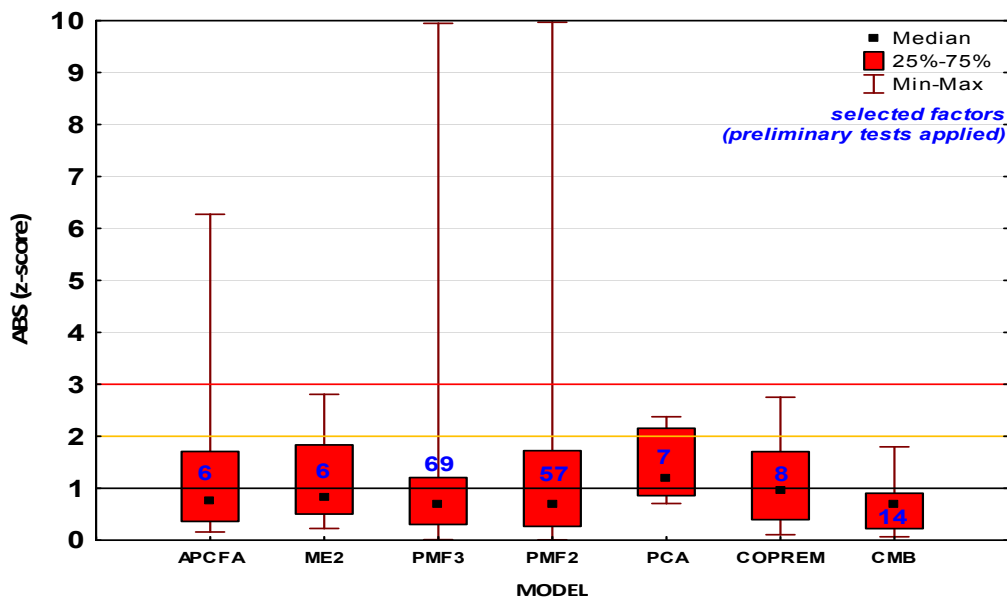


Figure 10.2.4: Boxplot summary of all proficiency tests, grouped by model, calculated only for source/factor profiles that passed the preliminary tests (number of tested factors/sources in blue).

A total of 182 factor/source profiles were reported by participants, two of which could not be attributed to any source category. Some profiles were tested in more than one source category. On the basis of the preliminary tests, 18 source profiles were rejected and two were rejected for one source category and accepted for another.

Of the 167 z-scores calculated for factor/source profiles in the performance test, 144 (86%) are acceptable, 10 (6%) are questionable and only 13 (7%) are unsatisfactory.

11. Number of factor/sources

The number of factor/sources reported in the different solutions vary between 6 and 13 (Figure 11.1). Unfortunately, there is no reference value for this parameter since the exact number of sources in a real-world dataset is unknown.

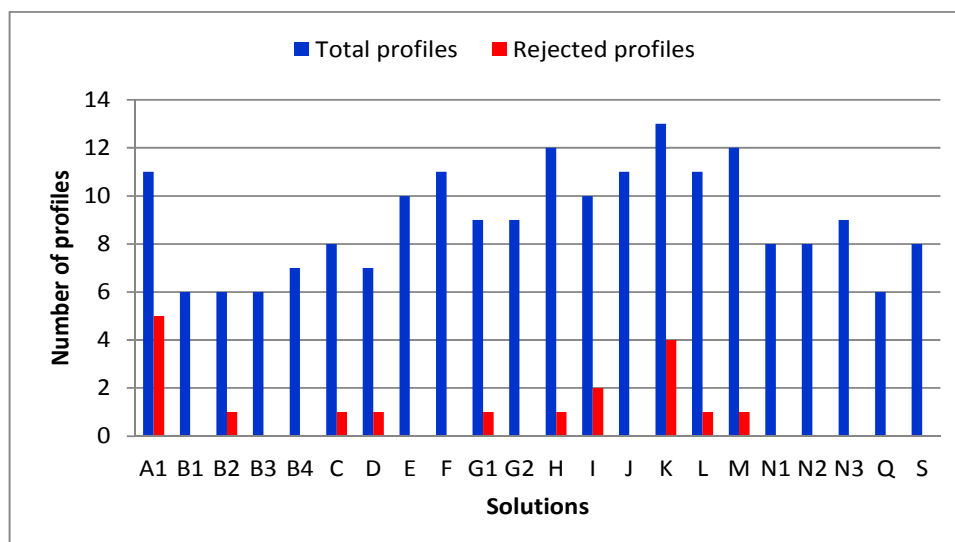


Figure 11.1 Total number of factor/sources reported in each solution and number of rejected profiles (CMB solutions include real and estimated sources).

The reference paper by Lee et al. (2006), in which the source apportionment was made using PMF on the inorganic species, reports 10 sources. If we pool all the solutions reported in this intercomparison the average number of factor/sources per solution is 9.0. Nevertheless, if we observe data grouped by model (Table 11.1) emerges that CMB solutions have on average 8.3 sources while factor analysis based models present on average 9.2 factor/sources.

Although the differences between models are small there are considerable differences between participants suggesting that the methodology applied by different practitioners has an impact on this parameter (see also Annex A).

MODEL	Total profiles	Solutions	Profiles per solution (avg.)	Rejected profiles (n)	Rejected profiles (%)
APCS	11	1	11.0	5	45
ME2	6	1	6.0	0	0
EPA PMF3	73	8	9.1	6	8
PMF2	55	6	9.2	3	5
PCA	7	1	7.0	0	0
COPREM	13	1	13.0	4	31
CMB	33	4	8.3	0	0

Table 11.1: Number of factor/source profiles reported for each model.

Concerning the reliability of the factor/sources, all those of the CMB passed the preliminary tests while the PMF variants show between 5 and 8% of rejected factors. The highest proportion of rejected factors is observed in APCS and COPREM (45% and 31%, respectively).

12. Conclusions

Obtaining a real-world database with all the necessary information and the appropriate quality standards was one of the most challenging tasks in the organization of this intercomparison. On this regard, a special acknowledgment goes to P.K. Hopke, J.J. Schauer and J.R. Turner for having made available unique data that constituted the basis for this exercise.

The new methodology demonstrated to be effective to quantitatively assess model performances. In particular, the performance test used for the evaluation of the intercomparison proved to be suitable to test the comparability between factors/sources on the basis of their fingerprints and time trends.

Nevertheless, due to the nature of real-world data it was possible only to evaluate each solution against the other solutions of the same category.

The test results indicate a good quantitative agreement between the source contribution estimation of the reported solutions. More precisely, an 86% of the factors/sources met the acceptability criteria indicating that the solution bias was consistent with the 50% standard uncertainty acceptability criterion. Moreover, many of the factors/sources reported by participants were comparable with those described by Lee et al. (2006) in the original publication of the source apportionment on the same database, using only inorganic species.

In the complementary tests was observed a considerable variability in the number of factors/sources between solutions but not between models. The average number of solutions was close to the one reported in the mentioned article by Lee et al.

Although some solutions over or underestimated total PM gravimetric mass, many of them reconstructed it satisfactorily.

These two tests are, however, to be considered a complement of the main performance test since a) the ability to reproduce the PM mass is a prerequisite but tells little about the accuracy in the source identification and quantification, and b) the actual number of sources is unknown in a real-world dataset and, therefore, there is no absolute reference value to evaluate this parameter.

In this exercise, EPA-PMF 3.0 and PMF2 were the most commonly used models and those with the best performances. Also CMB, showed a satisfactory performance. APCS, COPREM and ME-2 presented a satisfactory performance only after the exclusion of rejected profiles. PCA is the only model presenting the mean z-score above 1 and the upper quartile in the warning area. Nevertheless, it is not possible to draw conclusions about the performance of models that were used only in one or two solutions. More intercomparisons would be necessary to gather complete information on the performance of more models.

In order to put all participants at the same level, the database was distributed with some ancillary data but without disclosing the site and the sampling time. This choice put participants under conditions more difficult than those they find in current practice and was particularly critical for those applying the CMB method. On the other hand, this gave the chance to participants to demonstrate that on average they have good skills to deal with noisy and complex data.

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Annex A: Questionnaire and Future work

With the aim of investigating the connections between participant's methodological choices and results, a questionnaire about preliminary data treatment key tasks accomplished during model execution, and interpretation of results was distributed to them after the submission of the results.

The questionnaire also invited participants to give feed-back about the intercomparison organization and methodology.

The outcomes of these questionnaires are summarized in Tables A.1, A2.2 and A3.3.

Input data treatment	n. participants
Replacement of missing values with average values	11
Exclusion of missing values	1
Replacement of BDL values with MDL/2	11
Selection of species with the criterion S/N or <BDL	8
Recalculation of the uncertainties (extra down-weighting)	8
Identification of outliers	1
Add up EC and OC steps	5

Table A.1: Procedures used by the participants for data treatment prior running receptor models.

Most of the participants declare to use the Polissar's approach for DB data pre-treatment (Polissar et al., 1998). About one half of them claim to have performed species selection and/or to have recalculated the uncertainties.

Receptor modelling tasks	method	n. participants
Determination of the number of factors	$Q_{\text{robust}}/Q_{\text{theory}}$	4
	G space	2
SCE uncertainties	bootstrapping	14
	Standard dev. of computed factors	2
Rotational uncertainty check	Fpeak	2
Factor labeling	Source profiles from literature, SPECIATE	16
	Factor profiles from literature	16
Assessment of SCE	Analysis of scaled residuals	16
Validation of SCE	Correlation between source profiles and observed total mass vs. calculated total mass	16

Table A.2: Specific tasks performed by the participants during receptor modelling analysis.

All participants reported the methodology used to perform mandatory tasks like: estimation of output uncertainties and factor labeling. All declared also to have accomplished quality assurance and validation tests.

The determination of the number of factors is the one, among the key tasks, that received less attention by participants. Only 6 participants declare to have performed this operation. This may be associated with their difficulty to find a reference value for this parameter. Such methodological shortcoming revealed by the questionnaire matches the high variability in the number of factors retrieved in the reported solutions (Chapter 11).

Remarks from participants
Missing meteorological data: wind direction, temperature, humidity height of mixing layer
Data uncertainties were judged either too low or too high
Missing relevant chemical species such as: Na, Cl, Sb for marine and traffic sources
PAHs could be excluded
Missing identification of the sampling site
Preferred to have received non-pre-treated data
Additional info was only provided after participants' request
Difficult recalculating the uncertainties because of not clear identification of the geometric mean and no matching with the MDLs.

Table A.3: Remarks rose up by the participants after completing receptor modelling analysis.

Remarks from participants were of great help to assess the methodology used in the intercomparison and will be taken into consideration in the organization of future exercises. The next step is to organize an intercomparison exercise using a **synthetic database**. The advantage of this approach is the availability of known source profiles and contributions to be used as reference in the assessment of participants solutions.

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Abstract

Receptor models are commonly used to identify the sources of ambient particulate matter (PM) in Europe. However, the use of different tools and methodological approaches make it difficult to compare the results of different studies.

In order to promote harmonization in this field, an intercomparison exercise was organized and evaluated by the JRC with the collaboration of European experts in 16 institutions.

The test database consisted of 178 PM_{2.5} speciated samples deriving from two real-world re-arranged DB

Participants were asked to scrutinize the database in order to identify, solve and report typical imperfections of real world DBs (missing values, values below detection limits, outliers, unusual uncertainty patterns, etc...).

The reported solutions included the number and label of the identified sources, their contribution estimation (SCE) and uncertainty. The exercise was evaluated using a new methodology developed on purpose.

The majority of the solutions reconstructed the PM mass satisfactorily while the number of sources identified in the different solutions was variable. The correspondence of every source/factor to a source category was checked by comparing its chemical profile and time trend with all the other members of the same category and with reference source profiles, when available. The SCEs of the different solutions were compared with a reference value obtained by robust analysis (standard ISO 5725-5). The acceptability criterion was set to 50% standard uncertainty. More than 90% of the 182 tested profiles passed the preliminary tests and 86% of the assessed source/factor contribution estimations met the acceptability criterion. This result indicates a good general agreement between the performances of the different participants and models.

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new standards, methods and tools, and sharing and transferring its know-how to the Member States and international community.

Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security including nuclear; all supported through a cross-cutting and multi-disciplinary approach.

