Source Apportionment of Urban Road Dust Using Four Multivariate Receptor Models

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Source Apportionment of Urban Road Dust using Four Multivariate Receptor Models

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Abstract

Road dust is one of the biggest contributors to airborne particulate matter (PM) in many urban regions. Due to the inherent heterogeneity of road dust, it is important that its sources are identified and mitigated. Multivariate receptor models are used for source apportionment of PM in many cities. In recent years, these receptor models are finding more applications outside the scope of PM source apportionment. In this study, four multivariate receptor models (Unmix, Positive Matrix Factorization, Principal Component Analysis and Multiple Curve Regression) are used for source apportionment of road dust at Vellore City, India. The elemental composition of road dust samples from 18 locations and for three seasons (summer, winter, and monsoon) are measured using acid digestion followed by Inductively Coupled Plasma - Optical Emission Spectroscopy. Irrespective of models, results showed that crustal material (100% - 68%) and resuspended road dust (82% - 15%) are the biggest contributor to road dust in the study region. Brake wear, tire wear, biomass combustion, vehicular emission and industrial sources are some of the other sources identified by the receptor models. Receptor modeling performance of MCR and PCA models are unsatisfactory. PMF and Unmix models gave acceptable results. From comparing the performance characteristics, Unmix is found to be the ideal receptor model for this dataset. This research clarifies the constraints of different receptor models and the source apportionment information obtained is critical for development of future policy and regulation.

Keywords: Road dust; Receptor model; Source apportionment; Resuspended dust; Elemental composition.

1. Introduction

Chemometric methods of data analysis is a cornerstone for air pollution control in urban environments (Azid et al. 2015). Isolating and quantifying the contribution of various sources to pollution at a location is one of the most common applications of chemometrics in environmental data. This is commonly referred to as receptor modeling (Devi and Yadav 2018). Receptor modeling started gaining popularity during the mid-2000s and continues to be a major player in urban air quality management (Zhang et al. 2017). These models reconstruct the contribution of individual sources to pollution in a region using the ambient pollutant concentration information (Henry et. al., 1984) and are frequently used for source apportionment of particulate matter (PM) emissions (Heo et al. 2009).

Road dust is consistently seen in source apportionment studies irrespective of study location (Belis et al. 2014). Road dust is the loose, mostly crustal material settled in road surfaces that is resuspended by the action of wind or wake from vehicular movement (Abu-Allaban et al. 2003; Amato et al. 2009). Combustion and non-combustion vehicular emissions such as exhaust emissions, tire wear, brake wear and engine wear are the common source of road dust in urban environment (Denby et al. 2018). Non-vehicular sources of road dust include crustal material transported by wind (Mao et al. 2013), construction and demolition activities (Marín et al. 2011) and street sweeping (Amato et al. 2010). The heterogenous nature of road dust impacts human health necessitating effective qualitative and quantitative apportionment of the sources. This information is needed to develop effective control and mitigation strategies to reduce morbidity from exposure to road dust (Bartkowiak et al. 2017).

Toxicological studies have noted that these sources of road dust can release dangerously high amounts of potentially toxic elements (PTEs) (Arslan 2001) and polycyclic aromatic hydrocarbons

(PAH) (Khpalwak et al. 2019). Many of these chemicals are also classified as "probably carcinogenic to humans" by the International Agency for Research on Cancer (IARC 2020). Studies show that children are at a greater risk of being exposed to high concentration of PTEs and PAH since they spend a greater portion of their day outdoors (Zeng et al. 2019). Developmental disorders like impaired mental development (Isaac et al. 2012) and stunted growth (Zeng et al. 2019) are common in children exposed to elevated concentrations of PTEs.

Source apportionment of PM is studied extensively in research from around the world (Banerjee et al. 2015). However, application of these receptor models in source apportionment of road dust have garnered considerably less attention. Cities in developing countries tend to see even fewer studies. This is alarming because many of the world's most polluted cities are in developing countries, especially in South Asia. Vellore is a small tier - 2 city (MHRD 2015) in the South Indian state of Tamil Nadu. The city is spread over a land area of 87.92 km^2 and has a population of 177,230 (as per 2011 Census). For a semi-arid land locked city like Vellore, road dust is a major cause of concern. In this study, the results from four receptor models are compared viz., Unmix, Positive Matrix Factorization (PMF), Principal Component Analysis – Multiple Liner Regression Analysis (PCA-MLRA), and Multiple Curve Regression – Alternating Least Squares (MCR-ALS). The major objectives of this study are, (1) Identifying and apportioning the sources of road dust in the city, thereby helping future endeavors in regulation and policy, (2) Recognizing the constraints of different receptor models used in this study, and (3) Most importantly, this research could prove to be instrumental in reinvigorating receptor modeling studies on road dust.

2. Methodology

2.1. Sample Collection and Analysis

Figure 1 shows the sampling region and sampling locations. Deposited dust samples from the road surface are collected from 18 locations within Vellore City. Table 1 shows the various sampling locations. More information on the sampling region is explained in Jose and Srimuruganandam (2020). Road dust samples are collected from 27th and 28th of January 7th and 8th April and 22nd and 23rd May of 2018 corresponding to Winter, Summer and Monsoon Seasons. Vellore city does receive summer rains towards the end of May and early June. The samples for monsoon season are collected towards the end of May a proxy for monsoon season since rains are unceasing during monsoon season, which makes it nearly impossible to collect samples. The samples for monsoon season were collected after two weeks of sporadic rains. Approximate weights of the samples were taken in situ using a generic weighing balance. The weighed samples are then sieved manually as per ASTM C136 (ASTM 2001). The portion of the sample that passed through 75μm sieve is subjected to microwave digestion using a mixture of HCl and HNO_3 as per U.S.EPA 3050b procedure (U.S. EPA 1996) for direct energy coupling devices. The digested samples are analyzed for 25 elements (Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, Zn) by Inductively Coupled Plasma - Optical Emission Spectroscopy (Perkin Elmer, Avio - 200). Detailed information on sample collection, sample analysis and quality control can be found in Jose and Srimuruganandam (2020).

[INSERT FIGURE 1]

[INSERT TABLE 1]

2.2. Multivariate Analysis

In this study, the efficacy of four different multivariate receptor models for source apportionment of road dust are examined viz., PCA-MLRA, Unmix, MCR-ALS, and PMF.

PMF model is performed using pre-compiled binary available for Microsoft® Windows operating system from U.S. EPA. EPA-PMF v.5.0 is used for this study. The software is run atop Microsoft® Windows 10 (OS build 18363.836).

Pre-compiled binary for Unmix is available for Microsoft® Windows operating system from U.S.EPA. EPA-Unmix v.6.0 is used for this study. Since this binary is incompatible with modern operating systems, it is run in an Oracle VirtualBox virtual machine instance (1 logical processor and 1 GB RAM) on Microsoft® Windows XP (SP3).

MCR-ALS is performed using R, an open-source statistical modeling package (v.3.6.2) coupled with RStudio (v. 1.2.5) interactive development environment (IDE). ALS library available from the Comprehensive R Archive Network (CRAN) repository is used in this model.

Like MCR-ALS method, PCA-MLRA is done using R, (v.3.6.2) coupled with RStudio (v. 1.2.5) IDE. PCA and MLRA are done using functions available by default in R (prcomp and lm).

All receptor modelling processes in this study are performed on a ThinkPad T430 Personal Computer (Intel Core i5- 3320M 2.60GHz, 8GB RAM). A brief explanation on various multivariate receptor models used in this study is given below.

3. Theory of Receptor Modeling

Receptor models are mathematical model that are used to identify and quantify the contribution of different sources of a pollutant at a receptor location. These models use the chemical composition of a pollutant at a receptor location to identify its sources. This is in stark contrast to source-oriented models where the concentration at a receptor location is estimated if the properties of the source and meteorological conditions are known. The major advantage of using receptor model is that they use real measured ambient pollutant concentrations.

Most receptor models work by factoring a large concentration data matrix into two lower rank matrices. Since the number of samples are always greater than the number of variables, these equations cannot be solved uniquely. Receptor models are used to obtain the best possible solution. The difference between receptor models depends largely on the various approaches and constraints employed by these models to get a valid solution (Henry 1991). Since the value of concentration cannot be negative, non-negativity of mass concentration is a constraint used consistently in receptor models (Belis et al., 2014). However, non-negativity alone is seldom enough for a complete solution. Many other constraints are considered in modern receptor models like; measurement uncertainty, factor rotation and multi-dimensional edge detection (Pant and Harrison 2012). In this study, source apportionment of road dust collected from Vellore city of South India is studied by using different multivariate receptor models.

Meta-analysis of source apportionment conducted all over Europe show that the number of receptor modelling studies is more than all other source apportionments methods combined (Belis et al. 2014). Compared to other source apportionment methods, the location-first approach of receptor modeling makes them ideal to assess the compliance of a receptor location to air quality limits. Receptor-oriented models do not consider complex chemical and meteorological processes. These models therefore have very modest computational requirements compared to source-oriented models. Multivariate receptor models also negate the need for emission inventories thus reducing uncertainties related to it (Hopke 2016). The inability of model reactive species limits the use of receptor models to regional or urban scale. Application of receptor models necessitates the availability of quantitative data at the receptor and demands good knowledge of the atmospheric conditions and chemical nature of sources from the researcher.

It is hard to establish a minimum number of samples in advance, since that number would be dependent on the amount of information within the data set (Belis et al. 2014). Studies show that at least 50 chemically characterized samples are needed to run multivariate analysis. (Johnson et al., 2011). Other studies also mention that the number of samples should be approximately three times the number of variables (Thurston & Spengler, 1985). Also, small datasets from multiple sites in a region are used in previous source apportionment studies (Xie et al., 2012). All multivariate factor analysis works on the principle of matrix factorization (Hopke 2016). This can be expressed mathematically by the expression.

$$C_{(m\times n)} = G_{(m\times p)} \times F^{T}_{(n\times p)} + E_{(m\times n)} \quad (1)$$

where, the matrix *C* is the concentration of *n* elements collected at *m* locations, *F* is the factor matrix with *n* elements and *p* factors, *G* is the mass concentration matrix with *m* observations and *p* factors. The matrix *E* has information on the residuals from the model caused due to experimental and measurement errors. Different receptor models apply different constraints to *F* and *G* matrices to minimize the residuals in the *E* matrix.

3.1. Unmix

The Unmix method is a multivariate model with built-in non-negative constraints. It begins with singular variable decomposition (SVD) of the concentration matrix *C* and is represented by the equation below (Henry 2003).

$$C_{ij} = \sum_{i=1}^{p} \sum_{k=1}^{p} U_{ik}\, D_{kl} V_{lj} + E_{ij} \quad (2)$$

where C_{ij} is the input data, *U* and *V* are orthogonal $n \times n$ and $m \times m$ matrices. *D* is an $n \times m$ diagonal matrix. The Unmix model uses SVD to find the edges in an *m*-dimensional data space and reduce the dimensionality of data from *m* to *N*, where n is the number of sources identified.

Equation 2 is like the general receptor model equation (Equation 1). The exception is that in normal chemical mass balance approach, source composition is already known.

One of the major advantages of using Unmix model is that it has the non-negativity criteria build into model. This negates problems arising from negative mass concentrations. Also, since this model extracts all required constrains to solve the chemical mass balance equation from the data itself, measurement uncertainties are not required to run this model. However, since the model uses eigen vector analysis, it is not well suited for heteroskedastic data commonly seen in atmospheric modeling.

3.2. PCA

PCA is an eigen vector method of matrix factorization that is used to reduce many possibly correlated variables into a smaller number of uncorrelated principal components. In PCA method, the total concentration of each element *i* is assumed to be a sum of the elemental contribution from the different elemental sources *j*. Thus, a normalized concentration matrix can be written as,

$$Z_{ik} = \sum_{p}^{j=1} W_{ij} P_{jp} \quad (3)$$

Equation 2 can be rewritten in matrix terms as an analogue to equation 1 as,

$$[P]_{j\times\lambda} = [B]_{j\times i}[Z]_{i\times\lambda} \quad (4)$$

This equation (3) is now equivalent to equation (1). The matrix $[P]_{j\times i}$ is factorized based on eigen value decomposition. Absolute Principal Component Scores are calculated by subtracting an absolute zero principal component matrix from $[P]_{j\times i}$ matrix as shown in equation (4) (Thurston and Spengler 1985).

$$[APCS]^{*}_{p\times j} = [P]^{*}_{p\times j} - [P_o]^{*}_{p\times j} \quad (5)$$

Later, mass distribution for each day is calculated by multiple linear regression analysis of the APCS to total mass for each day as shown in equation (5).

$$M_k = \zeta_0 + \sum_{j=1}^{p} \zeta_j APCS_{jk}^{*} \quad (6)$$

Like Unmix, PCA model extracts all required constrains to solve the chemical mass balance equation from the data itself, measurement uncertainties are hence not used in this model. Also, PCA method does not require any specialized software. Many commercially available and open-source statistical packages have PCA model build into them. PCA is also an eigen vector decomposition method. Hence, the problems with heteroskedastic data haunts PCA. Unlike Unmix, PCA has no build in non-negativity constraints. This omission can lead to presence of negative mass concentration in source apportionment results. Although, PCA is generally not recommended for quantitative source apportionment, they can be used effectively for exploratory analysis.

3.3. MCR

MCR-ALS is a method used to recover pure response profiles of chemical components from an unresolved mixture without prior knowledge of its composition. This method is initially developed for gas chromatographs. However, this source apportionment is also a matrix factorization problem, MCR-ALS algorithm can be used. In the MCR-ALS model, the matrices *G* and *F* in equation (1) is calculated by minimizing the sum of squared residuals SSR (Tauler et al. 2009).

$$SSR = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(x_{ij} - \bar{x}_{ij}\right)^2 \quad (7)$$

In equation (6), x_{ij} is the measurement of j^{th} element in the i^{th} sample. Although this algorithm can work when both matrices are unknown, the problem can be further simplified by finding an

initial solution using a simpler algorithm like simple-to-use interactive self-modeling analysis (SIMPLISMA). Once matrix *F* is initialized, matrix *G* is calculated using:

$$G = XF(F^T F)^{-1} \quad (8)$$

Non negativity in *G* is obtained by minimizing the sum of residuals in matrix *X* such that all elements in matrix *G* is greater than zero. This *G* is then used to recalculate *F* using:

$$F^T = (G^T G)^{-1} G^T X \quad (9)$$

This iterative procedure continues until SSR value from two consecutive iterations fall below a preset value.

Unlike PCA and Unmix model, MCR model use alternating least squares for solving the chemical mass balance equation. Hence, this model is well suited for use in applications where heteroskedastic data is analyzed. This model also has the advantage that non-negativity criteria is built into it. All these advantages come at the cost of slightly higher computational requirements.

3.4. PMF

PMF is a purpose made receptor model that is developed by U.S. EPA for source apportionment applications. The general working of PMF model is like MCR-ALS model with the exception that the sum of squares of residuals SSR is minimized using the equation (Paatero and Tapper 1994):

$$SSR = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{X_{ij} - \sum_{k=1}^{p} G_{ik} . F_{kj}}{u_{ij}} \right]^2 \quad (10)$$

Like MCR-ALS model, PMF model is more suited for heteroskedastic data since it allows individual weighing of data points. Usually, this model tends to resolve more sources than the

224 other models tested here. The downside of this model is that it requires considerably higher
225 computational requirements compared to the other models.

226 **4. Results and Discussion**

227 Source apportionment is performed using the chemical composition of the collected silt samples
228 (fraction of road dust with size <75µm). Silt component of road dust is highest during the summer
229 season with 160g for 1kg of sample tested. This is followed by winter (152.2g) and monsoon
230 season (108.4g). The highest fraction of silt in road dust sample is at location 7, near Vellore
231 district administrative office (264g). Being an administrative center, this location experiences
232 considerable vehicular traffic. The sampling location is also located below an overpass thus
233 impeding air movement. Lowest silt fraction is at location 1 (88.37g) since this road has paved
234 sidewalks and is cleaned regularly. More information on chemical composition of analyzed road
235 dust and its seasonal variations is explained in Jose and Srimuruganandam (2020).

236 A total of six sources are identified by the four receptor models, viz., crustal material,
237 resuspended dust, tire and brake wear, biomass combustion, industrial sources, and vehicular
238 emission. Source apportionment by the individual receptor models is explained in more detail
239 below. It is to be noted that the sources are numbered for identification only and are not ranked in
240 by any means.

241 **4.1. Unmix**

242 For the Unmix model, 51 of the 52 observations are taken for consideration. One observation is
243 ignored (location 14 during winter season) to improve signal to noise ratio of the data. 100 feasible
244 solutions for unmix model are obtained from 218 runs. Run number 15 is chosen as the global
245 minima. The model identified five sources with a minimum R^2 value of 0.93 and a minimum signal

246 to noise ratio of 1.91. Source contribution of the five sources to different elements is shown in and
247 their contribution to different sources with different sampling locations is shown in Figure 2. The
248 scaled residuals are found to be between -3 and +3.

249 **[INSERT FIGURE 2]**

250 *4.1.1. Source 1: Resuspended Dust*

251 The first source accounts for all the Pb present in road dust of Vellore city. It also shows significant
252 contributions to nearly all elements. It contributes least to K (5%), Mg (5%), Mn (8%), and Sr
253 (8%). Low contribution to K would rule out biomass combustion as this source. High contribution
254 to Pb (100%), Rb (22%) and Li (21%) suggests that this source could be resuspended road dust.
255 The probable source of Pb in this fraction could be from automobile exhaust prior to the year 2000;
256 when leaded fuel was banned in the country (Miguel et al. 1999; Das et al. 2018). Since lead halide
257 salts from vehicle exhausts are largely insoluble, they tend to remain in the environment for a long
258 time (Habibi 1970). From Figure 2, it is visible that the contribution of this source to pollution is
259 considerably high during the summer season. The semi-arid summers in the region are the reason
260 for increased resuspension of road dust. Winter season shows a relatively consistent contribution
261 of this source throughout the study region. However, there are clearly defined hotspots during
262 summer and monsoon. Highways are the most obvious hotspots of this source as evident from
263 locations 6, 8, 9 and 10. However the presence of Pb in location 14 can have other sources since
264 lead-acid battery refurbishment shops operate regularly in this region (Jose and Srimuruganandam
265 2020).

266 *4.1.2. Source 2: Crustal Material*

Second source of road dust identified by Unmix shows significant contributions to almost all elements in the study region. With high contributions going to Al (50%), Ba (82%), Zn (71%), Mg (71%), Sr (74%) and Co (55%). This source is expected to be a combination of both tire wear and biomass combustion. High contribution to K and Mg show that biomass combustion could be a contributor to this source (Pio et al. 2008). All other elements with high contribution from this source suggest that tire wear is also a contribution to this source. Zn is a common tracer that is used for identifying contamination from tire wear (Kupiainen et al. 2005). Studies have shown that up to 1% of the tire tread material can be Zn (Councell et al. 2004). Co is added to the rubber matrix to promote its adhesive characteristics (Fulton 2005), thereby improving the strength of tire compound (Ooij 1984). Fluoride salts of Sr are used in some tire formulations for improving the stability of resins (Yasuda et al. 1990). Magnesium alloys and forged aluminum are both used in manufacture of engine blocks and pistons implying presence of engine wear in this source (Lakshminarayanan and Nayak 2011).

This source is found to contribute heavily to road dust in locations 3, 17 and 18. This is essentially a long stretch of road and thus tire wear can be a significant source of pollution in these locations. Locations 3 and 18 are adjacent to gas stations. Barium from diesel fuel additives and engine oil additives can also be contributing to the high levels of this source in these locations (Monaci and Bargagli 1997). There is a considerable seasonal variation of this source. Winter season shows the highest contribution whereas the monsoon season shows the lowest contribution.

4.1.3. Source 3: Break Wear

The third source shows high contribution to Fe (27%) along with a significant contribution to Al (7%), Li (14%) and Cu (8%) suggests that break wear can be a contributor to this source (Gramstat 2018). High contribution to Fe can be attributed to wear from brake disks and drums used in

290 automotive braking systems (Garg et al. 2000; Kukutschová and Filip 2018). This source shows
291 high contribution throughout all three seasons. The highest contribution is noted during the
292 summer season. Winter season also shows a similar distribution for this source. Lowest
293 contribution for this source is noted during monsoon season since the brake dust could be washed
294 off during monsoons. Considerable spatial variation is not exhibited by this source.

295 *4.1.4. Source 4: Vehicular Emissions*

296 Fourth source shows significant contribution to Cr (66%), Ni (58%), Mn (47%), Ga (45%) and Cu
297 (48%). This suggests that the fourth source of road dust is possibly from vehicular emissions.
298 Source apportionment studies generally consider Ni as an indicator for oil combustion (Thomaidis
299 et al. 2003; Peltier et al. 2009). Studies show that heavy duty diesel engines can release significant
300 quantities of Mn (Hilden and Bergin 1986) and Cu (Konstandopoulos et al. 1988) since they are
301 used as fuel additives. Cr coating is used in high power diesel engine piston rings to prevent wear
302 (Rastegar and Craft 1993). Traces of these elements are also usually present in engine oils used by
303 diesel engines. From Figure 2 contribution of this source to road dust is maximum during the
304 summer season. Winter and monsoon show nearly equal distribution throughout the study region.

305 *4.1.5. Source 5: Crustal Material*

306 Fifth source shows high contribution only to Fe (19%). Since Fe is one of the most abundant
307 elements on earth's crust (Turekian and Wedepohl 1961; Taylor 1964), it can be assumed that the
308 fifth source of road dust is crustal material. From Figure 2, contribution of crustal material to road
309 dust is minimal during the summer since vehicular emission and tire wear take a more prominent
310 place during this season. This source contributes high during the monsoon season. Rains during
311 monsoon season are expected to wash away pollutants from other sources.

312 **4.2. PMF**

313 Microsoft Windows binary for EPA PMF 5.0 provided by U.S.EPA is used for the PMF model.
314 Of the 52 samples, 14 samples are discarded to improve the signal to noise ratio of the model
315 (shown as empty circles in Figure 3). The number of bootstrap runs is kept 100 with a minimum
316 r^2 of 0.6. The Q-robust of the model is found to be close to Q-true, suggesting that results are
317 acceptable. Scaled residuals for this model is between -7 and 7.

318 **[INSERT FIGURE 3]**

319 *4.2.1. Source 1: Vehicular Emission*

320 First source shows high loading only for Ba (57%). It is also seen to contribute moderately to Co,
321 Sr, Mg and Zn. The high loading of Ba indicates that this source could be vehicular emission.
322 Studies have shown that Ba is an effective indicator for vehicular emission (Monaci and Bargagli
323 1997; Monaci et al. 2000). Barium fuel additives are used extensively in diesel engines to reduce
324 smoke from combustion (Glover 1966; Truex et al. 1980). Barium fluoride is also used in some
325 engine oils to improve its load carrying capacity (Hermant et al. 1986). Monsoon season shows
326 the highest contribution from this source (Figure 3) since other sources of road dust could have
327 been washed away. Location 17 shows extremely high contribution during winter season.
328 Similarly, high contribution was also identified by Unmix model (Figure 2). This could be an
329 isolated incident like an oil spill.

330 *4.2.2. Source 2: Biomass Combustion*

331 Second source shows a high contribution towards K. This is indicative that this source could be
332 from biomass combustion. Potassium (Andreae 1983) and Levoglucosan (Achad et al. 2018) are
333 the two most common indicators for biomass combustion. This source shows higher contribution

to road dust during the summer season due to the increased biomass load present in the road surfaces. As expected, contribution from this source is found to be higher during summer season and least during monsoon season (Figure 3). Contribution from this source is negligible during monsoon season since damp vegetation inhibits combustion.

4.2.3. Source 3: Resuspended Road Dust

The third source shows considerable contribution to Pb (71%), Ni (24%) and Cr (25%). It also contributes to most other elements that are analyzed. High contribution to Pb would suggest that this source is re-suspended road dust (Al-Chalabi and Hawker 1997; Wang et al. 2005). As stated before, Pb based antiknock agents have been phased out of the country since 2000 (Sharma and Pervez 2003). So, the contribution to Pb by this source can only be attributed to previously deposited Pb two decades ago. As noted in the unmix model, the contribution of this source to road dust in the region is greater during summer season due to the semi-arid conditions that are prevalent in the city during summer.

4.3.4. Source 4: Tire and Brake Wear

Fourth source shows high concentration to Cu (54%), Zn (29%), Cr (44%), and Ni (50%). Zinc is an indicator for tire wear (Wang et al. 2005) and copper is seen more in brake wear particles (Thorpe and Harrison 2008). As mentioned in previous models, Ni is an indicator for oil combustion (Galbreath et al. 2000) and Cr can be linked to vehicular exhaust (Testa 2004). This source can hence be concluded to be vehicular emission. From Figure 3 the contribution of this source to the road dust in this region is greater towards the city center compared to the outskirts. The increased traffic at this location can be the reason for this observation. Mean contribution from this source is found to be greater during the winter season. Although tire wear generally increases

during the summer season due to higher road temperature, the higher emissions from vehicle exhausts and brake wear could have offset this.

4.2.5. Source 5: Crustal Material

The final source of road dust identified by PMF shows high contribution to Al (39%), Ca (42%), Fe (44%), Mg (38%), Sr (44%) and Co (53%). Fe, Ca, and Al are the most abundant elements in the earth's crust (Yaroshevsky 2006) suggesting that the fifth source is crustal material. This source is found to contribute more to road dust during the winter season. The lowest concentration of road dust is identified at the bridge across river Palar (Location no. 4). Higher contribution of sources like tire and brake wear during summer season decreases the percentage contribution of crustal material during summer season. Lower road temperatures during monsoon season coupled with rains washing off smaller dust particles could be reason for high contribution of crustal material (Figure 3).

4.3. PCA-MLRA

PCA model is run using a custom R script. All 52 samples are used in this model. Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy is 0.56 for the collected data. This suggests a factor analysis can be performed with the data. Bartlett's test gave a significance level considerably lower than 0.05 suggesting that the variables are related, and factor analysis can provide useful information. Both the tests were performed using KMO and Bartlett test functions in 'psych' library available at CRAN. With a cut off eigen value of 1, PCA can extract 5 principal components (Table 2). The five principal components extracted accounted to 85% of the total variance.

[INSERT FIGURE 4]

4.3.1. Source 1: Crustal Material

The first principal component accounts for 25% of the total variance explained by PCA. This component shows high loading for Al, Sr, Mg, Cr, Fe and Mn. The major source of these elements in road dust is from crustal matter. Al and Fe are two of the most abundant elements present on earth's crust (Rudnick et al. 2019). This source is found to contribute significantly to road dust in the region throughout the year especially during the summer season (Figure 4). The dry summers in the study region can be contributing to this. Major hot spots for this source are along roads that lack a paved sidewalk or hard shoulders.

4.3.2. Source 2: Biomass Combustion

Second principal component accounts for 18% of the total variance and shows high loading for K and Li. High loading for K indicates presence of biomass (Yu et al. 2018). Hot spots for this source, largely concentrated along Gandhinagar main road (locations 2, 3, 17 and 18) show that biomass combustion has a higher contribution during monsoon season. This anomaly could be because other sources could also be included in this principal component. Previous studies have noted the presence of an unidentified source of Li in this region (Jose and Srimuruganandam 2020). Locations towards the south of the city show contribution from this source during monsoon season, which is in stark contrast to PMF model, where contribution from biomass combustion is largely absent during this season.

4.3.3. Source 3: Resuspended Dust

Third component shows high loading for Mg, Sr, Cr, Cu, Ni and Pb. This source accounts for 16% of total variance and contribute more during the winter season. High loading for Pb suggests that the third source is from re-suspended road dust. Two of the biggest hot spots of re-suspended road

399 dust according to PCA-MLRA are Palar river bridge (location 4) and highway underpass (location
400 15).

401 *4.3.4. Source 4: Crustal Material*

402 Fourth principal component also shows high loading for Ca and Fe. Suggesting that this source is
403 also crustal in origin. This source contributes more to road dust during the winter season, with
404 contributions greater towards the south of city, suggesting that contribution from resuspended dust
405 might also be accounted in this source (Figure 2). This source has negligible contribution to road
406 dust during summer and monsoon seasons.

407 *4.3.5. Source 5: Tire Wear*

408 Fifth principal component accounts for 8% of the total variance. This component shows high
409 loading for Ba, Cu and Zn. High loading for Zn and Cu suggests that the source is likely from tire
410 wear (Kupiainen et al. 2005). Ba is usually present in vehicular emissions. The presence of Ba in
411 suggests that this source could be a combination of both tire wear and vehicular emissions. This
412 source has exceptionally low spatial variation and is distributed equally throughout the study
413 region. As seen in Unmix and PCA models, contribution is higher during summer season and least
414 during monsoon season (Figure 4). High vehicular traffic combined with impeded ventilation
415 could be the reason for higher contribution of this source in location 7 (Figure 4).

416 **4.4. MCR-ALS**

417 The MCR-ALS model is run using the 'ALS' library provided by CRAN. For running the MCR
418 model, an initial solution is necessary. This solution will help in reducing the number of iterations
419 necessary before reaching a satisfactory solution. Since the SIMPLISMA model did not have an
420 equivalent under CRAN, the results from the PCA model are used as an initial solution for the

MCR-ALS model. The model converged in 14 iterations with non-negativity criteria for both matrices. This model could extract only three sources from the receptor concentration data. The deviation of data from ideal bilinear behavior can be the reason for poor source apportionment results. The initial differential residual (RD) is 0.85. After 14 iterations alternating between optimizing S and C matrices, the RD value dropped below the default threshold of 0.001. The scaled residual in this model lies below ±3.

[INSERT FIGURE 5]

4.4.1. Source 1: Industrial Source

The first source shows contribution to Al and Mg. Presence of this source close to location 17 suggests that this source could be of industrial origin. There is an industrial estate towards east of location 17 which can contribute to pollutants in this location. This source has a higher contribution during summer and least contribution during monsoon season (Figure 5). Summer season shows high contribution of this source in locations 1, 2, 4, 5 and 7. Winter contribution is greater at locations 2, 7 and 17. Contribution from this source must be studied further by dispersion modeling methods.

4.4.2. Source 2: Crustal Material

Second source contributes to the entirety of Fe, Li and K. It also shows significant contribution to Ca, Ga, Ni, Na and Sr. Presence of high contributions to Ca and Fe would suggest that this source is of crustal origin. As discussed in previous models, the mean contribution of this source to road dust is greater during monsoon season due to wash off soil from sidewalks. Other sources like brake wear and tire wear are washed away by rains during the summer where re-suspended dust is

found to contribute more. Contribution from this source is least during summer season due to contribution from resuspended dust and tire and brake wear as seen in Figure 5.

4.3.3. Source 3: Resuspended Dust

This source is found to contribute more to Pb, Rb, Zn, Cr, Co, and Al. Presence of these elements suggests that this source is largely from re-suspended road dust. Like other models in this study, contribution from this source is greater during summer season. MCR model shows no contribution from this source during winter season. Contribution from this source is found to be greater at locations that lack a paved sidewalk (Figure 5).

4.5. Seasonal Variation of Sources

Unmix, PMF and MCR-ALS models show that contribution of crustal materials to road dust is found to be greater during monsoon season. Only PCA-MLRA model shows higher contribution during summer season. Considering that PCA-MLRA model overestimates the contribution of this single source considerably, the results obtained from it can be erroneous. The other three models attribute lowest contribution to summer season. As mentioned in previous sections, this can be attributed to increased tire and brake wear during summer season.

High contribution of resuspended road dust during summer season is identified by all four models. Drier road conditions during summer season can lead to increased resuspension of road dust particles. Likewise, all four models identified that the contribution of resuspended road dust is least during monsoon season owing to the wet deposition of resuspended dust when in contact with rains.

Contribution of tire and brake wear is found to be nearly equal during summer and winter seasons and lowest during monsoon seasons. Summer contribution is slightly higher due to

increase in tire wear resulting from the higher road temperatures. Winter contributions are equally high due to stable atmospheric conditions that are observed during winter months. Tire and brake wear particles tend to be very small and hence can be easily washed away. This would explain the low concentration during monsoon season.

Unmix is the only model that could identify contribution from vehicular emissions. This source shows high contribution during summer season. Winter and monsoon concentrations are nearly equal. Biomass combustion on the other hand have contradicting results from two models. PMF model shows high contribution of biomass burning during summer season. This is the expected result since biomass combustion is highly unlikely during monsoon season. However, this anomaly is observed in PCA-MLRA. Presence of elements like Li and In in this source suggests that the specific principal component is a combination of sources.

4.6. Spatial Distribution of Sources

The models identified six sources in total: crustal matter, re-suspended road dust, biomass combustion, tire and brake wear, vehicular emission and industrial. Of these sources, crustal matter and re-suspended road dust is identified by all the models. Tire wear, brake wear or a combination of both is identified by three models (Unmix, PCA and PMF). Two models (PCA and PMF) identified biomass as a source of pollution in the region. Industrial source is identified by MCR-ALS model and vehicular emission is identified by Unmix model. The spatial distribution of various sources quantified by the source apportionment models are shown in Figure 6.

[INSERT FIGURE 6]

Crustal source is identified by all four receptor models. The PCA model placed the highest contribution on crustal source. Lowest contribution is apportioned by the PMF model. The PCA model shows exceptionally low spatial variance in this source. The contribution of this source is found to vary

from 84% to 94%. Unmix model shows slightly higher spatial variance in source contribution from crustal matter (37% to 62%). Hot spots identified are along the main road (locations 15 and 16). The PMF model also shows similar hot spots. The contribution of crustal material according to the PMF model is considerably low compared to other models. MCR model showed the highest variance in contribution from this source (between 65% and 100%). From Figure 3 and Figure 4, both PMF and Unmix models show high contribution from crustal material during monsoon season. Higher contribution is noted in roads that lack a paved sidewalk (locations 9, 10 and 13).

Re-suspended road dust is another source identified by all four receptor models. The contribution of resuspended road dust is estimated to be between 1% and 16%. Highest contribution to the source is estimated by the PMF model. As per the PMF model, the contributions varied from 2% to 23%. The highest contributions are noted at highways (locations 6 and 8). Lowest contribution is noted at Gandhinagar main road (location 17). Unmix model also identified location 8 as a hotspot for this source. Lowest mean contribution is obtained from the PCA model. Three of the four models show highest contribution from resuspended road dust during summer and lowest contribution during winter (Figures 2, 3 and 5). PCA apportioned the least contribution from resuspended dust during summer season. Figure 4 shows that PCA overestimated the contribution from crustal material in all three seasons.

Unmix model shows relatively high contribution for tire and brake wear (17% to 44%). Lowest contribution to this source is noted by the PCA model. Unmix and PMF models show high contribution of tire and brake wear during summer season and lowest during monsoon season (Figure 2 and 3). Biomass combustion is identified by both PCA and PMF models. PMF model shows higher contribution for this source during summer season. PMF model apportioned negligible contribution form this source during monsoon season while PCA model apportioned highest contribution for this source during monsoon season. The principal component representing contribution from biomass could be a composite of multiple sources. Lowest biomass concentration is noted at lorry owner's association petrol pump (location 18). Vehicular emission is identified in the Unmix model and Industrial source by MCR-ALS model. The industrial source

512 is found to contribute higher towards the north of the city and vehicular emission towards the south of the
513 city. Summer season experiences highest contribution from this source and monsoon season the least.

514 Three receptor models (PMF, Unmix and PCA) identified five sources each, while MCR-
515 ALS can only identify three sources (Figure 5). The implementation of MCR-ALS model available
516 in CRAN is designed specifically for spectral analysis, which limits its use in cases where deviation
517 from ideal bilinear behavior is possible. The results from PCA model are unsatisfactory and
518 pollution from most of the sources are attributed to a single source (Crustal) for all three seasons
519 (Figure 4). A KMO sample adequacy of 0.56 is classified as miserable by Henry Kaiser. This
520 would suggest that although some information can be extracted by PCA, the model is ill suited for
521 the data at hand. PMF model did an admirable job in source apportionment of road dust with the
522 detriment that many locations during all three seasons had to be ignored due to them being outliers.
523 Though its performance characteristics are acceptable, the residuals for many species in PMF are
524 considerably greater than all other models in this study. Samples collected from different locations
525 can add uncertainty that is not addressed by PMF model. Of the four models tested, Unmix model
526 is found to give the best source apportionment result, with excellent performance characteristics
527 and lowest scaled residuals of the bunch.

528 **5. Conclusion**

529 Road dust is a significant source of PM in an urban environment. Source apportionment of road dust is thus
530 essential for effectively controlling urban air quality. Receptor models are some of the most robust
531 frameworks available for source apportionment. In this study, the source apportionment performance of
532 four receptor models viz. Unmix, PMF, PCA and MCR-ALS methods are studied and compared. Road dust
533 samples are collected form 18 sampling locations within the study region and analyzed using ICP-OES.
534 The resulting elemental composition data is then used for receptor modeling studies.

Unmix model extracted five sources (resuspended dust, tire wear, brake wear, vehicular emission, and crustal material). The PMF model also managed to extract five sources for road dust in the region (vehicular emission, biomass combustion, resuspended dust, and crustal material). Although the PCA method extracted five sources, two sources are found to be of the same composition. The four sources classified by PCA model are crustal material, biomass burning, resuspended dust and vehicular emissions. The MCR-ALS model identified an industrial source, crustal source, and resuspended dust. All four models identified crustal material as the predominant source of road dust in the region. Of the four models tested, UNMIX model is found to give the best results for this dataset.

Source apportionment results are expected to be helpful for setting future policy and regulation. This study also brought forth the limitations of different receptor models when applied to road dust. Multivariate receptor models can be immensely powerful tools for controlling and mitigating health effects from urban road dust. More studies comparing the source apportionment performance of receptor models are thus necessary.

Declarations

Author Contributions

Jithin Jose*:* Conceptualization, Data curation, Methodology, Investigation, Formal Analysis, Software, Validation, Visualization, Writing – original draft. ***B. Srimuruganandam****:* Project administration, Conceptualization, Methodology, Resources, Supervision, Visualization, Validation, Writing – review & editing.

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Compliance with Ethical Standards

The authors declare no conflict of interest.

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738 **Figures**

751 **Tables**

754 **Supplementary Tables**

Table S4: Correlation between unmix models

Table S5: Scaled residuals from Unmix model

Table S6: PMF Source contribution (no contribution shown by -999)

Table S7: PMF Source composition (units in mg/kg)

Table S8: Source contribution from PCA model

Table S9: Source loading from MCR-ALS

Table S10: Source contribution from MCR-ALS

Table S11: Scaled residuals from MCR-ALS model

Table S12: Residuals for PMF model

Figures

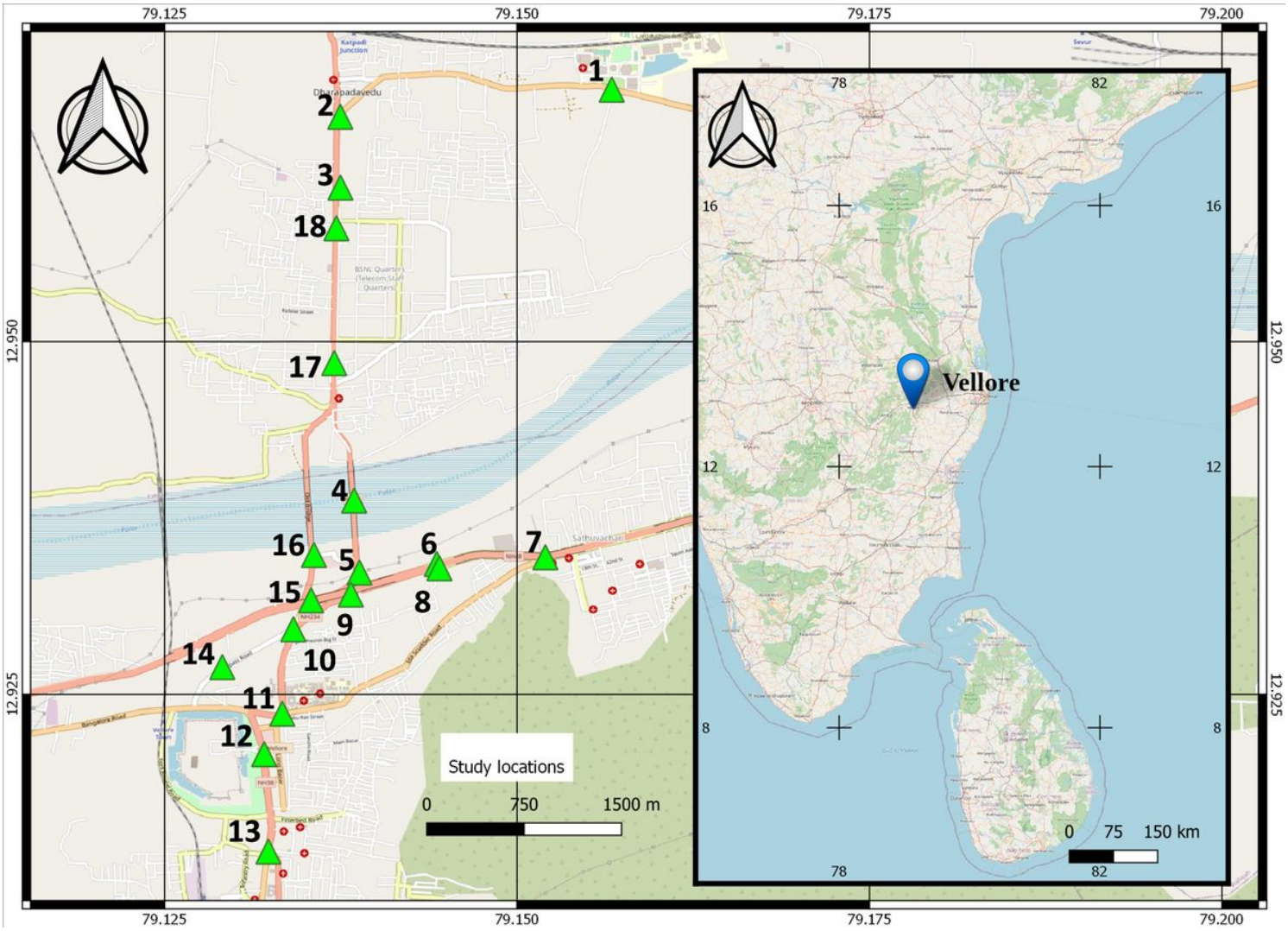

Figure 1

Sampling locations

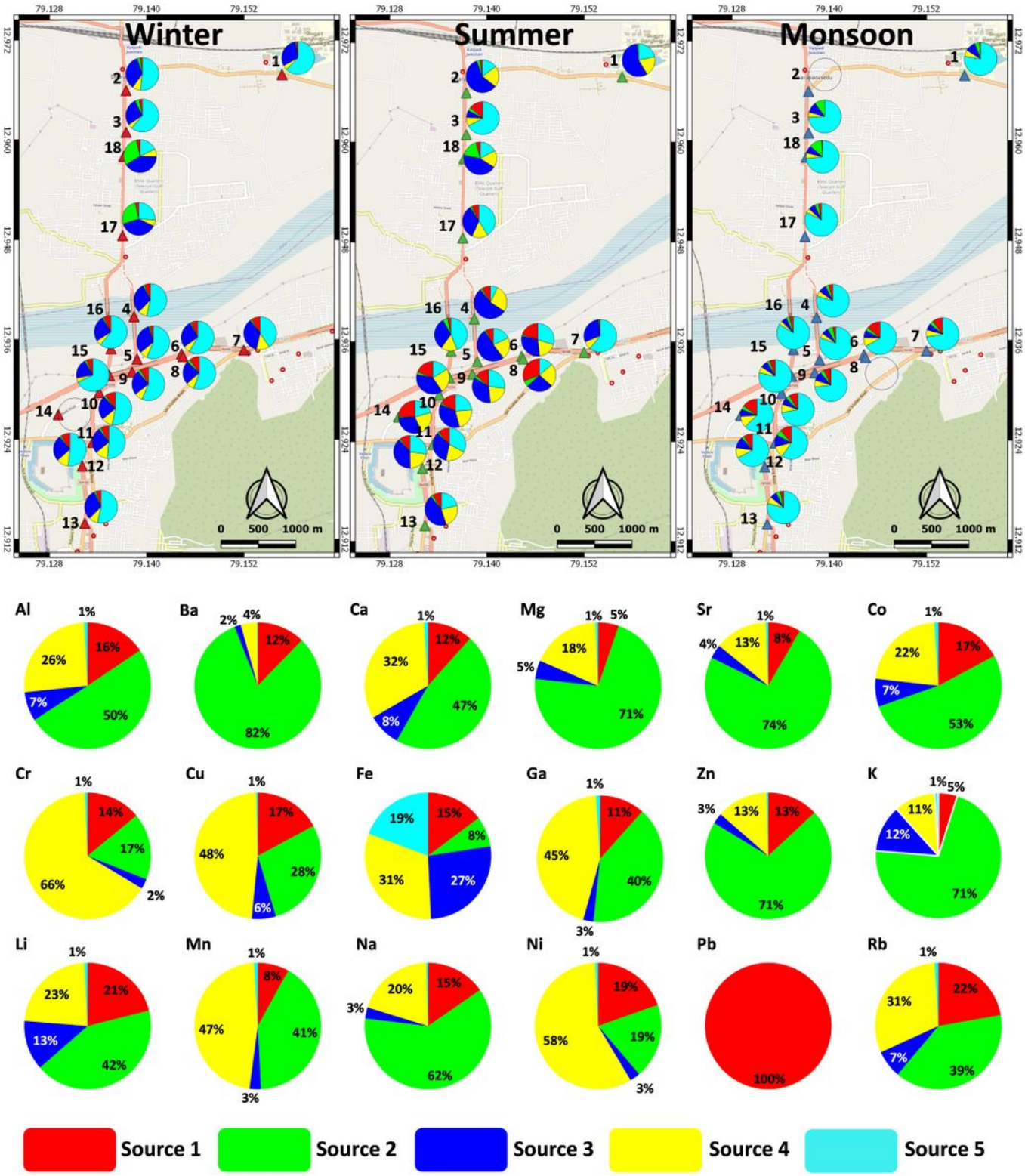

Figure 2

Source contribution in study locations (above) and source contribution by elements (below) from the Unmix model

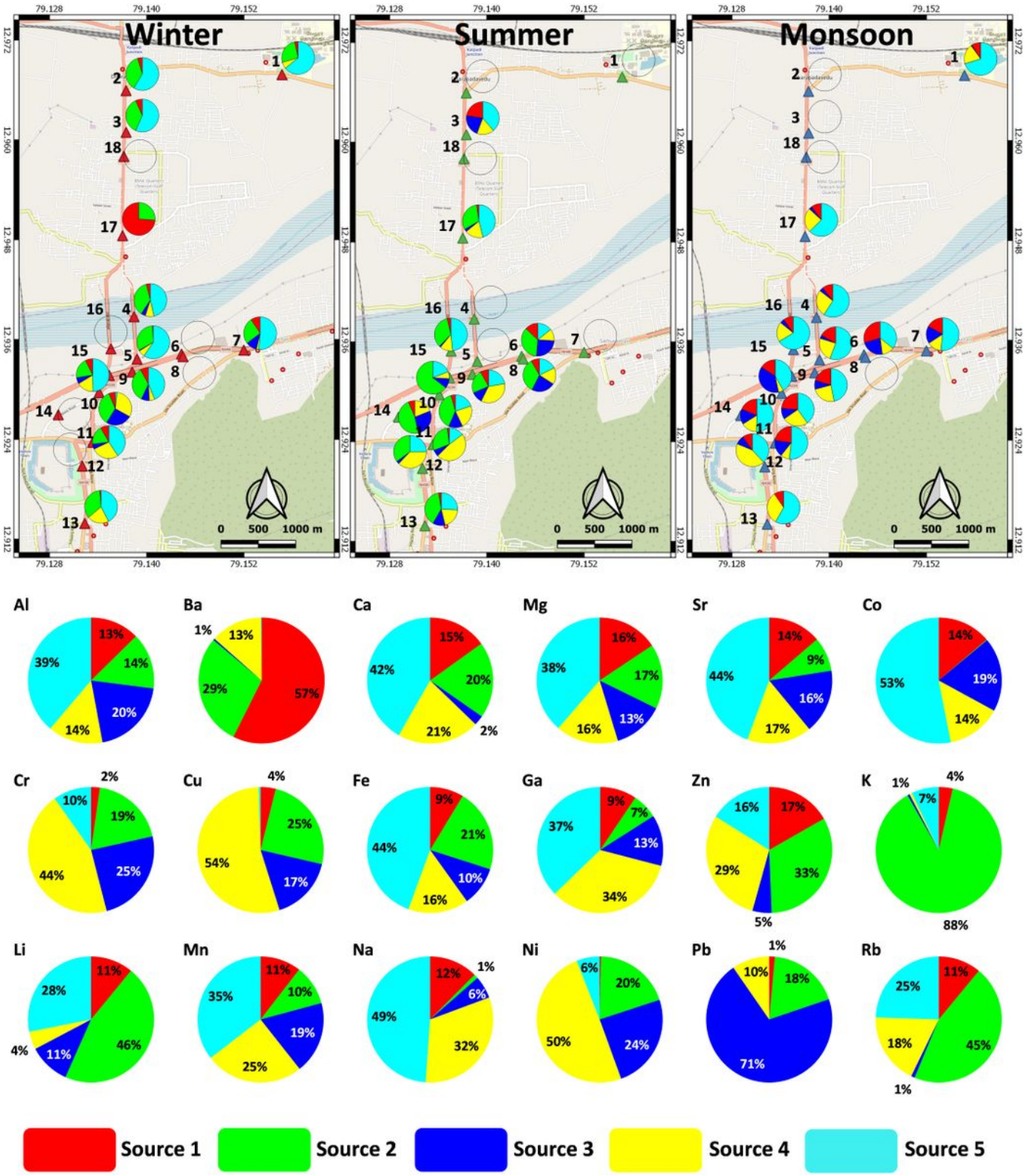

Figure 3

Source contribution in study locations (above) and source contribution by elements (below) from the PMF model

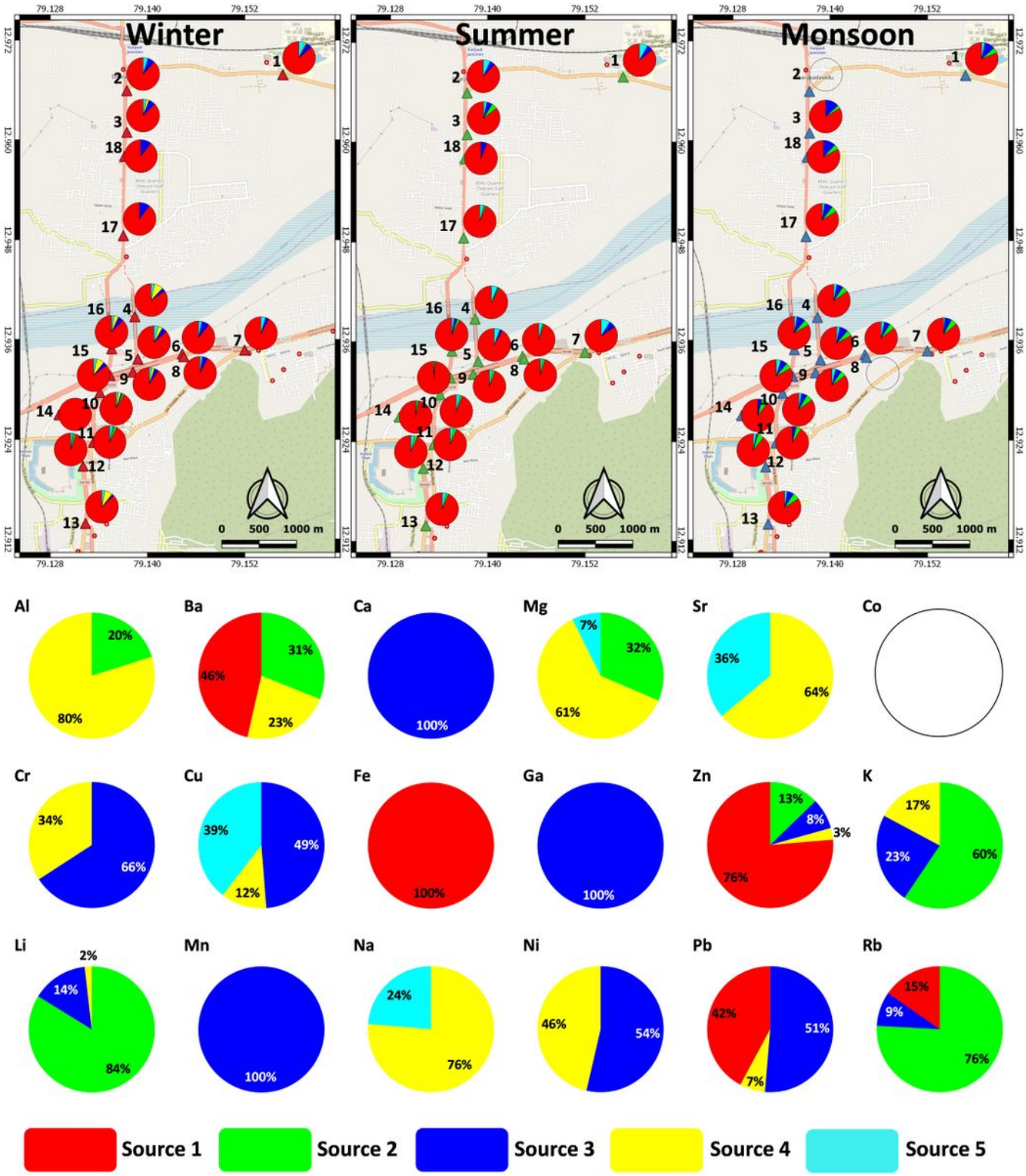

Figure 4

Source contribution in study locations (above) and source contribution by elements (below) from the PCA model

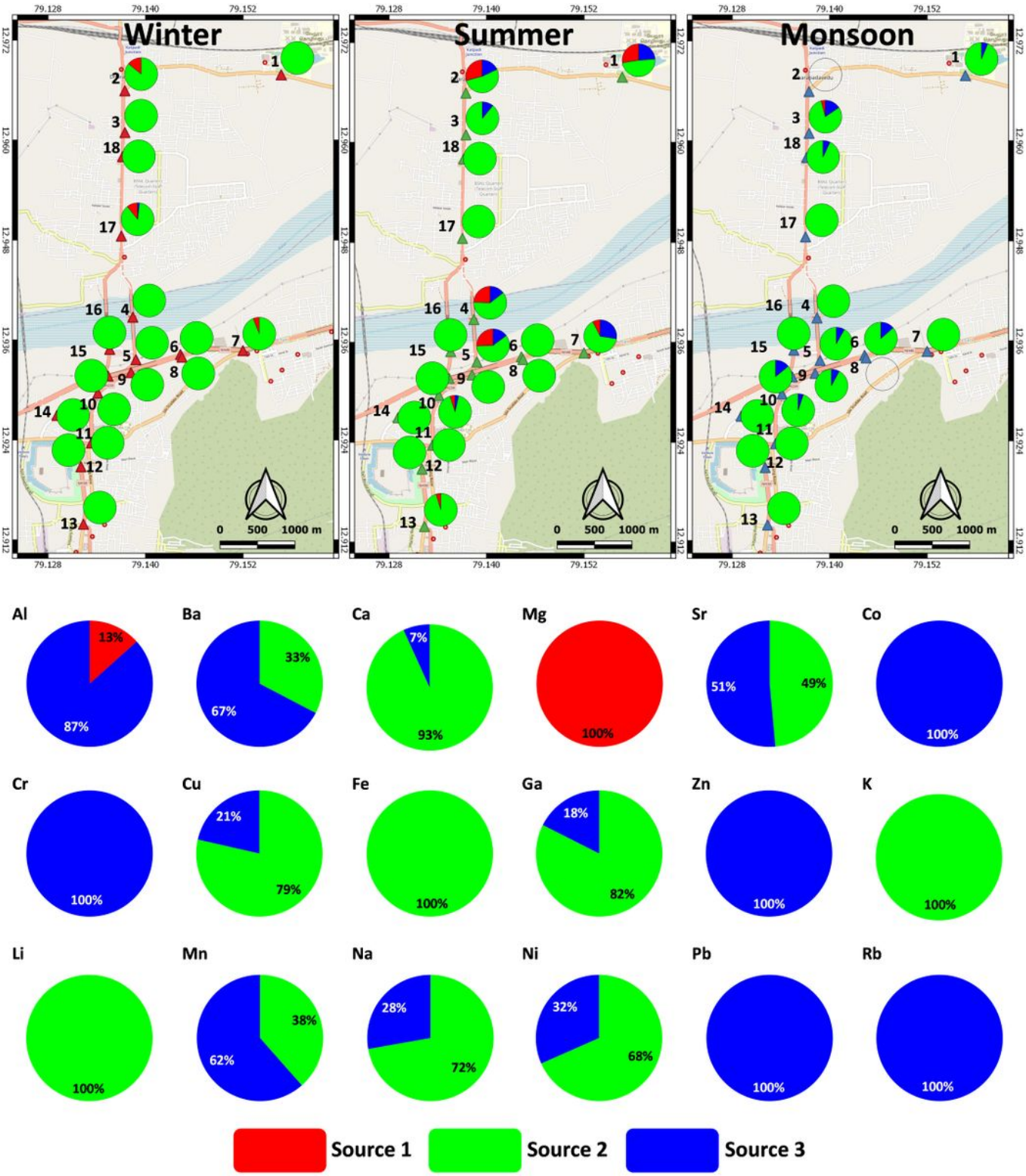

Figure 5

Source contribution in study locations (above) and source contribution by elements (below) from the MCR model

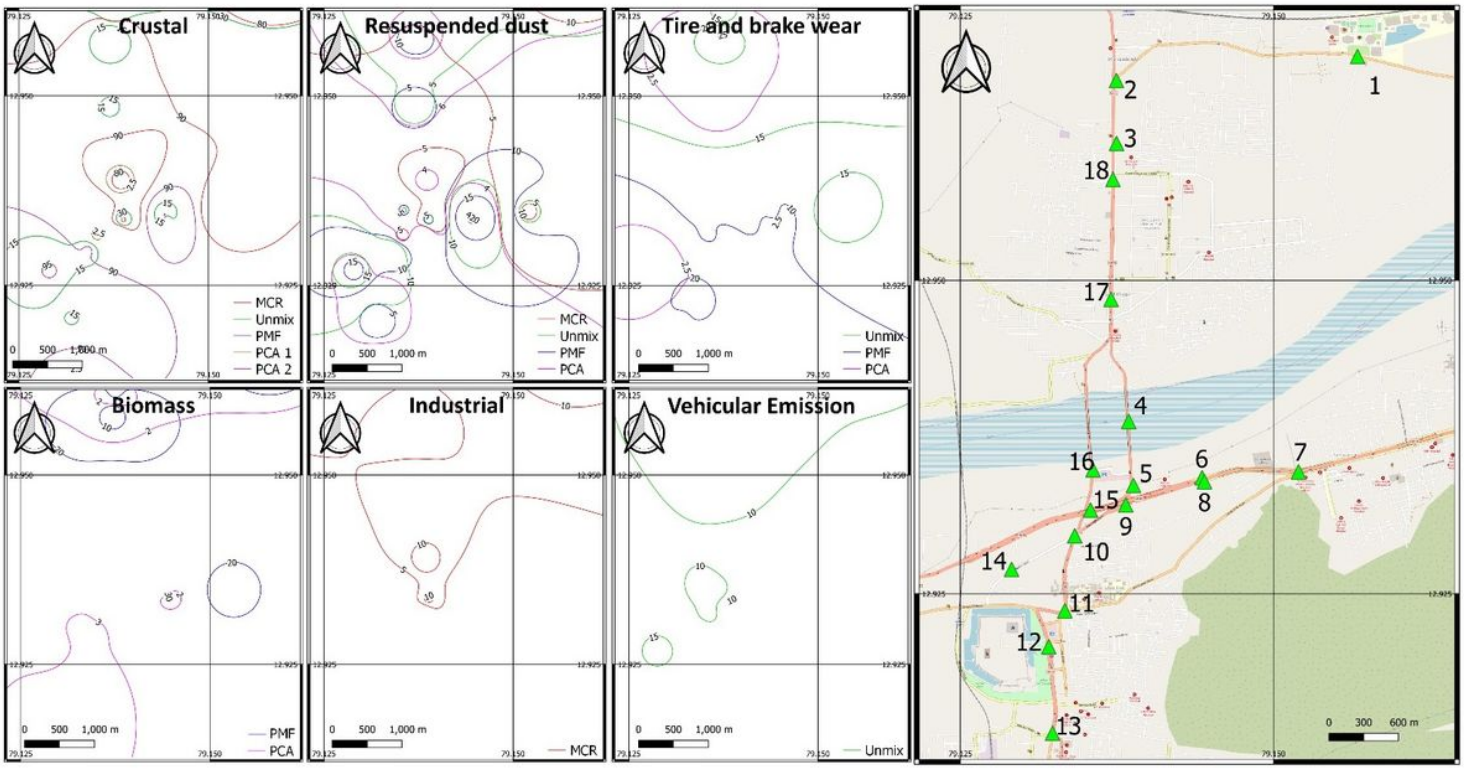

Figure 6

Distribution of sources in the study region. Lines represent the contribution of individual sources as calculated by different receptor models. Map on the right shows the different sampling locations. Explanation of sampling locations is provided in Table 1. (Units in % contribution)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- TableS1.docx
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- TableS3.docx
- TableS4.docx
- TableS5.docx
- TableS6.docx
- TableS7.docx
- TableS8.docx
- TableS9.docx
- TableS10.docx
- TableS11.docx

- TableS12.docx