

The Use of Principal Component Analysis for Source Identification of PM_{2.5} from Selected Urban and Regional Background Sites in Poland

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Abstract. The paper reports the results of the measurements of water-soluble ions and carbonaceous matter content in the fine particulate matter (PM_{2.5}), as well as the contributions of major sources in PM_{2.5}. Daily PM_{2.5} samples were collected during heating and non-heating season of the year 2013 in three different locations in Poland: Szczecin (urban background), Trzebinia (urban background) and Złoty Potok (regional background). The concentrations of PM_{2.5}, and its related components, exhibited clear spatiotemporal variability with higher levels during the heating period. The share of the total carbon (TC) in PM_{2.5} exceeded 40% and was primarily determined by fluctuations in the share of OC. Sulfates (SO₄²⁻), nitrates (NO₃⁻) and ammonium (NH₄⁺) dominated in the ionic composition of PM_{2.5} and accounted together ~34% (Szczecin), ~30% (Trzebinia) and ~18% (Złoty Potok) of PM_{2.5} mass. Source apportionment analysis, performed by PCA-MLRA model (Principal Component Analysis – Multilinear Regression Analysis), revealed that secondary aerosol, whose presence is related to oxidation of gaseous precursors emitted from fuel combustion and biomass burning, had the largest contribution in observed PM_{2.5} concentrations. In addition, the contribution of traffic sources together with road dust resuspension, was observed. The share of natural sources (sea spray, crustal dust) was generally lower.

1 Introduction

Air pollution by particulate matter (PM) is one of the most serious environmental problems of all developed and developing countries [1]. Much attention is paid to fine PM fractions – PM_{2.5} (particles with aerodynamic diameter ≤ 2.5 μm), mainly due to their harmful impact on human health [2, 3]. What's more, fine particulates are capable of long-term persistence in the air, affect climate, ecological conditions and visibility [4, 5]. PM_{2.5} are complex mixtures, originating either directly from natural and anthropogenic sources, such as biomass burning, vehicle exhaust and industry, or as secondary pollutants through heterogeneous chemical reactions in the atmosphere [6-8]. Carbonaceous matter (elemental carbon – EC, organic carbon – OC) and inorganic ions, have the highest

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contribution to PM mass [9, 10]. The latter, especially sulfates (SO_4^{2-}), nitrates (NO_3^-) and ammonium (NH_4^+), are an important constituent of the secondary inorganic aerosol (SIA) [11, 12]. This component greatly affects the concentration and composition of fine PM, both in areas remote from emission sources, as well as in urban areas [10-14].

The PM concentrations and chemical composition can vary significantly in time and space, which depend on the main emission sources and chemical reactions occurring in the atmosphere [12, 15]. Therefore, it is necessary to further study the chemical characteristics and sources of $\text{PM}_{2.5}$ in as many sites as possible. The research on a spatial and seasonal variation of PM constituents in different types of measurement sites is particularly important for Central and Eastern Europe where knowledge about PM chemical compositions is still very limited [16].

Characterizing and evaluating the contribution of the different aerosol sources can constitute the basis for planning efficient strategies of air quality management [4]. Commonly used methods of source apportionment are receptor models (RMs), which use the chemical speciation of aerosols collected at the receptor to infer the contribution of the possible sources to the ambient concentration of particulate matter and their chemical composition [7]. Several receptor models have been devised and widely used, such as chemical mass balance [17], positive matrix factorization [18] and principal component analysis [17, 19].

Taking into account the above considerations, the aim of the following study was to analysed concentrations and chemical compositions of $\text{PM}_{2.5}$ samples from 3 different measurement sites in Poland. The preliminary assessments of the $\text{PM}_{2.5}$ sources were also performed and its relative contribution to observed $\text{PM}_{2.5}$ concentrations were determined.

2 Materials and methods

2.1 $\text{PM}_{2.5}$ sampling and chemical analysis

Research material were $\text{PM}_{2.5}$ samples from 3 air quality monitoring stations pertinent to Regional Inspectorate for Environmental Protection (RIEP), located in Trzebinia (urban background), Szczecin (urban background) and Zloty Potok (rural background) [Fig. 1]. The study included 2 periods of 2013 year, representing the heating (I-III) and non-heating (V-VII) season. 24 hours PM samples were collected on quartz fiber filters with the use of low-volume samplers. Mass concentration of $\text{PM}_{2.5}$ was determined by the gravimetric method, according to the standard PN-EN 14907:2006b. Ambient air quality – Standard gravimetric measurement method for the determination of the $\text{PM}_{2.5}$ mass fraction of suspended particulate matter.

The methodology followed was already presented in details in previous papers [eg. 10] and is briefly described below. A 1.5-cm² piece was cut out from each filter and was analysed for the OC and EC concentrations. Carbonaceous matter content was determined by thermal-optical carbon analyser with FID detection – Model 4L Main Oven Assembly, manufactured by Sunset Laboratory Inc. In this study, the analysis was performed using the "EUSAAR_2" protocol, which has been developed as a proposed standard method for European measurement stations under the EUSAAR (European Supersites for Atmospheric Aerosol Research) project [20]. The remaining part of the filter was used to analyse water-soluble inorganic ions: Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} . The ion content was determined by ion chromatograph manufactured by Herisau Metrohm AG (Switzerland), equipped with conductivity detector. Chromatographic separation was performed on anion- and cation-exchange columns (respectively Metrosep A Supp 3 or 5 and Metrosep C3 or C4).

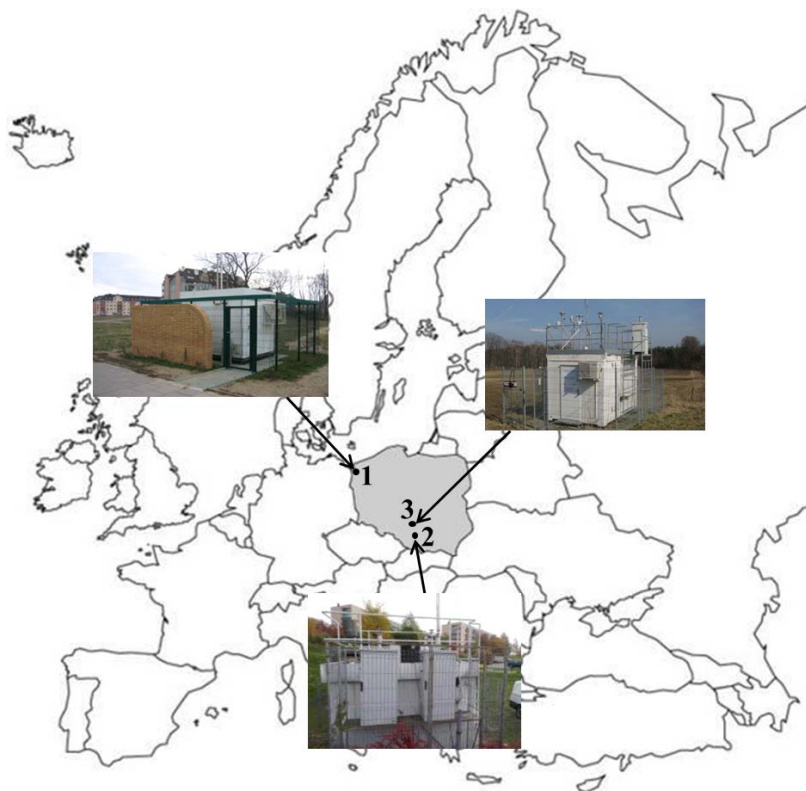


Fig. 1. Location of measurement sites: 1) Szczecin ($14^{\circ}39'48''\text{E}$; $53^{\circ}22'51''\text{N}$); 2) Trzebinia ($19^{\circ}28'41''\text{E}$; $50^{\circ}09'23''\text{N}$); 3) Złoty Potok ($19^{\circ}27'29''\text{E}$; $50^{\circ}42'38''\text{N}$)

2.2 Principal Component Analysis/Multiple Linear Regression (PCA-MLR)

A preliminary source identification study of the water soluble ionic species and the carbonaceous matter was carried out by the principal component analysis coupled with multilinear regression analysis (PCA-MLRA) [21]. The PCA-MLR is an important receptor model that has been applied in several studies [17, 19, 22]. This model does not require information on source profiles. The source categories can be identified according to the PM ambient dataset, and the contribution of each source category can be also estimated [22].

All the computations were performed using the software package Statistica 12.0 (Stat Soft company). PCA was performed separately for both measuring periods. The necessity of separate treatment of heating and non-heating seasons results from the differences in the meteorological situation and changes in the emission profile (especially increased activity of anthropogenic sources during heating season) which have together a significant impact on PM concentrations and chemical composition.

Eleven parameters were included in the analysis (NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , Cl^- , K^+ , Mg^{2+} , Ca^{2+} , EC, SOC i POC). The exceptions were $\text{PM}_{2.5}$ samples from Złoty Potok, where Ca^{2+} and Mg^{2+} ions were not taken into account, due to a large number of results below the detection limit. Bearing in mind the chemical behaviour of organic carbon [11], the secondary organic carbon (SOC) and primary organic carbon (POC) were considered as independent variables. The method for the determination of SOC and POC content in $\text{PM}_{2.5}$ was specified in previous works [11].

In this study, the decision of selecting the number of principal components relied on Kaiser criterion (factors having an eigenvalue greater than 1.0) [21]. The interpretation of the principal components was based on the variables with factor loadings with absolute values greater than 0.6. The contribution of each source to the PM burden was quantitatively assessed by the means of MLRA procedure proposed in [21].

3 Results and discussion

3.1 Characterization of PM_{2.5} and major components

The daily mean concentrations of PM_{2.5}, as the concentration of its related components, ranged in wide limits of values and exhibited spatial and seasonal variations. Much higher PM_{2.5} concentrations were found during the heating period than the non-heating one, with the values respectively: 24.4 and 8.7 µg/m³ (Szczecin), 39.2 and 16.7 µg/m³ (Trzebinia), 34.0 and 16.3 µg/m³ (Złoty Potok). These differences can be attributed to unfavourable meteorological conditions in winter (lower wind speeds and mixing heights, frequent temperature inversions) and, what is more important, an increase in the activity of local emission sources of PM, especially biomass burning and fossil fuel combustion in domestic furnaces and in small local heating plants [10-12].

The concentrations of total carbon (TC) in PM_{2.5}, averaged for a whole measuring period, equalled 6.65 µg/m³, 11.03 µg/m³ and 10.05 µg/m³, respectively for Szczecin, Trzebinia and Złoty Potok. The total carbon (TC) content in PM_{2.5} mass exceeded generally 40% and was primarily determined by fluctuations in the share of OC, which was generally above 30% of the PM_{2.5} mass. On average, water-soluble ions contribute above one-third by weight to PM_{2.5}, with the exception of a rural background station in Złoty Potok (averaged contribution ~20%). At all measurement sites, ionic composition of PM_{2.5} was dominated by SO₄²⁻, NO₃⁻, and NH₄⁺. Combined share of the above mentioned ions was (on average) ~34%, ~30% and ~18% of PM_{2.5} mass, respectively in Trzebinia, Szczecin and Złoty Potok. The SIA mass contributions to PM_{2.5} at all sites were similar during heating and non-heating period, opposite to TC contribution, which was quite higher during heating period.

The obtained results were compared with the values observed at selected urban and regional background sites in Europe [Fig. 1.]. It should be mentioned that concentrations of main components in analysed PM_{2.5} samples were comparable for Trzebinia and Złoty Potok sites from Southern Poland – one of the regions of Poland with the highest degree of urbanization and pollution of all the components of the environment [11].

The combined share of secondary inorganic ions in PM_{2.5} from investigated areas was lower (eg. Birmingham [14], Corso Firenze [24], Melpitz [27]) or comparable (Madrid [25], Barcelona [26], Rotterdam [23]), conversely to TC shares. Mean seasonal contribution of TC in PM_{2.5} from Szczecin and Trzebinia sites were relatively higher than those observed in urban background sites specified in Fig. 1. In the case of regional background site in Złoty Potok the higher TC share in PM_{2.5}, in comparison with other similar sites, was particularly evident. The dominance of carbonaceous matter content in PM_{2.5} mass from Polish measurement sites is due to the unique position of coal as an energy source, especially in power generation sector, and the wide use of biomass (mainly in rural areas) in the low-efficient furnaces, which results in the combustion conditions favorable the emissions of substances rich in organic carbon. Moreover, the contribution of industrial emission (e.g. cocking plants, iron works, waste incineration plants) to particulate pollution in Poland is also high against other European countries [10-12, 19].

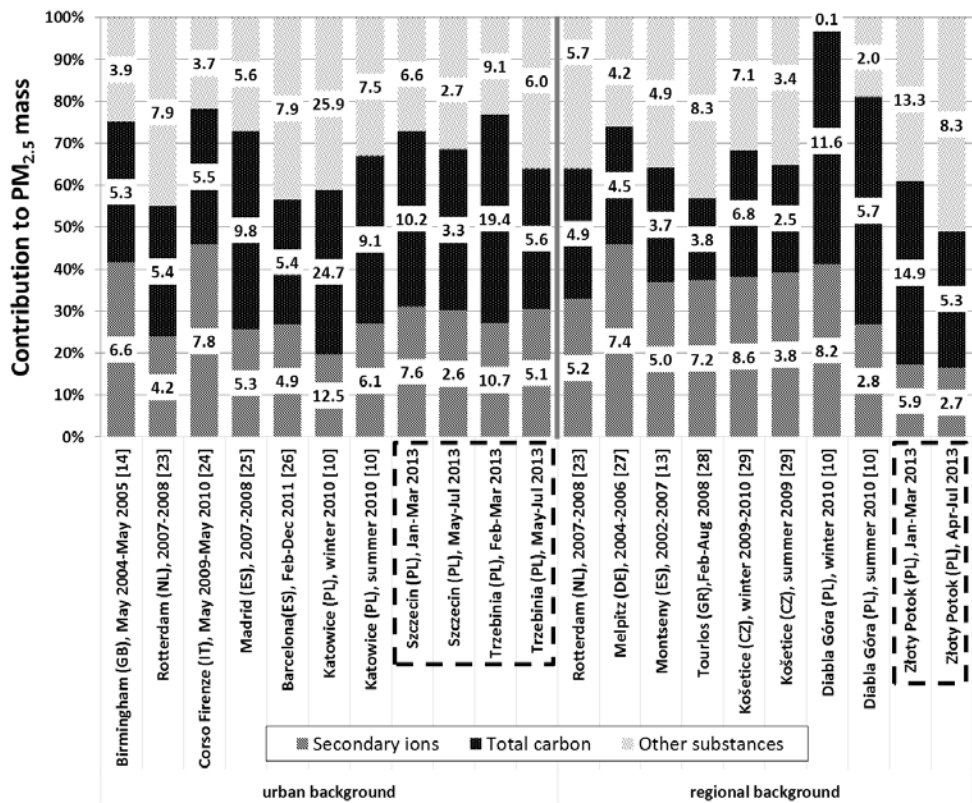


Fig. 1. Contributions of secondary inorganic ions and total carbon to fine particulate matter mass from selected urban and regional background sites in Europe (the grey line on the graph separates urban and regional background sites; 3 sites under the consideration of this study are distinguished by the black dotted lines)

3.2 Source identification of PM2.5

Table 1 shows a number of principal components (PC) for PM_{2.5} samples from analysed measurement sites. The main statistical parameters of extracted components – initial eigenvalue, and variance explained (%), as well as the contribution of these components to observed PM_{2.5} concentrations, was also presented.

In the case of Szczecin site, PCA-MLRA model allowed to extract 3 and 4 principal components, respectively in the heating and non-heating period, explaining up to ~76% and ~86% of the total variance. During the heating period, the main contribution in the PM_{2.5} concentrations showed sea spray (PC3: Na⁺, Cl⁻), with the average value ~46%. The first component (NO₃⁻, SO₄²⁻, NH₄⁺, and SOC) (~28%), suggested the role of secondary aerosols, which results from the oxidation of gaseous precursors emitted from fuel combustion processes [19]. A comparable contribution (average: ~26%) was noted for vehicle emissions along with road dust resuspension (PC2: EC, POC, Ca²⁺, Mg²⁺). During the non-heating period, the highest share in the observed PM_{2.5} concentration (~47%) was identified for secondary aerosol (PC2 : SO₄²⁻, NH₄⁺, SOC). The combustion of solid fuels, identified by PC3 (EC, POC), equalled on average ~28%. The share of secondary nitrate (PC4: NO₃⁻), as well as mixed natural sources (sea salt and mineral dust) (PC1: Cl⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺) was significantly lower.

Table 1. Varimax rotated factor loadings for PM_{2.5} ambient dataset in Szczecin, Trzebinia and Złoty Potok

<u>Szczecin</u>	Heating season			Non-heating season			
No. of components	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	PC 4
Components	NH₄⁺, SO₄²⁻, NO₃⁻, SOC	Mg²⁺, Ca²⁺, EC, POC, K⁺	Na⁺, Cl⁻	Cl⁻, K⁺, Mg²⁺, Ca²⁺, Na⁺	NH₄⁺, SOC, SO₄²⁻	EC, POC	NO₃⁻
Initial eigenvalue	5.53	1.57	1.24	4.94	1.82	1.67	0.99
Variance explained	50.30	14.28	11.27	44.92	16.56	15.21	9.00
Contribution [%]	27.83	25.73	46.45	10.02	47.28	28.56	9.11
<u>Trzebinia</u>	Heating season			Non-heating season			
No. of components	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	
Components	NH₄⁺, SO₄²⁻, NO₃⁻, K⁺	EC, POC	SOC, Cl⁻, Na⁺, Ca²⁺, Mg²⁺, K⁺	EC, POC, K⁺, Na⁺	NH₄⁺, SO₄²⁻, Ca²⁺, SOC	NO₃⁻, Cl⁻	
Initial eigenvalue	5.08	1.68	1.62	3.42	1.95	1.46	
Variance explained	46.16	15.28	14.73	31.08	17.73	13.30	
Contribution [%]	48.23	9.06	42.71	67.84	23.45	8.71	
<u>Złoty Potok</u>	Heating season			Non-heating season			
No. of components	PC 1	PC 2		PC 1	PC 2	PC 3	
Components	NH₄⁺, SO₄²⁻, NO₃⁻, SOC, K⁺	Cl⁻, Na⁺, EC, POC		EC, POC, NH₄⁺, NO₃⁻	SOC, SO₄²⁻, Na⁺	Cl⁻, Na⁺, NO₃⁻	
Initial eigenvalue	5.98	1.09		3.42	1.58	1.27	
Variance explained	66.40	12.13		37.97	17.51	14.12	
Contribution [%]	44.28	55.72		51.63	38.28	2.38	

*Note: The variables with factor loadings greater than 0.6 are in bold

At Trzebinia site, 3 principal components were identified both in the heating and non-heating period, explaining ~76% and ~62% of the total variance, respectively. During the heating period, the dominant sources of PM_{2.5} were associated with the combustion of fuels, represented by PC1 (~48%) and PC3 (~43%). PC1 was high loaded with NO₃⁻, SO₄²⁻, NH₄⁺ and K⁺, and therefore might showed a combined contribution of secondary inorganic aerosol and biomass burning. PC3 (SOC, Cl⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺) would pointed out the role of municipal combustion sources (presence of fly ashes particles, typically enriched in alkaline metals). Moreover, the contribution of primary emissions (combustion of fuels eg. in vehicle engines) (PC2: EC, POC) was found. During the non-heating period, the largest contributor in observed PM_{2.5} concentrations (~68%) was a vehicle traffic accompanied by road dust resuspension (P1: EC, POC, Na⁺, K⁺). Secondary aerosol (PC2:

SO_4^{2-} , NH_4^+ , Ca^{2+} , SOC), originating from transformations of gaseous PM precursors emitted in coal combustion processes, has played a minor role (average: ~23%). Factor 3 (NO_3^- , Cl^-) could represent open burning processes as well as wood combustion and/or waste incineration.

With regard to the regional background station in Złoty Potok PCA-MLRA model allowed to extract 2 and 3 principal components, respectively for the heating and non-heating period, explaining ~56% and ~70% of the total variance. During the heating one, the large source of $\text{PM}_{2.5}$ was secondary aerosol formation after gaseous emission from different sources (PC1: NH_4^+ , SO_4^{2-} , NO_3^- , SOC; ~44%). The dominant source of $\text{PM}_{2.5}$ was traffic sources (road salt and emissions from car engines, often outdated and with high emission rates), represented by PC2 (Na^+ , Cl^- , EC, POC; ~56%). A significant role of traffic sources, along with secondary ammonium nitrate, in the observed $\text{PM}_{2.5}$ was found also during the non-heating season – PC1 (NO_3^- , NH_4^+ , EC, POC; ~52%). A slightly lower share was recorded for secondary aerosol (PC2: SO_4^{2-} , SOC), with an average contribution ~38%. A small proportion was found for factor 3 (NO_3^- , Na^+ , Cl^-), which could present the contribution of wood burning, or, what is more likely, the shares of particles of natural origin, which have been changing in the atmosphere during transportation.

4 Conclusion

$\text{PM}_{2.5}$ samples were collected at two urban background (Szczecin, Trzebinia) and one regional background (Złoty Potok) measurement sites and analysed for the main chemical components (OC, EC, NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , Cl^- , K^+ , Mg^{2+} , Ca^{2+}). Much higher $\text{PM}_{2.5}$ concentrations, as well as concentrations of carbonaceous matter and water-soluble ions, were recorded during the heating period, due to the changes in the emission profile and unfavourable meteorological conditions. Comparing the obtained results with the data recorded on different urban and rural background sites across Europe, it was found that SIA contribution in $\text{PM}_{2.5}$ mass from investigated areas is lower or comparable, while the share of total carbon was relatively high. In the latter case, it is due to the existing structure of energy consumption in Poland, with a dominance of fossil fuels and the wide use of biomass (especially in rural areas) in the low-efficient furnaces.

PCA-MLRA model allowed for sources identification of $\text{PM}_{2.5}$ from investigated areas. The chemical composition of $\text{PM}_{2.5}$ appeared to be influenced mainly by secondary aerosols, emitted from fossil fuel combustion, vehicle exhaust, as well as biomass burning. The seasonal variability of secondary aerosol contribution was quite different for selected sites. For urban background site in Szczecin, higher share of this $\text{PM}_{2.5}$ source was identified during the heating period. Opposite situation was noted in the case of Trzebinia and Złoty Potok sites, localised in Southern Poland – one of the regions of Poland with the highest degree of urbanization and pollution of all the components of the environment.

A large contribution of traffic sources along with road dust resuspension was also identified by PCA-MLRA model, especially in the case of Złoty Potok site. Natural sources (sea spray, crustal dust) had, in general, a minor contribution to the observed $\text{PM}_{2.5}$ composition. The exception was Szczecin site, localised in the West Pomeranian Province – one of the regions of Poland with the lowest emissions of PM and its gaseous precursors.

This work was supported by the Polish National Science Centre partly under PRELUDIUM funding scheme 2nd edition, Project no. UMO-2011/03/N/ST10/05542. The results presented in this work will be included in PhD thesis of the author. The author would like also to thank Prof. Dr Eng. Katarzyna Juda-Rezler, the dissertation supervisor, and Dr Eng. Krzysztof Klejnowski, the auxiliary supervisor, for comprehensive assistance during the realisation of the work, as well as Dr Eng Magdalena Reizer for help in the interpretation of the results and Dr Eng Barbara Mathews for conducting the analysis of $\text{PM}_{2.5}$ chemical composition.

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