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Załącznik 4

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Abstract

1. Name and family name:

Lucyna Samek

2. Acquired honours, awards and academic degrees - including their name and the places and years they were achieved as well as the title of the doctoral dissertation:

Education

1. 1977+1981: High School, Liceum Ogólnokształcące, Myslenice, Major in Mathematics and Physics.
2. 1981+1986: university studies, Faculty of Material Engineering and Ceramics, AGH University of Science and Technology, Krakow, Department - Chemistry, Specialization – Ceramic.
3. 1987+1991: doctoral studies, Faculty of Material Engineering and Ceramics, AGH University of Science and Technology.

Degrees and titles

1. 1986: MSc in Chemistry, specialization: Ceramics, Faculty of Material Engineering and Ceramics, AGH University of Science and Technology, Krakow.
2. 1991: PhD in Technical Sciences, Faculty of Material Engineering and Ceramics, AGH University of Science and Technology, Krakow. Title of doctoral dissertation: "Synthesis, structure and properties of fluoro - zirconate glasses". Supervisor: Professor J. Wasylak.

3. Information regarding up to date academic appointments:

1. February 2002+present: assistant professor, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow.



2. October 2000+January 2002: post - doctoral studies, Laboratory of Micro and Trace Analysis, University of Antwerp, Belgium.
3. September 1995+September 2000: assistant professor, Faculty of Nuclear Physics and Technology, AGH University of Science and Technology, Krakow.
4. October 1992+September 1995: assistant professor, Faculty of Material Engineering and Ceramics, AGH University of Science and Technology, Krakow.
5. November 1987+September 1991: doctoral studies, Faculty of Material Engineering and Ceramics, AGH University of Science and Technology, Krakow.

4. Indicated accomplishments* resulting from article 16 act 2 from March 14th 2003 concerning academic degrees and titles as well as degrees and titles obtained in the arts (Dz. U. 2016 r. poz. 882 ze zm. w Dz. U. z 2016 r. poz. 1311.):

a) the title of the academic/arts achievement,

Studies of Particulate Matter and the Receptor Modelling of their Emission Sources

b) (author/authors, title/titles of publications, year of publication, publisher),

1. **SAMEK L.**, Chemical characterization of selected metals by X-ray fluorescence method in particulate matter collected in the area of Krakow, Poland, *Microchemical Journal*, 2009 vol. 92 iss. 2, s. 140–144, <http://www.sciencedirect.com/science/article/pii/S0026265X09000228/pdf?md5=930ddfff85d862e322e41942b6c40bd3&pid=1-s2.0-S0026265X09000228-main.pdf>

IF=2.579 (lista A czasopism MNiSW, 2009): **20.000**.
My contribution to the creation of this work (100%) consisted in the organization of a measurement station, selection of parameters for sampling, seasonal collecting of air particulate matter separated into three grain fractions, optimization of measurements on an X-ray fluorescence spectrometer, determination of concentrations of elements in each fraction by X-ray



fluorescence. My contribution also consisted in preparing a review of the literature and carrying out the interpretation of the results obtained, writing the article.

2. **SAMEK L.**, Lankosz M., Seasonal variation of the elemental composition of particulate matter collected in a small town near Warszawa, Poland, *Nukleonika: the International Journal of Nuclear Research/Institute of Nuclear Chemistry and Technology*, Polish Nuclear Society, National Atomic Energy Agency, 2011 vol. 56 no. 1, s. 57–64. **IF=0.389** (lista A czasopism MNISW, 2012): **15.000**.
My contribution to this work consisted of planning sampling, performing elemental composition analyzes by X-ray fluorescence and conducting tests. I also carried out interpretations of the results obtained. I prepared the text of the publication and conducted a discussion with the reviewers. I estimate my participation at 90%.

3. **SAMEK L.**, Source apportionment of the PM10 fraction of particulate matter collected in Kraków, Poland, *Nukleonika: the International Journal of Nuclear Research/Institute of Nuclear Chemistry and Technology*, Polish Nuclear Society, National Atomic Energy Agency, 2012 vol. 57 no. 4, s. 601–606. NUTECH-2011: Proceedings of the International Conference on Development and Applications of Nuclear Technologies: 11–14 September 2011, Kraków, Poland. **IF=0.507** (lista A czasopism MNISW, 2012): **15.000**.
My contribution to the creation of this work (100%) consisted in the evaluation of the usefulness of quartz filters for the purpose of fluorescent analysis of air pollutants, performing elemental analyzes of PM10 fractions collected on quartz filters, using statistical methods (PCA-Principal Component Analysis and MLRA-Multilinear Regression Analysis) to determine the sources of air dust pollution and their percentage share in the mass of the PM10 fraction. I prepared the manuscript of the publication and carried it throughout the entire publishing process.

4. **SAMEK L.**, Furman L., Kawik T., Weinogorska K., Application of X-ray fluorescence method for elemental analysis of PM2.5 fraction, *Nukleonika: the*



International Journal of Nuclear Research/Institute of Nuclear Chemistry and Technology, Polish Nuclear Society, National Atomic Energy Agency, 2015 vol. 60 iss. 3, s. 621-626.

IF=0.546 (lista A czasopism MNiSW, 2015): **15.000.**

My contribution to this work consisted of planning sampling and elemental composition analyzes. I made gravimetric and elemental analysis by X-ray fluorescence. I interpreted the results and prepared the manuscript of the publication and carried it through the entire publishing process. I estimate my participation at work at 70%.

5. **SAMEK L.,** Gdowik G., Ogarek J., Furman L., Elemental composition and rough source apportionment of fine particulate matter in air in Cracow, Poland, Environment Protection Engineering, 2016 vol. 42 no. 1, s. 71–83. **IF=0.514** (lista A czasopism MNiSW, 2016): **15.000.**

My contribution to this work consisted in planning sampling, performing elemental composition analyzes using X-ray fluorescence and statistical analysis. I partially did gravimetric and elemental analysis as well as statistical analyzes. I also conducted interpretations of the results obtained and prepared the manuscript. I conducted a discussion of the results and sent for publication. I estimate my participation at work at 70%.

6. **SAMEK L.,** Overall human mortality and morbidity due to exposure to air pollution, International Journal of Occupational Medicine and Environmental Health, 2016 vol. 29 no. 3, s. [1–10]. W bazie Web of Science zakres stron: 417–426.

IF=0.930 (lista A czasopism MNiSW, 2016): **15.000**

My contribution to the creation of this work (100%) consisted in planning the research, preparation of the given concentrations from WIOS, getting acquainted with the AirQ program and making calculations. I prepared a literature review on the impact of air pollution on human health. I conducted a discussion of the results obtained and wrote a manuscript of the publication.

7. **SAMEK L.**, Stęgowski Z., Furman L., Preliminary PM_{2.5} and PM₁₀ fractions source apportionment complemented by statistical accuracy determination, *Nukleonika: the International Journal of Nuclear Research*, Institute of Nuclear Chemistry and Technology, Polish Nuclear Society, National Atomic Energy Agency, 2016 vol. 61 no. 1, s. 75–83. Warsaw medical physics meeting 2014: 15–17. May 2014, Warsaw, Poland. **IF=0.760** (lista A czasopism MNiSW, 2016); **15.000**
My contribution to the planning, preparation of the data from WIOS conditioning program AirQ making calculations. I prepared a literature review on the impact of air pollution on human health. I conducted a discussion of the results obtained and wrote a manuscript of the publication.
8. **SAMEK L.**, Stęgowski Z., Furman L., Fiedor J., Chemical content and estimated sources of fine fraction of particulate matter collected in Krakow, *Air Quality, Atmosphere and Health*, 2017 vol. 10 iss. 1, s. 47–52. Publikacja dostępna online od: 2016-05-10. tekst: <https://goo.gl/orgJM>
IF=2.662 (lista A czasopism MNiSW, 2017); **25.000**.
My contribution was to plan my research. I carried out an analysis of the elemental composition of the PM_{2.5} fraction by X-ray fluorescence. I made calculations of BC concentration in the PM_{2.5} fraction. I prepared the data for PMF analysis. I partially did a statistical analysis of the PMF. I conducted a discussion of the results obtained, prepared a manuscript of the publication and carried it through the entire publishing process. I estimate my participation at 70%.
9. **SAMEK L.**, Stęgowski Z., Furman L., Styszko K., Szramowiat K., Fiedor J., Quantitative assessment of PM_{2.5} sources and their seasonal variation in Krakow, *Water, Air and Soil Pollution*, 2017 vol. 228 iss. 8 art. no. 290, s. [1–11]. Publikacja dostępna online od: 2017-07-21. tekst: <https://goo.gl/mWLGVG>.
IF=1.769 (lista A czasopism MNiSW, 2017); **25.000**.
My contribution was to plan my research. I carried out an elemental composition analysis by X-ray fluorescence. I made calculations of BC concentration in PM. I prepared the data for statistical analysis and partially did it. I prepared a review of



literature. I interpreted the obtained results of both elemental, ionic and statistical analysis. I wrote an article. I estimate my participation at 60%.

10. **SAMEK L.,** Stegowski Z., Styszko K., Furman L., Fiedor J., Seasonal contribution of assessed sources to submicron and fine particulate matter in a Central European urban area, *Environmental Pollution* 241 (2018) 406-411, **IF=4.358** (lista A czasopism MNISW, 2017): **40.000.** *My contribution consisted in planning the tests (sampling, gravimetric analysis, elemental and ionic composition analysis and statistical research). I made gravimetric analysis and elemental composition analysis by X-ray fluorescence. I made calculations of BC concentration in particulate matter. I partially did a statistical analysis of the PMF. I interpreted the obtained results of both elemental, ionic and statistical analysis. I wrote an article. I estimate my participation at 60%.*

c) describing scientific/art aim the above mentioned papers and obtained results together with describing their applications.

The series of 10 publications presented above include the works written by me. In order to create them by myself, I planned the course of the research, made the gravimetric analyzes, elemental composition analyzes by X-ray fluorescence method and statistical analyzes. Participation of the co-authors was limited to the implementation of specific tasks initiated by my ideas. Statements about the scope of work carried out within the framework of a specific publication have been obtained from all co-authors and can be found in Annex No. 6

Introduction

Air particulate matter (APM) is a mixture of solid and liquid particles suspended in the air [1, 2]. This definition of APM is used by the World Health Organization and the European Environment Agency. The size of particulate matter grains ranges from a few nanometers to about 100 micrometres. Considering the size of the particulate matter grains, we can divide them into fine (fine) and coarse (coarse). The fine fraction

contains grains with a diameter of not more than 2.5 μm , while the coarse fraction contains grains with a diameter of more than 2.5 μm and not more than 10 μm . These fractions differ in chemical composition, physical properties and emission sources. The current division of air particulate matter includes TSP (Total Suspended Particulate) and PM₁₀, PM_{2.5}, PM₁ and PM_{0.1} fractions. These are granulometric fractions of PM (Particulate Matter) containing particles with aerodynamic diameter less than or equal to 10 μm , 2.5 μm , 1 μm and 0.1 μm , respectively. TSP is the total air particulate matter. Division into grain fractions depends on their impact on human health. Larger particles are retained in the nasopharyngeal cavity and excreted. The PM₁₀ fraction enters the trachea and bronchi (upper respiratory tract), the PM_{2.5} fraction travels to the pulmonary alveoli (lower respiratory tracts), whereas the PM₁ fraction reaches the alveoli and the blood. Emission sources are also linked to the size of the grains. Natural and anthropogenic sources of air particulate matter can be distinguished. Both natural and anthropogenic sources can be primary and secondary. From primary sources, the pollution is emitted directly into the atmosphere, while secondary pollutants are created in chemical reactions taking place in the atmosphere. The natural primary sources of air pollution include volcanic eruptions, forest fires, sea salt and mineral dust (from the soil). Primary anthropogenic sources include industrial dust (including energy, mining and construction). Natural secondary contaminants include sulphates from biogenic gases, sulphates from volcanic SO₂, organic volatile compounds, nitrates from NO_x. Anthropogenic secondary sources include SO₂ sulphates, biomass burning, nitrates from NO_x, and anthropogenic organic volatile compounds.

The chemical composition of air particulate matter is also very important. The air particulate matter is composed of elemental and organic carbon, sulphate, nitrate, ammonium, phosphate, chloride, potassium, calcium, magnesium and various organic compounds. Among the elements present in the environment there are main, minor and trace elements [3]. Concentrations of main elements in the environment range from several to several dozen percent. These include elements such as: carbon (C), hydrogen (H), nitrogen (N) and oxygen (O). The concentration of sub-elements in the environment does not exceed several percent. Sub-elements include: calcium (Ca), chlorine (Cl), potassium (K), magnesium (Mg), sodium (Na), phosphorus (P) and sulfur (S). Trace elements occur in the environment in concentrations below 0.1%. About 40 trace elements are present in the atmospheric air: silver (Ag), aluminum (Al), arsenic



(As), gold (Au), bar (Ba), bromine (Br), cadmium (Cd), cerium (Ce), cobalt (Co), chromium (Cr), cesium (Cs), copper (Cu), europium (Eu), iron (Fe), gallium (Ga), hafnium (Hf), mercury (Hg), indium (In), lanthanum (La), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), palladium (Pd), platinum (Pt), rubidium (Rb), rhodium (Rh), antimony (Sb), scandium (Sc), selenium (Se), silicon (Si), samarium (Sm), tin (Sn), strontium (Sr), tantalum (Ta), thorium (Th), titanium (Ti), tal (Tl), uranium (U), vanadium (V), tungsten (W), yttrium (Y), zinc (Zn), zirconium (Zr). Silicon is rarely treated as a trace element. Elements such as Ni, Cd, As and especially Pb have a negative effect on human health. Permissible concentrations of these elements are included in EU directives and national regulations [4, 5, 6]. The concentrations of these elements in the PM₁₀ fraction are determined by the Voldvodship Inspectorates for Environmental Protection. The analysis of the composition of other elements is not routinely carried out. Groups of scientists in the world (including Poland) conduct such research [7-14, IB1-IB10]. The results of these analyzes are used, inter alia, for the receptor modeling of pollutant emission sources [15-20, IB3-IB5, IB7-IB10] and for the characterization of particulate matter for further research aimed at human health [21-25].

The identification of sources of air pollution and the estimation of their contribution in the mass of PM can be conducted using various receptor methods based on immission measurements [18, 26-31]. Chemical components in these methods are identifiers of particular sources of pollution. The PCA (Principal Component Analysis) method was first used by Thurson and Spengler to estimate sources of pollution in Boston [32, 33]. Interesting examples of PCA applications in environmental sciences can be found in the following literature [34, 35]. These analyzes include the application of Factor Analysis, which is used to study the correlation between the concentrations of elements at the sampling point (at the receptor) [18, 36]. In the PCA method, the elements are listed and, as a consequence, probable sources are identified. The main disadvantage of PCA is the fact that it can lead to negative values of the contribution of factors. However, PCA remains widely used in studies identifying sources of pollution [17, 37, 38, 39]. Another receptor method used to determine the sources is PMF (Positive Matrix Factorization) [40, 41]. In this method, the contribution of factors can only take zero or positive values. In my case, I use EPA PMF which uses the method developed by Paatero and Tapper and modified by Paatero and Hopke [42, 43]. In this program, the



concentration of chemical components and the uncertainty of their determination are used to determine the contribution of factors [44, 45]. The receptor methods are based on the chemical composition of the collected APM at the site of immission. Individual chemical components are the identifiers of pollution sources. In Poland, these methods are not widely disseminated. According to my findings, the PMF analyzes made by me are among the first or even the first such studies in Poland.

The aim of my research was:

Determination of concentrations of elements by X-ray fluorescence method in fine and coarse fractions and fraction with grain diameter of over 10 μm of air particulate matter with an attempt to indicate their origin in the urbanized (Krakow) and suburban (Swierk) areas.

Determination of element concentrations by X-ray fluorescence method and ion concentrations in the PM₁₀, PM_{2.5} and PM₁ fractions collected in the urbanized area (Krakow).

Modeling with PCA, MLRA and PMF receptor methods, which allowed to determine probable sources of air pollution and their contribution to the PM₁₀, PM_{2.5} and PM₁ fractions collected in the urbanized area (Krakow).

Achieving the above-mentioned goals is a significant contribution to research into air pollution and identification of the emission sources. This is important in works aimed at reducing the level of pollution.

Publications [IB3-IB10] were created during the implementation of regional projects TC (Technical Cooperation) of the International Atomic Energy Agency located in Vienna. I was the initiator of the above-mentioned projects. In 2009, I started the implementation of a project in which 9 scientific institutions and universities together with the Environmental Protection Agencies from 9 European countries decided to participate. I organized a working meeting in Krakow and became the leader of this international project. More and more in the awareness of air quality institutions, the view is emerging that these issues should be considered as global phenomena, not local ones. As I mentioned, in the first cycle of projects related to air pollution participated 9 countries (scientific institutions, environmental protection agencies, universities). Interesting results led to the continuation of research, which resulted in the second

edition of projects concerning air quality research. The number of participants increased to 16. We implemented the next two-year cycle of the program and in the current cycle (2018-2019) participate already 20 European and Asian countries. In this project I fulfill the role of coordinator and project leader. The implementation of projects involves cooperation of the participating units. Each research center performs works related to the implementation of the project at home, and then workshops are organized at which the obtained research results are presented and discussed. Initially, we organized summer and winter PM10 sampling campaigns, we analyzed the elemental composition of these samples by analytical methods available to the research unit. These were primarily nuclear and X-ray fluorescence methods. The PM10 fraction was collected in rural and urban areas (for comparison). Meteorological parameters were also monitored. The results of elemental composition analysis, together with meteorological data formed the basis for the use of receptor modeling methods to identify sources and estimate their contribution. According to my findings, the PMF analyzes made by me are among the first or even the first such studies in Poland. Research conducted as part of our regional projects was also unique for Central Europe, Southern Europe and selected Asian countries. The research strategy consisted in developing activities aimed at optimal use of the workshop and research tools as well as the development of a methodology understandable and accepted by individual units. The high quality of the research results obtained by us was influenced by the comparative tests organized as part of the projects. They were carried out in the field of sampling, elemental composition analysis and finally estimation of pollution sources by PMF receptor modeling. From 2014, daily PM2.5 samples are collected throughout the year (every third day) by research units in 16 countries. The elemental composition of the PM2.5 fraction is determined by analytical methods available by participants. The next stage of projects involves the use of the PMF receptor method to identify sources of pollution. During the implementation of projects, trainings in the field of chemical analyzes and receptor modeling as well as air mass transport are organized. Experts are invited to cooperate with the Joint Research Center (JRC-European Commission). A manuscript has now been written covering research conducted by all project participants (16 European and Asian countries) and was sent for publication in the journal Environment International. During the implementation of projects at the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, many master's



and engineering theses were created. I was the supervisor of the above-mentioned works. The research was captured and noticed by the medical community.

The general description of own research

The presented cycle of publications implements the objectives listed before. A detailed description of my own research is provided in the next part of abstract. Below is a general description of the research.

The concentrations of elements depend on the place of sampling and on the day of collection related to the season of the calendar year. For samples collected in Krakow at the AGH, I observed higher concentrations of K, Ca, Mn, Fe, Cr, Cu, Zn, Br and Pb in comparison to samples taken in Swierk near Warsaw. Samples were collected using the same equipment. It should be noted that the samples came from similar periods (2007-2008 Krakow, 2008-2009 Swierk).

For both locations Ca, Mn, Fe appeared in higher concentrations in fractions with grain sizes above 10 μm . For Swierk samples, high correlation coefficients between concentrations of these elements were observed, which would indicate a common origin. The source of these elements may be dust carried away from the soil. For Krakow, the origin of dust can also be associated with the steel industry. However, in the fine fraction, Br and Pb occurred with high correlation coefficients. These elements may indicate the origin of road transport and / or municipal emissions.

The following observations were made for the PM₁₀ fraction. In the winter period concentrations of PM₁₀ fractions collected at the AGH University of Science and Technology in Krakow were more than twice as high as in summer (2010, 2011, 2012).

The concentrations of elements in the PM₁₀ fraction collected in Krakow (at the AGH, in Krowdrza, in Nowa Huta) are below the limit values given by the Ministry of the Environment [6].

For samples of the PM₁₀ fraction collected at the AGH in Krakow, concentrations of the following elements K, Ti, Mn, Fe, Cu, Zn were lower in winter in 2012 compared to the winter of 2011.

For samples of PM₁₀ fractions collected at the AGH in Krakow, concentrations of the following elements: Cl, Ca, Zn, Br, Sr, Pb were higher in winter 2012 than in the summer of



2010. Concentrations K, Ti, Mn, Fe, Cu were higher in summer compared to winter for the same samples.

The following observations were made for the PM_{2.5} fraction.

PM_{2.5} fraction concentrations collected at the AGH University of Science and Technology in Krakow did not change significantly in 2011, 2013 and 2016, both for summer and winter. In winter more than twice as high concentrations of PM_{2.5} fraction were observed than in summer.

Higher concentrations of the following elements in the PM_{2.5} fraction were observed in the above mentioned samples Cl, K, Zn, Br, Pb in winter compared to the summer. Concentrations of Ca and Mn were comparable in summer and winter. However, Cu and Fe concentrations in the PM_{2.5} fraction were higher in the summer.

The following observations were made for the PM₁ fraction.

PM₁ fraction concentrations collected at the AGH University of Science and Technology in Krakow were higher in winter than in the summer of 2016-2017. Higher concentrations of the following elements Cl, K, Fe, Cu, Zn, Br, Pb were observed in winter compared to summer. The Ca concentration for these samples was higher in the summer.

The concentrations of the majority of the elements studied are higher in the PM₁₀ fraction compared to their concentrations in the PM_{2.5} fraction.

The concentrations of the majority of elements in the PM_{2.5} fraction are higher than in the PM₁ fraction. This indicates the presence of most elements in larger grains.

The PCA and MLRA receptor method used to identify PM₁₀ fraction sources of air pollution indicated two factors (Krowodrza, Nowa Huta) and three factors (AGH, Krakow) respectively. Each factor was assigned two or more probable sources of pollution, assisted by elements as identifiers of individual pollution sources.

The PCA and MLRA methods were used for samples of PM₁₀ fractions collected at AGH. The calculations were performed both in STATISTICA and MATLAB. The MATLAB program additionally uses procedures to determine the uncertainty of factor contribution. For both of the above calculations, similar categories of sources were obtained. In MATLAB, the categories for the first factor were poorly separated (three likely sources were assigned to them).

For the PM_{2.5} fraction collected at the AGH in 2011-2012, 2012-2013, PCA and MLRA analyzes were performed, and the PMF analyzes for samples collected in 2016-2017. In the initial period, three factors were separated, and in 2016-2017 four. Several sources have

been assigned to one factor. The research results complement each other. On the basis of statistical analyzes of PCA MLRA and PMF, similar categories of sources and similar values of their contribution to the PM2.5 fraction were obtained. It is worth noting that in 2016-2017, in addition to the elements, the concentrations of ions in the samples were determined. This helped in the separation of another factor associated with secondary aerosols.

Parallel to the PM2.5 fraction, results for the rarely measured PM1 fraction were obtained. The concentrations of elements, ions along with the PMF modeling were performed. The same number of factors as for the PM2.5 fraction was obtained. The shares of sources are now different. The largest share in the PM1 fraction are secondary aerosols (sulphates and nitrates), less transport and the smallest combustion processes - compared to the PM2.5 fraction.

For the PM2.5 fraction collected at the urban background station in the years 2014-2015, 8 factors were obtained by the PMF modeling method on the basis of elemental composition analyzes. Complementing the analysis with ion composition, the best parameters were obtained for six factors. Each factor was assigned one source category. In this way, the contribution of the following sources was determined: combustion processes, secondary aerosols (sulphates, nitrates), biomass combustion, industry, traffic and unidentified.

The AirQ program (Issued by the WHO) was effectively used to estimate the health effects of exposure of people living in Krakow on air pollution.

The detailed description of own research

The elemental analysis of particulate matter

I carried out research work on airborne particulate matter mainly in Krakow. The work [IB1] contains the results of research carried out in Krakow in 2007-2008. Samples were collected seasonally every day for a week in each season. Air dust samples were separated into grain fractions, with grain sizes below 2.5 μm (fine fraction), between 2.5 + 10 μm (coarse) and the third fraction with grain sizes above 10 μm . Research carried out with a division into grain fractions was one of the first in Poland. In air pollutants, the separation into grain fractions is important. Small dusts most often attack the human respiratory system (they reach the lower parts of the respiratory system and blood) and can cause many diseases (eg asthma, respiratory tract cancer) and can also affect the condition of historic buildings. The coarse fraction enters the upper respiratory tract (trachea) and is removed

from it. The elemental composition of air particulate matter in each grain fraction was determined by X-ray fluorescence. At the same time, I determined the concentrations of the following elements found in APM: K, Ca, Ti, Ni, Cr, Mn, Fe, Cu, Br, Pb and As. European regulations and national regulations adapted to them give limit values of the concentrations of elements in particulate matter with particle sizes up to 10 μm due to human health. The X-ray fluorescence method allows simultaneous determination of concentrations of many elements. Determining the correlation dependence between concentrations of elements in dust pollution and meteorological parameters allows for a broader interpretation of the results obtained, related to the possibilities of their transport and origin. The applied analytical method allows to determine the concentrations of elements in individual grain fractions. During the winter of 2007, high levels of elements in air particulate matter appeared (low wind speed at the time meant that the dust persisted in the air for a long time). In May 2007 the wind speed was high, the city was clearly air-conditioned and low concentrations of elements were observed. There was a strong correlation between concentrations of Ca, Mn, Fe, which would indicate that they could have come from the same source. There were also correlations between Pb and Br concentrations, which would also indicate a common source.

I also conducted similar studies in the towns of Swierk and Otwock as part of the AGH project with the Institute of Nuclear Chemistry and Technology and published the results in [IB2]. In the years 2008-2009 in Swierk, I collected samples of air pollutants seasonally. They included three grain fractions: fine (with a grain diameter of not more than 2.5 μm) coarse (with a grain diameter between 2.5 and 10 μm) and the third fraction with a grain size above 10 μm . Samples were collected daily for one week in four seasons of the calendar year. High concentrations of fine fractions were observed in February 2009 and April 2008. Ca, Fe and Mn concentrations showed the same trend and occurred mainly in the large grain size fraction. High concentrations of these elements occurred mainly during the days when the wind was blowing from the south-east at a speed of 2m / s. The calculated correlations between the concentrations of these elements indicated a high correlation coefficient in the range of 0.8-0.9. High correlation coefficients may indicate a common source of origin. These elements are part of the mineral part (soil) of air pollutants and can also be part of soil and / or airborne dust. The other analyzed elements did not show any correlation. High potassium levels were observed in the winter in the three fractions collected. Potassium is an indicator of biomass burning, which would indicate the fact that



biomass is burned in furnaces used to heat homes during the winter season. High concentration of copper was observed in February 2009 in the coarse fraction, while in the remaining seasons copper was evenly distributed in all fractions. Zinc showed similar concentrations in all fractions during all seasons. Higher concentrations of lead and bromine were observed in fine and coarse fraction.

The Identification of emission sources of particulate matter by PCA (Principal Component Analysis) and MLRA (Multilinear Regression Analysis); and determination of their contribution to PM mass

Subsequent works [IB3, IB4, IB5, IB7] included: sampling of PM₁₀ and PM_{2.5} fractions using the reference method at the AGH University of Science and Technology in Krakow, determination of air particulate matter concentration and analysis of their elemental composition by X-ray fluorescence. In [IB3], the samples originated from the districts of Krakow Krowdrza and Nowa Huta. Statistical methods of PCA and MLRA (PCA-Principal Component Analysis and MLRA-Multilinear Regression Analysis) were used to identify pollution sources and estimate their contribution to air pollution. In [IB3] I presented the results of research carried out in Krakow in the winter of 2010. Samples of air pollutants of the PM₁₀ fraction were collected every day for a month in Nowa Huta and Krowdrza simultaneously, by the Voivodship Inspectorate of Environmental Protection (WIOS) in Krakow. By X-ray fluorescence method I marked elemental composition of PM₁₀ samples. Next, to the results of the elemental composition analysis, I used statistical methods to identify pollution sources and estimate their contribution. The elements were indicators of individual sources of air pollution. The concentrations of the analyzed elements were particularly high in Nowa Huta, but their values did not exceed the limit values given by the Ministry of the Environment [6]. The concentrations of Ti, Cu, Br and Pb for both locations had comparable values. The concentrations of K, Ca and Zn were twice as high for Nowa Huta, Cr concentrations, Mn three times, and for Fe up to four times higher concentration values were observed for Nowa Huta. On the basis of statistical analysis, I received two factors identifying sources for both locations. One characterized by the elements: Pb, Br, Zn, Cu, As identifies the source related to combustion processes (coal, fuels) and road transport. The indicators of the second factor were the elements: Ca, K, Fe. This factor is probably related to the industry and wood burning. Using the MLRA method,



I determined the contribution of individual sources in air pollution. For Nowa Huta, the average monthly share of the factor related to industry and wood burning was 28.5%; combustion of coal and fuels, and transport of 53.1%, while the contribution of the unidentified factor was 18.3% (secondary aerosols). For Krowodrza, the average monthly contribution of the factor related to industry and wood burning was 46.1%; combustion of coal and fuels, and transport 50.1%, whereas the share of the unidentified factor was only 3.5% (secondary aerosols). In the days when the outdoor temperature decreased, the contribution of the factor associated with the coal combustion processes increased, reaching even the value of 85%.

Papers [IB4, IB5] contain the results of elemental composition analysis of the PM_{2.5} fraction collected at the AGH University of Science and Technology in Krakow in 2011, 2012 and 2013. Additionally, the paper [IB5] presents a statistical method for the analysis of pollution sources. Samples were collected in two summer and winter seasons. Average concentrations of PM_{2.5} fractions during winter are 3-4 times higher than during the summer (50-75 μg / m³ in winter and 16 μg / m³ in summer). Average K concentrations were much higher in winter than in summer (733 ng / m³ and 171 ng / m³ in 2011 and 2012 and 1666 ng / m³ in winter and 123 ng / m³ in summer 2013). The probable K source can be associated with wood and biomass burning processes. Br and Pb concentrations are about 3 times higher in winter than in summer (30-38 ng / m³ in winter and 13-15 ng / m³ in summer for Pb and 8 - 21 ng / m³ in winter and 4-8 ng / m³ in summer for Br). These elements may come from the combustion of fuels. In 2011 and 2012 and 2013, the average concentrations of all analyzed elements are much higher in winter than in summer. The exception is Fe and Cu in 2013, when I observed higher concentrations of these elements in the summer of 2013. Interesting was one of the observations namely, during the inflow of air masses from the north-west direction on February 10, 2011 high concentrations of Zn, Br and Pb were observed. About 50 km north-west of Krakow a lead-zinc-lead industry is located. Based on the obtained concentrations of elements in two seasons, winter 2011 and summer 2012, I used the statistical methods of PCA and MLRA to identify the sources of pollution and determine their shares in the mass of the PM_{2.5} fraction. These were preliminary studies involving a small amount of data and therefore the obtained results of the receptor method used are an estimation rather than a thorough analysis. I received two factors in both seasons. In winter, the following elements were indicators for one factor: K, Ca, Fe, Cu, Zn and Sr, to which I assigned the following



sources: municipal emission as well as steel and cement industry. For the second factor, the identifiers were: Br and Pb. For this factor, the transport (communication source) can be assigned as the emission source. In contrast, in the summer the indicators of the first factor were the following elements: Zn, Br and Pb and I attributed to it transport as the source of emission (communication source). The second factor in the summer was related to the elements Ca, Mn, Fe and Sr, which talk about the cement and steel industry. I determined, by the MLRA method, the average contribution of sources in the total PM_{2.5} mass in winter and summer. The contribution of the communication source in the winter period was 37.8%, and in the summer - 53%, in the PM_{2.5} fraction. Municipal emissions and winter industry accounted for 49.2%, and municipal emissions in the summer were not identified while the industry share was 18%. In the second half of February, air temperatures were well below 0°C, the contribution of municipal emissions and industry was significant from 69 to 84%. During the days with higher air temperature, the share of these sources was significantly lower (from 2 to 44%). In winter, the share of unidentified sources was 13%, and in summer - 29%. These sources may include, but are not limited to, secondary aerosols (sulphates, nitrates, organic carbon).

In [B7] I used statistical methods of PCA, FA and MLR to identify and estimate the contribution of sources in the PM₁₀ and PM_{2.5} fractions. The samples of PM₁₀ and PM_{2.5} fractions were collected at the AGH University of Science and Technology in Krakow seasonally in the years 2010 to 2013. I carried out an elemental composition analysis using the X-ray fluorescence method. I observed the chlorine in winter; in the summer the concentration of this element was below the limit of detection. Chlorine can come from sprinkling roads and pavements with salt and / or municipal emissions. For potassium, the winter / summer concentration ratio was 0.76-1.5 for the PM₁₀ fraction. On the other hand, for the PM_{2.5} fraction it changed in the range of 9.2-13.5. Potential sources of potassium could be: municipal emission, combustion processes and biomass burning. Calcium concentrations for the PM₁₀ fraction were comparable in winter and summer. During winter the calcium concentration was twice as high as in summer 2010 and winter 2011. For PM_{2.5} fractions, Ca concentrations were comparable in winter and summer, while in 2013 winter / summer values were 3.0. Titanium I observed only in the PM₁₀ fraction. The concentration of Mn was higher in PM₁₀ than PM_{2.5}. The concentration of iron in PM₁₀ in the summer of 2010 was comparable with the winter of 2011. In contrast, in the winter of 2012 the concentration of Fe was twice as low as in previous years. The concentration of



Fe in the PM2.5 fraction in the summer was twice as high as in the winter. The concentration of Cu in the PM2.5 fraction in winter was five times lower than in the summer. In addition, the Cu concentration was higher in the PM10 fraction compared to the PM2.5 fraction. The concentration of zinc in both fractions was higher in winter than in summer. In PM10, the winter / summer value was 5.2 and 7.8 for Br. In the PM2.5 fraction, bromine concentrations were comparable in winter and summer. A similar trend was observed for Pb. After applying statistical methods, I received three factors for both fractions. The variance for the first factor was 68.6% for the second 29.7% and the third factor had variances of 1.2% for the PM10 fraction. Characteristic elements for the first factor were: K, Mn, Fe, Cu and Pb. These elements showed high correlation coefficients. Based on these elements, I identified three sources; combustion processes (municipal emission, biomass combustion (K, Fe)), steel industry (Fe, Mn), Cu presence may indicate a source related to the wear of brake pads. Potassium can be assigned to municipal emissions and biomass burning. The contribution of factor one was in the range of 60-90%. For the second factor, the indicators were Ca, Cr and Sr. They can be assigned to the cement and metallurgical industry as well as soil dust. The share of the second factor was 3% at the beginning of the research, and then 15% in 2012. The third factor was Zn and Pb. I have assigned it to zinc-lead plants located near Krakow. These elements can also be assigned to transport. The share of this factor was 3-20%. The trajectories have shown that on the days when we have a large share of this factor, the masses of air were flowing from the north-west, where the lead zinc plants are located. Good separation of sources of pollution was not obtained (in one factor there are three sources), but the positive result of the statistical analyzes was determination of uncertainties. The zero factor is responsible for secondary aerosols and its share is 4-18% in the PM10 fraction. Statistical analyzes for the PM2.5 fraction were also indicated by three factors. The first factor characterized by Ca, Fe, Cu and Sr can be attributed to two sources - industry (steel, cement) and transport. The second factor identified the following elements K, Rb Zn and Pb; it may be associated with combustion and road transport. The third factor (Mn, Fe, Br, Zn and Pb) can identify the source associated with road dust. The zero factor indicates unidentified sources. The contribution of this source is 1-4% in winter and 2-8% in summer. The share of the first indicator factor for industry and transport was 70-80%. (75.1% - winter, 80% summer). The contribution of the second factor was 10-30% in winter and 5-20% in summer (on average 20.5% winter, 12.1% summer). The share of the third factor was 2-7% in summer and 1-5% in winter. My



other PM_{2.5} fraction studies presented in [IB5] show results from winter 2011 and summer 2012. In winter, the factor responsible for municipal emissions and industry was characterized by elements K, Ca, Fe, Zn, Sr and its average contribution was 49.1%. The contribution of the second factor responsible for transport (Br, Pb) was 37.8% and the unidentified source was 13%. In the summer, transport (Cu, Br, Pb) indicated a share of 53%, industry (Ca, Mn, Fe, Sr) - 18%, and unidentified sources at 29%.

The Identification of emission sources of particulate matter by PMF (Positive Matrix Factorization) and determination of their contribution to PM mass

In subsequent papers [IB8] and [IB9], I present the results of research including a more advanced receptor method PMF-(Positive Matrix Factorization) for determination of sources. Research covers a much longer sampling period. Daily PM_{2.5} dust samples were collected throughout the year 2014-2015, every third day at the Krakow urban background station. A total of 194 samples of the PM_{2.5} fraction were collected and analyzed. In work [IB8] elemental composition analyzes (Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb) and coal (Black Carbon) were made, and on this basis probable sources of pollution using the PMF method were estimated. However, in [IB9] the analyzes of PM_{2.5} fractions were extended to ion analyzes (Na⁺, K⁺, Ca⁺⁺, NH₄⁺ cations and NO₃⁻, SO₄⁻, PO₄⁻, Cl⁻ anions). This study also used the PMF method for analyzing sources of pollution. The concentration of PM_{2.5} fraction is more than four times higher in winter than in summer and twice in autumn and spring. Only in summer, the concentration of PM_{2.5} fraction is below the limit value of 25 µg / m³. Concentrations of such elements as: Cl, K, Br, Pb, Cu and Zn showed high seasonal variability. High concentrations of Cl and K were observed in the winter. These elements can come from the combustion of coal and biomass. Depending on the season, the Cu / Zn concentration ratio was in the range of 0.009-0.16. The value of 0.3 shows that Cu and Zn are a transport (communication) indicators [46]. The Cu / Pb ratio was 0.43 in spring and 0.46 in autumn. In summer, 0.69 and very low in winter, 0.28. The ratio of these elements' concentrations to transport (communication) is 2.3-3.0 [46]. Such results indicate that there is also another source of lead, especially in winter. The Pb / Br value was 1.64-1.85 and remained stable throughout all seasons. Ca and Ti indicated high concentrations in the spring, probably due to the significant amount of construction work emitting dust. The indicators of the steel industry are Fe, Mn, while the transport - Cu, Zn and Pb [46]. Kabata Pendias reports that the indicator of non-steel metallurgical industry



may be Cu, Zn, Pb, As, Cr, Ni, Co [3]. Oil burn indicators according to Kabaty Pendias are Ba, Co, Ni, V, Cr and Mn [3]. Yu and co-authors give K as an indicator of biomass burning [11]. The confirmation of this information is the work of Viana and co-authors [18]. The results of receptor modeling of pollution sources together with their contribution to the PM_{2.5} fraction are shown in Figure 1. The PMF method yielded 8 factors and one source was assigned to each factor. Table 1 gives factors with assigned sources and their contribution to the PM_{2.5} fraction. In the previous work [18], the results obtained in the years 2012-2013 of PCA and MLRA analyzes for the PM_{2.5} fraction showed that in the winter the share of municipal emissions and industry is 49.2%, and road transport is 37.8%. In this work [18] covering the years 2014-2015, the contribution of road transport for the PM_{2.5} fraction in winter is similar and amounts to 36.5%, while the municipal emission is 25% and the steel industry 3.4%, the metallurgical industry - not steel 18% (total municipal emissions and industry - 46.4%). In the summer period, in the previous work [18], the share of road transport for the PM_{2.5} fraction was 53% (40-60%) while in this work for the PM_{2.5} fraction this share is 62.9%. The share of the industry was 18% for the PM_{2.5} fraction in the work [18], and in [18] 20.3%. The results indicate a large convergence of results obtained using both receptor methods (PCA and MLRA; PMF). It is worth noting that the PMF method is a more comprehensive method and contains results covering the whole year, while [18] contains results covering monthly periods of PM_{2.5} sampling (a month in summer, a month in winter). High seasonality was observed for the factor 6 associated with the combustion processes of coal and biomass, indicating a large contribution in winter. The contribution of road transport has remained stable throughout the year.

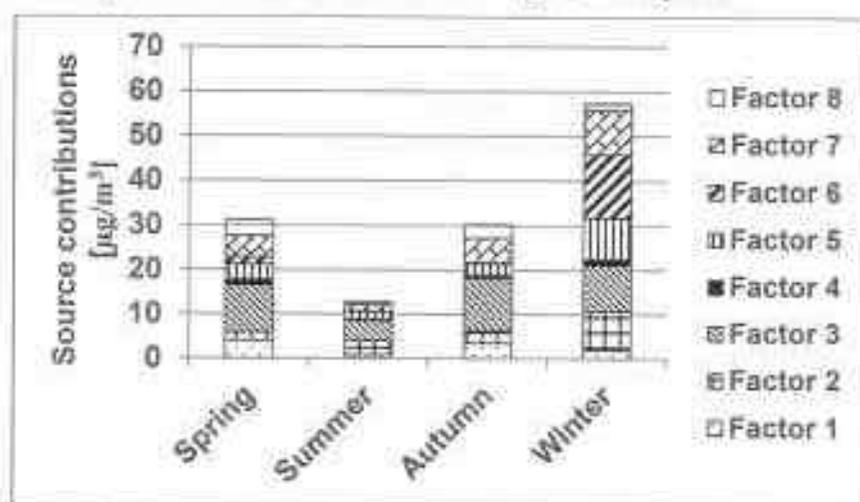


Fig.1. The contribution of factors to PM_{2.5} fraction in Krakow in 2014-2015

Table 1. The factors with assessed sources and indicators together with contribution to PM2.5 fraction in Krakow in 2014-2015.

Factor number	Assessed source	Indicators	The source contribution (%)			
			Spring	Summer	Autumn	Winter
1	Steel industry	Mn, Fe, Zn, Br, Pb	13	11,7	7	3,3
2	Traffic (diesel)	Ni, BC, BS	6,2	24,9	9,5	15,7
3	Traffic (gasoline)	Cr, Cu, Br, BC, BS	33,7	35	39	17,8
4	Dust resuspension	Cu	4	3,2	2,2	2,3
5	Construction work, soil	Ca, Ti, Cr, Mn, Fe, Ni	10,8	13	8,5	10
6	Combustion of coal, biomass	Cl, K	5	0,3	0,9	24,6
7	Metallurgical industry (No steel)	Zn, Br, Pb	15,7	11	18	18
8	Non identified sources		11,2	5	9,9	2,4

In [IB9], I published the results of extended tests on the analysis of ion concentrations and re-applied the PMF method to modeling pollution sources. The average annual results of concentrations of elements and ions were compared with data from other European and Asian cities. The most similar concentrations of elements and ions in Krakow are those obtained for Milan. The exception is chlorine, whose concentration in Krakow is 5 times higher than in Milan and half as much as in Beijing. Ammonium ions have comparable concentrations in Krakow and Milan. However, nitrate ions have higher concentrations in Milan, and sulphate ions in Milan. In work [IB9], the most optimal solution from PMF analysis showed 6 factors. For the first factor, the indicators were: Cl⁻, NO₃⁻, Zn, Br, Pb, Cu. The following sources have been assigned to it: combustion of coal (Cl⁻) [32, 42], waste (Cu, Mn, Pb, Zn, Cl, Br) [17, 47] as well as emissions from cars (NO₃⁻, Cu, Zn, Pb) [10]. The second factor was assigned to the secondary source of nitrates (NH₄⁺, K⁺, Na⁺, NO₃⁻). Jeong together with co-authors gave NH₄⁺, NO₃⁻, Cl⁻ as the identifiers of secondary nitrate aerosols [27]. Ammonium nitrate is formed from NO_x emitted from transport, biomass burning and industry [26]. Nitrates combine with ammonia, potassium and sodium. The third factor (SO₄²⁻, NH₄⁺) was identified as secondary sulfates. It is created from the agricultural origin of NH₄⁺ and SO₂ derived from the combustion of coal, biomass and natural gas used for industrial and domestic purposes. Secondary aerosols can be considered as regional pollution, compounds transported over long distances or anthropogenic origin. The fourth factor identified by K⁺, Cu, Pb, Fe is related to the combustion of biomass. Manousakas together with co-authors gives biomass identifiers as K, BC [30] and Almeida together with co-authors only K as an index of biomass burning [37]. The fifth factor (Cr, Fe, PO₄³⁻, Ca₂⁺, Na⁺) was identified as industry / soil dust. Viana together with co-authors give indicators Al / Si / Ca / Fe, Ti, Sr, Mg as soil dust (urban dust, street dust) [18]. Cr and Fe come from industry, especially steel or non-steel metallurgy present in Krakow. Road transport is the sixth source identified. The main indicators are: BC, Ti, Sr, Cu, Zn, Mn. Viana together with co-authors gives C, Fe, Ba, Zn, Cu, Cr, Mn as markers of road transport [18]. Cr, Cu, Zn are recognized as road transport indicators [30]. Figure 2 presents a comparison of the determined and modeled concentration values of PM_{2.5} fraction. In contrast, Figure 3 shows the contribution of individual sources in the PM_{2.5} fraction for each month in 2014-2015 in Krakow. The results indicate that in the winter months the dominant sources are combustion processes and secondary aerosols. In January, combustion processes of 27.2 µg / m³ have a large contribution; secondary nitrates-11.4 µg / m³ and secondary sulphates

-10.5 $\mu\text{g} / \text{m}^3$. In the summer, secondary aerosols also contribute to the presence of gases produced by car engines. In August, the share of secondary sulphates was 2.7 $\mu\text{g} / \text{m}^3$ (i.e. 27% of PM2.5) and secondary nitrates were 1.4 $\mu\text{g} / \text{m}^3$ (that is 14% of PM2.5). The high proportion of sulphates in the winter indicates the increasing consumption of solid fuels used to heat homes during the stagnant winter conditions. Similar results were received by Jeong and co-authors in Edmonton [27]. Biomass combustion is used to heat homes and in combined heat and power plants. The share of this source in August is 1.4 $\mu\text{g} / \text{m}^3$ and in January 10 $\mu\text{g} / \text{m}^3$. The source associated with road transport remains stable and amounts to 1.6-4 $\mu\text{g} / \text{m}^3$. However, dust from the soil and industry come to 0.5-1.2 $\mu\text{g} / \text{m}^3$. Similar observations were made by the authors of the works [11, 26, 27]. If we compare the contribution of individual sources in different cities, we can see the similarity of results for Krakow and Milan. Both cities are located in the lowlands with emerging mists, surrounded by mountains that create a natural barrier that protects against the main air circulations.

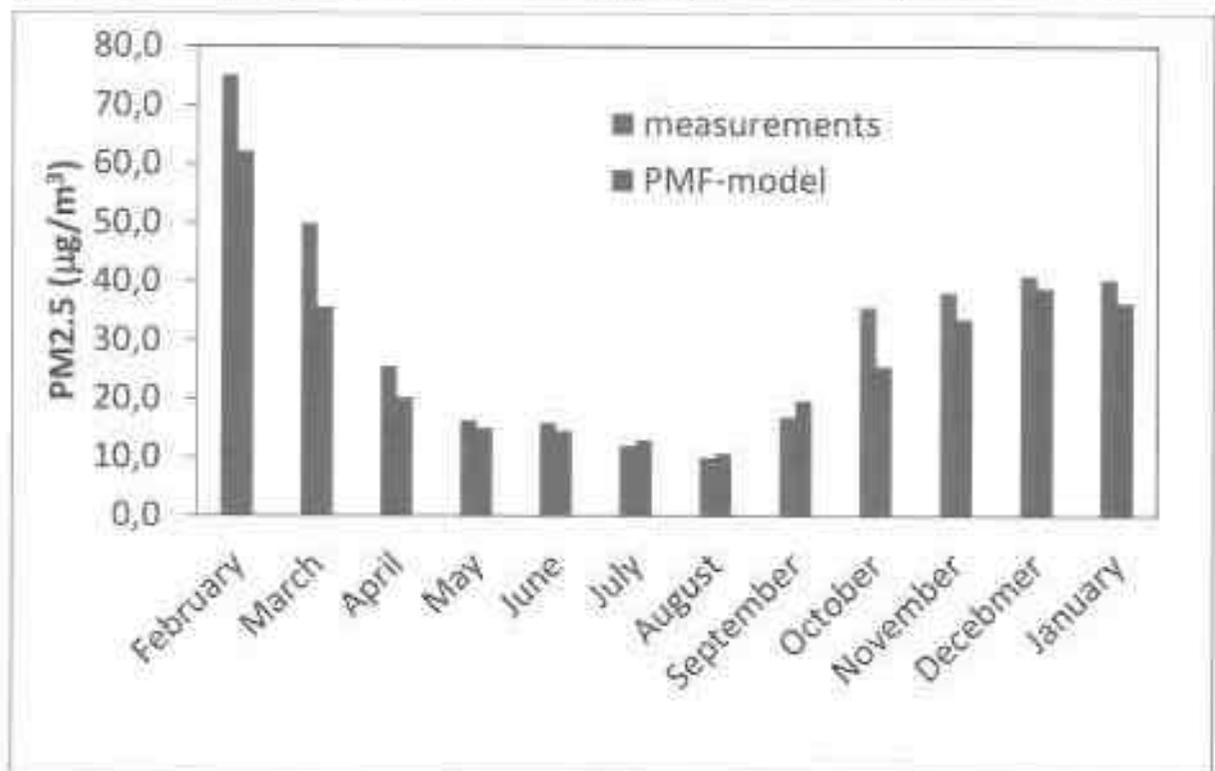


Fig. 2. The average monthly measured and modeled by PMF concentration of PM2.5 fraction in Krakow in 2014-2015.



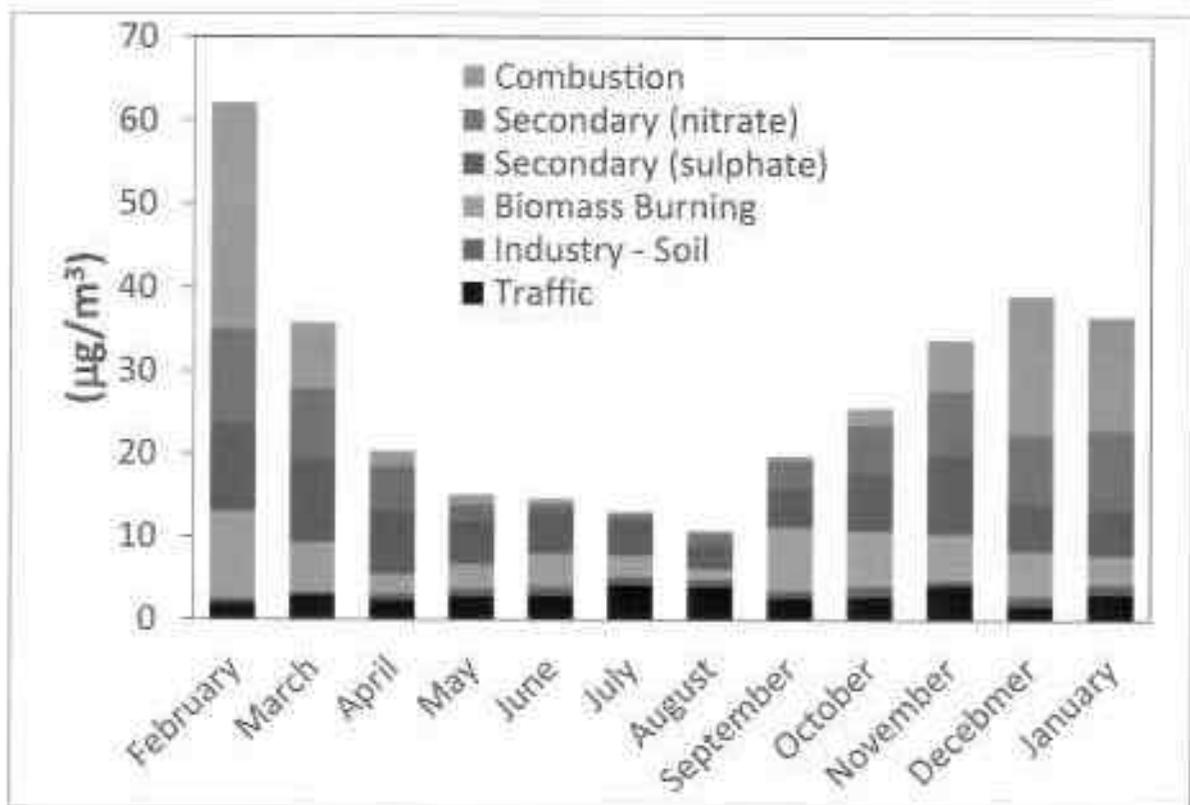
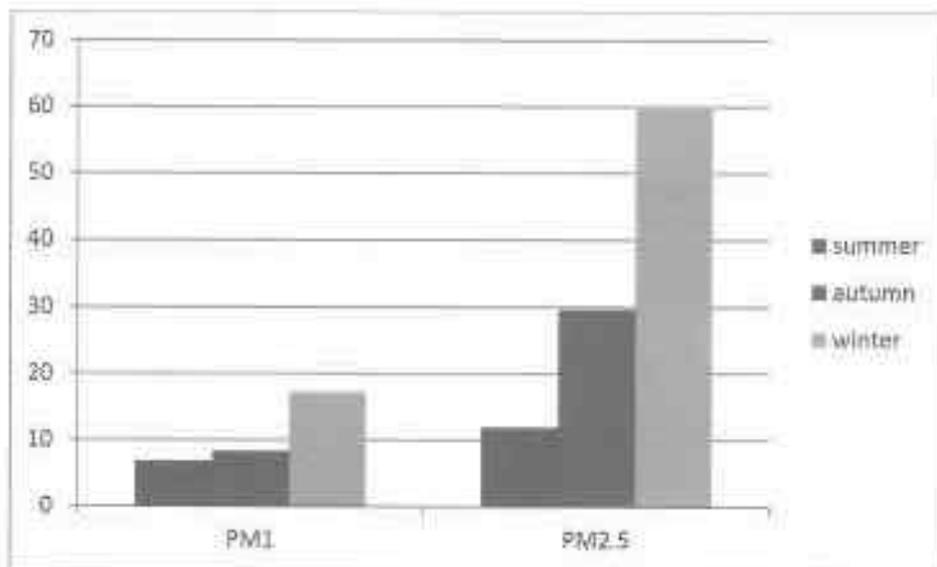


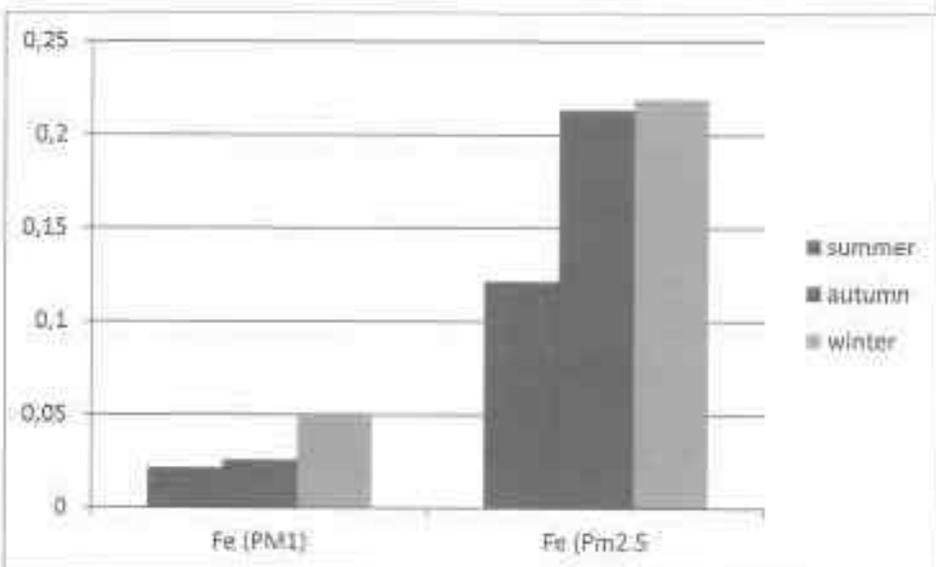
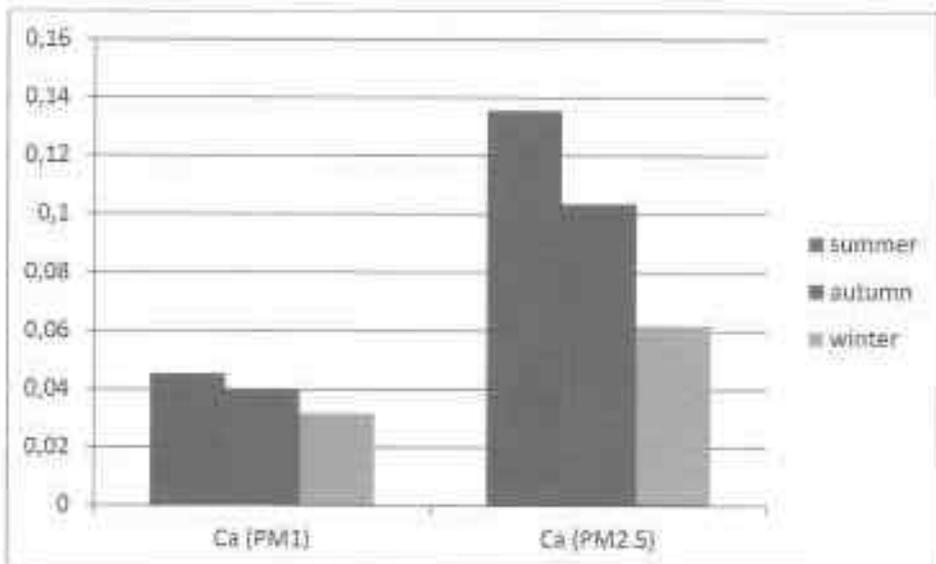
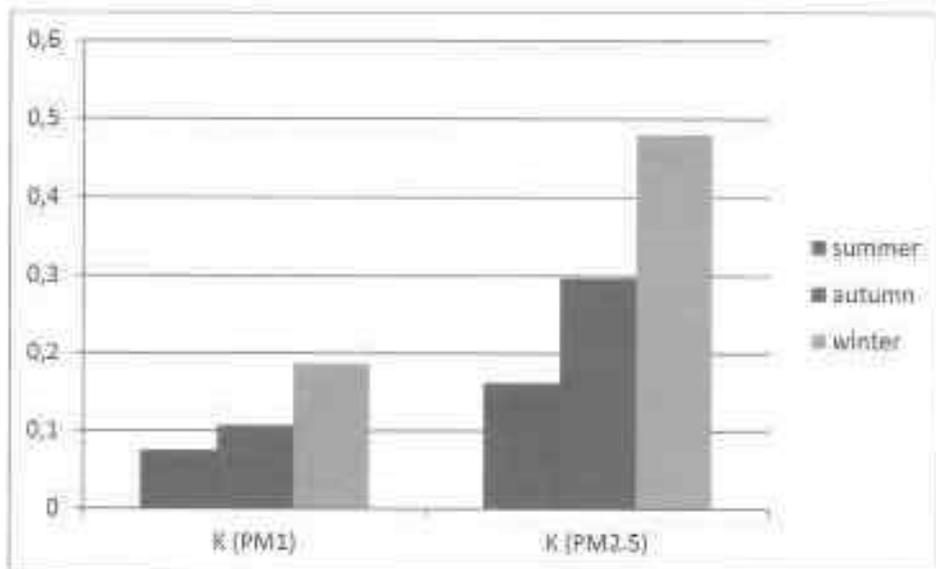
Fig. 3. The contribution of the sources modeled by PMF in PM2.5 fraction in Krakow 2014-2015.

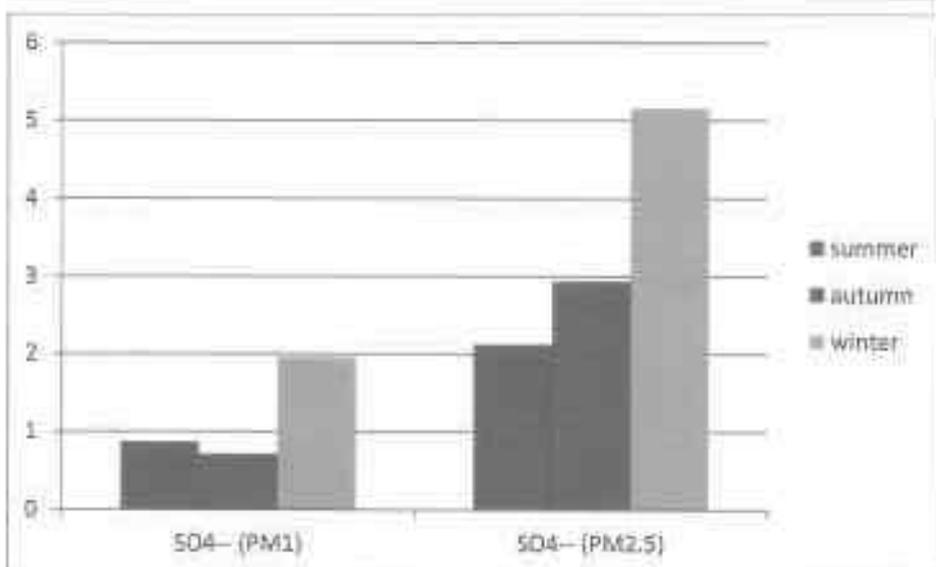
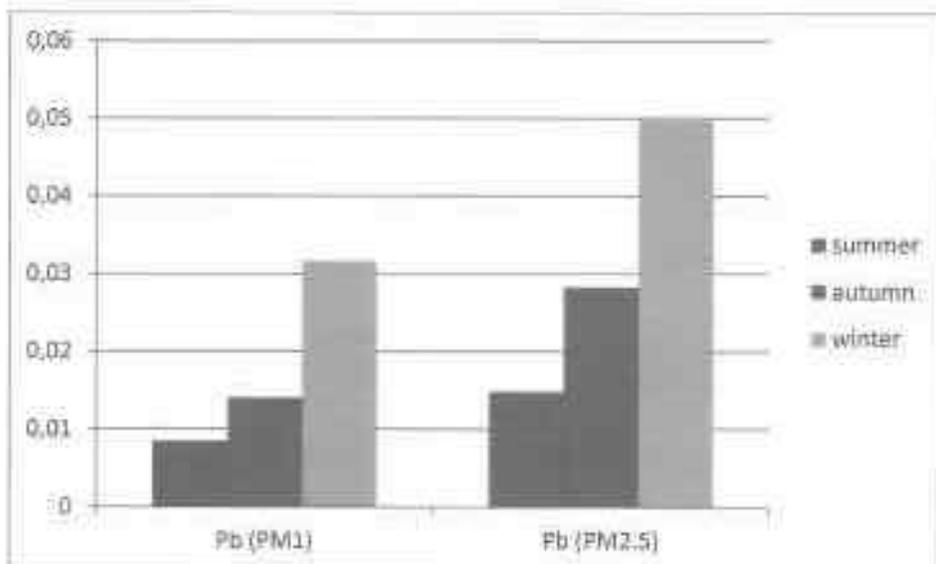
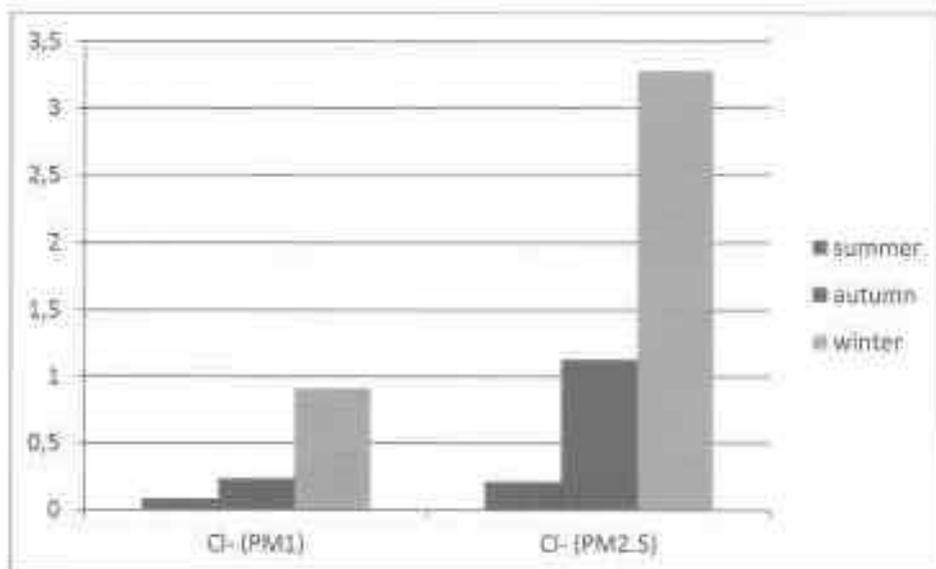
The highest seasonal variation was demonstrated by combustion processes (from 0.17 to 27 $\mu\text{g} / \text{m}^3$). In winter, the contribution of this source to the PM2.5 fraction in Krakow was 40%. Biomass combustion and secondary aerosols also showed high seasonal variability (in summer, 10 times smaller share than in winter). In the winter season, the contribution of these four sources to the PM2.5 fraction was in the 88-96% range, and in the summer 60%. Soil dust, industry and road transport did not show any significant seasonal variation.

In the next paper [IB10] I presented the seasonal variability of concentrations of PM1 and PM2.5 as well as their chemical composition along with estimated sources of air pollution. Samples PM1 and PM2.5 were collected from July 2016 to February 2017 at the AGH in Krakow. I determined concentrations of 16 elements, 8 ions and BC for each sample. Using concentrations, I used PMF receptor modeling to determine the sources of pollutant emissions. The concentrations of PM1 and PM2.5 were the highest in the winter and were respectively 17.3 $\mu\text{g} / \text{m}^3$ and 60 $\mu\text{g} / \text{m}^3$ for the PM1 and PM2.5 fractions. For the PM2.5 fraction a similar value was obtained in the previous work [IB9] of 57 $\mu\text{g} / \text{m}^3$ in 2014

for the urban background station. In summer, concentrations of PM1 and PM2.5 fractions amounted to $6.9 \mu\text{g} / \text{m}^3$ and $12 \mu\text{g} / \text{m}^3$. In the work [18] for the PM2.5 fraction in summer, a concentration of $12.7 \mu\text{g} / \text{m}^3$ was obtained. For Zabrze, Rogula-Kozłowska together with co-authors [13] received for PM2.5 $18.44 \mu\text{g} / \text{m}^3$ in summer and $66.85 \mu\text{g} / \text{m}^3$ in winter in 2009. Rogula-Kozłowska and Klejnowski [14] published for the PM1 fraction in Zabrze the value of $16.66 \mu\text{g} / \text{m}^3$ in summer and $60.17 \mu\text{g} / \text{m}^3$ in the winter of 2009. In this study, much lower concentrations of the PM1 fraction were observed. The fraction of PM1 fraction in the PM2.5 fraction was 60% in summer and 30% in winter. In my subsequent studies, this share was 60-70% in spring 2015 and 2016 [12]. The concentration of PM1 fraction increased slightly in the winter whereas the concentration of PM2.5 fraction increased significantly in the winter. High seasonal variability of PM is characteristic for Poland and other Central European countries where energy production is based on burning fossil fuels, mainly coal. Fig. 4 shows the concentrations of selected elements and ions in the two fractions PM1 and PM2.5.







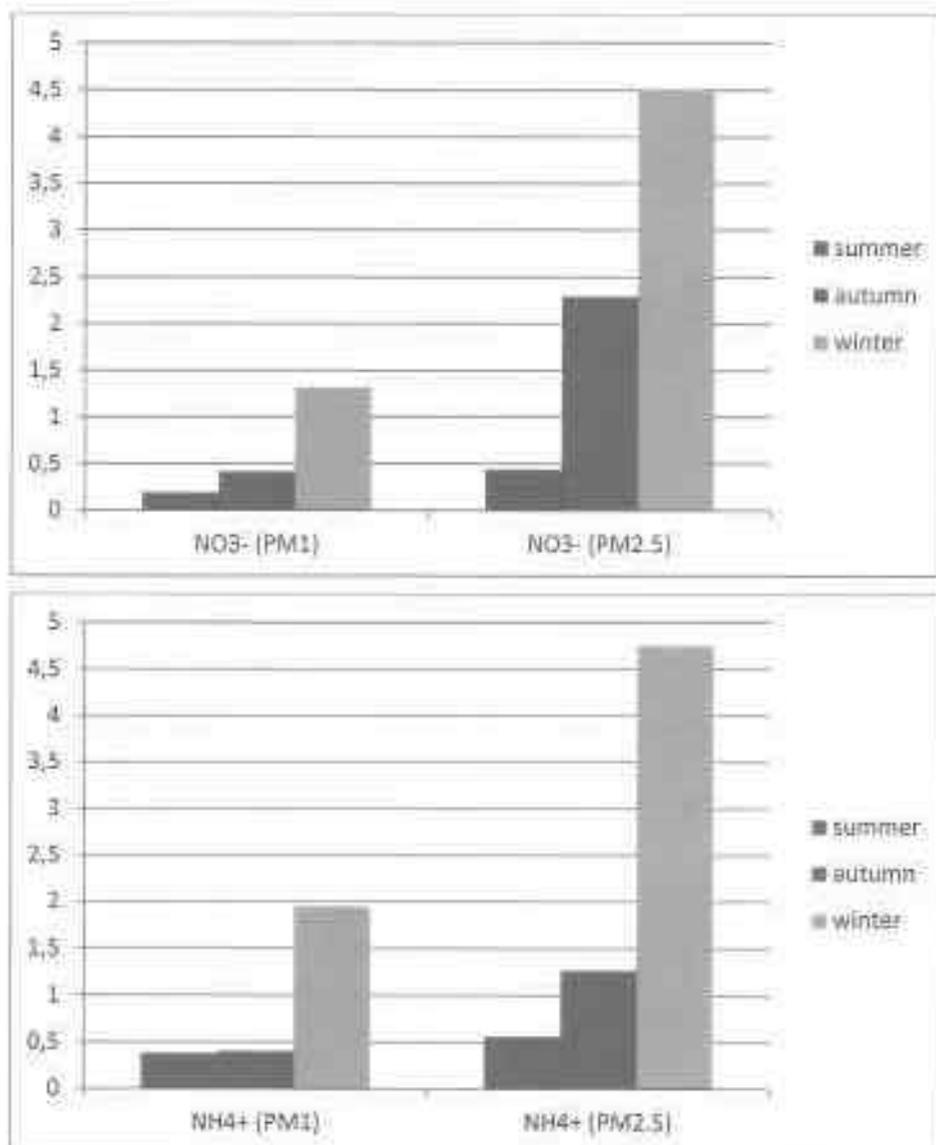


Fig 4. The average seasonal concentrations of some elements and ions in PM_{10} and $\text{PM}_{2.5}$ in 2016-2017.

The potassium content in the PM_{10} / $\text{PM}_{2.5}$ fractions is about 36-46%. This indicates that potassium is present in a larger amount in the $\text{PM}_{2.5}$ fraction. This element is an indicator of biomass burning. The Cl^- in winter concentration was $0.91 \mu\text{g} / \text{m}^3$ and $3.28 \mu\text{g} / \text{m}^3$ in the PM_{10} and $\text{PM}_{2.5}$ fractions, respectively. In summer, the concentration of chlorine ions is very low. The value of PM_{10} / $\text{PM}_{2.5}$ for Cl^- in winter is 30%, which indicates that this ion accumulates mainly in the $\text{PM}_{2.5}$ fraction. Chloride can come from domestic furnaces (burning coals and rubbish) and / or sprinkling sidewalks and streets in winter. The NO_3^- concentration in winter was $1.32 \mu\text{g} / \text{m}^3$ and $4.5 \mu\text{g} / \text{m}^3$ for the PM_{10} and $\text{PM}_{2.5}$ fractions.

respectively. In the summer the concentrations were much lower $0.19 \mu\text{g} / \text{m}^3$ and $0.44 \mu\text{g} / \text{m}^3$ for the PM1 and PM2.5 fractions, respectively. The PM1 / PM2.5 value for NO_3^- was similar to that for chlorine. Similar trends were observed for SO_4^- and NH_4^+ ions. The concentrations of sulphate ions were in winter $2.0 \mu\text{g} / \text{m}^3$ and $5.6 \mu\text{g} / \text{m}^3$ for the PM1 and PM2.5 fractions, respectively. In summer, $0.87 \mu\text{g} / \text{m}^3$ and $2.12 \mu\text{g} / \text{m}^3$ in the PM1 and PM2.5 fractions, respectively. The share of SO_4^- PM1 / PM2.5 was 40%. However, the share of ammonium ions was 69% in winter and 40% in summer (PM1 / PM2.5). The Fe concentration was in winter $0.05 \mu\text{g} / \text{m}^3$ and $0.22 \mu\text{g} / \text{m}^3$ for the PM1 and PM2.5 fractions, respectively. In the summer, $0.02 \mu\text{g} / \text{m}^3$ and $0.12 \mu\text{g} / \text{m}^3$ in the respective PM1 and PM2.5 fractions. The PM1 content in PM2.5 for Fe was 20%, which proves that iron is mainly present in the PM2.5 fraction. Another trend was observed for Ca: The summer concentration was higher than in the winter. The concentration was: in the summer of $0.05 \mu\text{g} / \text{m}^3$ and $0.14 \mu\text{g} / \text{m}^3$ and in winter $0.03 \mu\text{g} / \text{m}^3$ and $0.06 \mu\text{g} / \text{m}^3$ for the PM1 and PM2.5 fractions, respectively. The proportion of PM1 in PM2.5 for Ca was 34% in summer and 51% in winter. Calcium is an element originating mainly from the soil. The concentration of BC in the summer was $1.15 \mu\text{g} / \text{m}^3$ $1.29 \mu\text{g} / \text{m}^3$ for the PM1 and PM2.5 fractions; in winter, $1.95 \mu\text{g} / \text{m}^3$ and $3.25 \mu\text{g} / \text{m}^3$ for the same fractions. The share of PM1 in PM2.5 for BC was 90% in the summer and 60% in winter. This would indicate that BC is mainly in the sub-micron fraction.

PMF receptor modeling was used to obtain common sources of both fractions. Table 2 shows the contributions of individual sources.

Table 2. The contributions of particular sources to PM1 and PM2.5 fractions in Krakow in 2016-2017.

PM1 [$\mu\text{g}/\text{m}^3$]				
The source	Indicators	Summer	Autumn	Winter
Coal and biomass combustion	Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , BC, Br, Pb, Cu, Zn	0.19 (3%)	1.4 (17%)	4.8 (27%)
Secondary aerosols	SO ₄ ²⁻ , NH ₄ ⁺ , NO ₃ ⁻ , BC, Cu, Fe, Br	3.4 (49%)	3.1 (37%)	11 (63%)
Traffic, soil, industry	Cu, Zn, Br, Pb, BC, NO ₃ ⁻ , NH ₄ ⁺ , Ca, Fe	1.4 (19%)	1.7 (21%)	1.8 (10%)
Not identified		2.0 (29%)	2.2 (25%)	—
PM2.5 [$\mu\text{g}/\text{m}^3$]				
The source	Indicators	Summer	Autumn	Winter
Coal and biomass combustion	Cl ⁻ , NO ₃ ⁻ , BC, Cu, Zn, Br, Pb, K	0.85 (8%)	9.2 (31%)	31 (53%)
Secondary aerosols	SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , BC, K, Fe, Cu	7.1 (57%)	8.5 (29%)	17 (28%)
Traffic, soil, industry	Cu, Zn, BC, Pb, NO ₃ ⁻ , Ca, Fe, K	4.7 (37%)	7.9 (27%)	7.0 (12%)
Not identified		—	4.1 (13%)	4.3 (7%)

The first factor was assigned to the emission source associated with the combustion processes. The indices were Cl⁻, NO₃⁻, SO₄⁻, Br, Pb, Cu, Zn, BC for the PM_{2.5} fraction. For the PM₁ fraction, SO₄⁻ was not present as an identifier. Similar identifiers were found in the previous work [IB9] for the PM_{2.5} fraction. In the PM₁ fraction Cl⁻ correlates with Zn, Br, Pb. In the PM_{2.5} fraction, SO₄⁻ strongly correlates with Br, Cl⁻ NO₃⁻ and Cl⁻ correlates with Zn, Br, Pb. The second factor was identified as secondary aerosols (sulphates and nitrates). The main identifiers were: SO₄⁻, NH₄⁺, NO₃⁻ and BC, Ca, Fe, Br. In this work, sulphates and nitrates appeared as a common source (one factor), in the previous work [IB9], for the PM_{2.5} fraction, were separated. It is worth noting that in [IB9] results from the urban background station were included. NH₄⁺ correlates with Cl⁻, NO₃⁻, SO₄⁻, Br for both investigated fractions. The third factor includes three likely sources of emissions: road dust for which the identifiers were NO₃⁻, BC, Br, Pb, Cu, Zn; industry for which the identifiers were: Fe, Ca, Zn, Pb and soil dust with identifiers such as Ca and Fe. Pb correlates with BC, K, Cu, Br, Rb for both fractions. Zn correlates with Fe, Cl⁻ for both fractions. BC correlates with Cl⁻, Zn, NO₃⁻, Cu for both fractions. The seasonal contribution of the identified sources to the mass of the PM₁ fraction was different from the PM_{2.5} fraction due to the diverse origin and time of lifting of both fractions. In the summer, combustion processes had a very small contribution, in the autumn they were growing and in winter they reach the highest value of 4.8 µg / m³ for the PM₁ fraction, which was 27% of its mass and 31 µg / m³ for the PM_{2.5} fraction, which accounted for 53% of its mass. This source is associated with the combustion of low-quality coals (soot, sulfur compounds, chlorine, silicon, trace elements), waste (municipal, rubber, plastics) in poorly efficient old domestic kilns and the combustion of biomass. The concentration of secondary aerosols in the PM₁ fraction was 3.4 µg / m³ in summer, 3.1 µg / m³ in autumn and 11 µg / m³ in winter. Their contribution to PM₁ fraction in winter was the largest 63% later in summer 49% and in autumn 37%. For the PM_{2.5} fractions, the concentration of secondary aerosols was 7.1 µg / m³ in summer, 8.5 µg / m³ in autumn and 17 µg / m³ in winter. The contribution of secondary aerosols in the PM_{2.5} fraction was 59% in the summer, 29% in autumn and 27% in winter. Higher contribution values of secondary aerosols in PM_{2.5} fraction in the summer indicate more intensive changes of gaseous precursors in summer than in winter. For the PM₁ fraction, the same trend was observed for Zabrze and Birmingham. In the summer, for the PM_{2.5} fraction, the contribution of secondary aerosols amounted to 23.3% for Zabrze [13, 14], 39.3% for Helsinki, and 41.4%

for Athens [48]. Similarly, in winter in Zabrze 15.9% [13.14], Duisburg 39.5%, Prague 34%, Amsterdam 39% [48]. The annual average for Zurich was 45% [49] and Barcelona 30% [50]. The obtained results indicate a smaller contribution of secondary aerosols in Krakow than in other European cities. These aerosols are derived from the processing of SO_2 and NO_x . SO_2 is oxidized to SO_3 or liquid SO_4^- ions, and then neutralized to $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 . In contrast, NO_x is photochemically oxidized to HNO_3 followed by NH_4NO_3 . The value of the ratio of the equivalent concentration ($\text{NH}_4 / \text{SO}_4^- + \text{NO}_3^-$) is equal to 1.08 in summer and 1.74 in winter for the PM1 fraction. This means that the amount of NH_4 is sufficient to neutralize H_2SO_4 and HNO_3 . For the PM2.5 fraction, the ratio is 0.61 in summer and 1.46 in winter. This means that sulphates and nitrates are fully neutralized in winter by ammonia. However, in summer the conditions are not conducive to the formation of NH_4NO_3 in the air. Other compounds in summer may be formed such as NaNO_3 or $\text{Ca}(\text{NO}_3)_2$. In the summer for the PM2.5 fraction the value of $\text{NH}_4 / \text{SO}_4^-$ was 0.71 and in winter - 2.45. In summer, the sulphates are only partially neutralized in the PM2.5 fraction. At low NH_3 concentrations, the neutralization of sulfuric acid by ammonia is favored over the formation of ammonium nitrate. There is a reaction of ammonia with nitric acid. Another factor describing the three sources showed a similar concentration in all seasons. The concentration in the PM1 fraction was $1.4 \mu\text{g} / \text{m}^3$ in the summer, $1.7 \mu\text{g} / \text{m}^3$ in the autumn and $1.8 \mu\text{g} / \text{m}^3$ in the winter. On the other hand, in the PM2.5 fraction the concentration was $4.7 \mu\text{g} / \text{m}^3$ in the summer, $7.9 \mu\text{g} / \text{m}^3$ in the autumn and $7.0 \mu\text{g} / \text{m}^3$ in the winter. The percentages are 37% in the summer, 27% in autumn and 12% in winter in the PM2.5 fraction. The PM1 / PM2.5 ratio for the source associated with the combustion processes was 15% in all the seasons tested. For the third factor, this value was 20-30%. In contrast, for secondary aerosols PM1 / PM2.5 in winter was 65%, in summer 48% and in autumn 35%. In summary, by means of PMF modeling, three factors were obtained, which were assigned appropriate sources of pollution. In winter, the share of combustion processes and secondary aerosols was 90% in the PM1 fraction and 81% in the PM2.5 fraction. In the summer, combustion processes are 3-6% in both fractions. In the summer, the proportion of secondary aerosols was 50% for both fractions. Transport, industry and soil dust did not tend to change their seasonal contribution.



The health effects of air particulate matter

In [IB6], I determined through the AirQ program (Air Quality) developed by the WHO, the impact on human health in Krakow exposed to given pollution (based on PM10, PM2.5, NO_x and SO₂ dust concentrations alone). Pollution concentrations were collected from WIOS in Krakow. The studies covered the years from 2005 to 2013. The total mortality due to the PM10 exposure in 2005 was 41 premature deaths per 100,000 inhabitants and decreased in 2013 to 30.1 premature deaths per 100,000 inhabitants. Figure 5 presents comparative results of the calculated effects of the health impact of Krakow residents exposed to PM10 fractions.

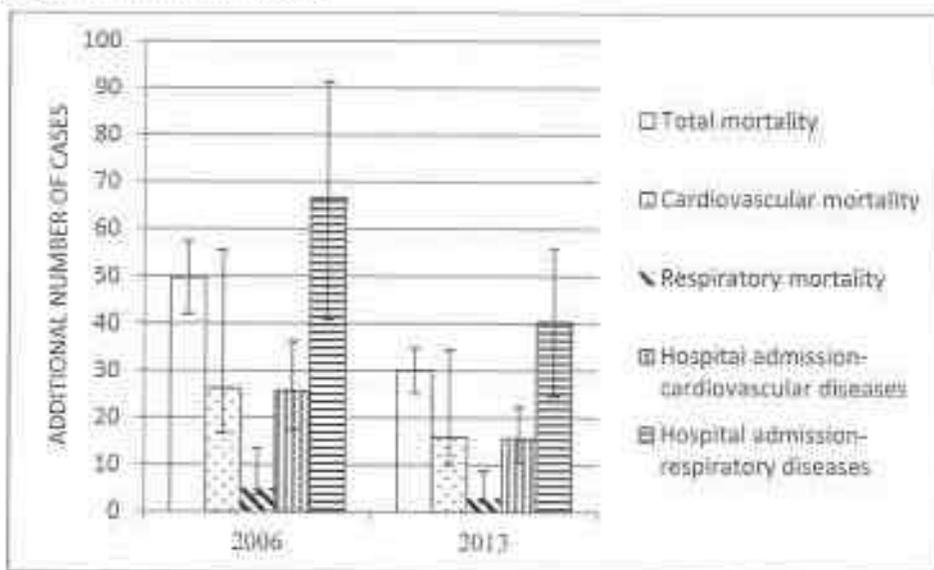


Fig. 5. comparative results of the calculated effects of the health impact of Krakow residents exposed to PM10 fractions (additional number of cases per 100 000 inhabitants).

Most cases were recorded in 2006 and the lowest figures in 2013. The number of cases in 2013 was twice lower than in 2006. Mortality due to cardiovascular diseases reached 50% of the total mortality in 2006 and 2013. However, mortality due to respiratory diseases reached the value of 10% of total mortality. Estimated mortality due to cardiovascular diseases was comparable to the number of visits to the hospital due to cardiovascular diseases. While the number of visits due to respiratory diseases was 13 times greater than the number of deaths due to this. Similar calculations have been made for several cities in Italy, where lower total mortality rates were obtained for most cities than for Krakow. Only for Milan the total mortality rate exceeded those for Krakow [51].

Summary

The following elements were found in air pulverized pollutants: Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, As, and Pb. The concentrations of these elements were determined by X-ray fluorescence.

Comparison of concentrations of elements in the PM₁₀ fraction of particulate pollutants collected at the industrial station and residential area indicated differences in concentrations of many elements. The Ti, Br, Pb and Cu concentrations were similar for both locations. The concentrations of K, Ca and Zn were twice as high for Nowa Huta, Cr concentration, Mn three times, and for Fe up to four times higher concentration values were observed for Nowa Huta compared to Krowodrza. The concentrations of elements in PM₁₀ are high, but do not exceed the limits given by the Ministry of the Environment. The applied statistical methods of PCA and MLRA suggest that the main sources of PM₁₀ fraction of air pollutants in Krakow are coal combustion processes, traffic, industry and secondary aerosols (mainly in Nowa Huta).

Seasonal comparison of element concentrations in the PM₁₀ and PM_{2.5} fractions indicated high concentrations of Cl and K, Br and Pb in winter.

Based on the PCA and MLRA studies in 2011 and 2012 (For PM_{2.5} samples from the AGH site) it was found that in winter the factor responsible for municipal emissions and industry was characterized by elements K, Ca, Fe, Zn, Sr and its average share was 49.1%. The contribution of the second factor responsible for transport (Br, Pb) was 37.8% and the unidentified source was 13%. In the summer, transport (Cu, Br, Pb) indicated a contribution of 53%, industry (Ca, Mn, Fe, Sr) - 18%, and unidentified sources at 29%.

In the work including surveys carried out in 2014-2015 (for PM_{2.5} samples taken at the urban background station) and PMF modeling, the contribution of road transport for the PM_{2.5} fraction in winter is similar and amounts to 36.5%, while the municipal emission is 25% and 3.4% for steel industry and metallurgical industry, not steel - 18% (Total municipal and industrial emissions - 46.4%). In the summer for the PM_{2.5} fraction the contribution of traffic is 62.9%. The industry contribution was 20.3% for the PM_{2.5} fraction. The results indicate a large convergence of results obtained using both receptor methods (PCA and MLRA: PMF). It is worth noting that the PMF method is a more comprehensive method and contains results covering the whole year, while [IB7] contains results covering monthly periods of PM_{2.5} sampling (one month in summer, one month in winter). A high seasonality



was observed for the factor 6 associated with the combustion processes of coal and biomass, indicating a large contribution in winter. The contribution of road transport has remained stable throughout the year.

Another approach in the PMF method was to include the results of the ionic composition analysis. The results, taking into account the ions, indicate that in the winter months the dominant sources are combustion processes and secondary aerosols. In January, combustion processes of $27.2 \mu\text{g} / \text{m}^3$ have a large contribution; secondary nitrates - $11.4 \mu\text{g} / \text{m}^3$ and secondary sulphates - $10.5 \mu\text{g} / \text{m}^3$. In the summer, secondary aerosols also contribute to the presence of gases produced by car engines. In August, the contribution of secondary sulphates was $2.7 \mu\text{g} / \text{m}^3$ (i.e. 27% of PM_{2.5}) and secondary nitrates were $1.4 \mu\text{g} / \text{m}^3$ (that is 14% of PM_{2.5}). The high proportion of sulphates in the winter indicates the increasing consumption of solid fuels used to heat homes during the stagnant winter conditions. The highest seasonal variation was demonstrated by combustion processes (from 0.17 to $27 \mu\text{g} / \text{m}^3$). In winter, the contribution of this source in the PM_{2.5} fraction in Krakow was 40%. Biomass combustion and secondary aerosols also showed high seasonal variability (in summer, 10 times smaller share than in winter). In the winter season, the share of these four sources in the PM_{2.5} fraction was in the 88-96% range, and in the summer 60%. Soil dust, industry and road transport did not show any significant seasonal variation.

Summarizing the results of the two PM_{2.5} and PM₁ fractions, in 2016-2017, three factors were assigned by means of PMF modeling, which assigned in turn the appropriate sources of pollution. In winter, the contribution of combustion processes and secondary aerosols was 90% in the PM₁ fraction and 81% in the PM_{2.5} fraction. In the summer, combustion processes are 3-6% in both fractions. In the summer, the proportion of secondary aerosols was 50% for both fractions. Transport, industry and soil dust did not tend to change their seasonal contribution.

The categories and contribution of sources designated for samples collected in 2014-2015 and 2016-2017 are convergent. The sources of measurement uncertainties have not been assigned to the contribution, but they constitute the spread of results in the measurement period and depend on many factors. They depend, among others, on meteorological conditions: wind speed, wind direction, humidity, ambient temperature and emission levels of individual sources on a given measurement day.



Research plans:

- Physico-chemical characteristics and receptor modeling of the PM₁₀ fraction for two selected monitoring stations in Krakow (traffic station and residential development area).
- Extending analyzes of all fractions with analysis of organic, inorganic carbon and C-14 isotope. Consideration of the listed components in receptor PMF modeling.
- Application of mass balance modeling (Chemical Mass Balance).

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5. Review of additional research accomplishments:

After obtaining the PhD title in 1991 I realized a research project run by Scientific Research Committee. I played the role of the organizer and main participant of the project. The research subject was connected with my previous activity and was called "Halide glasses for optoelectronic and electronic". It focused on the technology of production of fluoro - zirconate glasses modified with nitrogen, the evaluation of the influence of N on the structure of fluoro - zirconate glasses and their chemical, physical and optical properties. The research findings which resulted from the project were presented in numerous publications [IIA2, IIA3, IIE4, IIE5, IIE6]. These research studies were innovative. It was the first composition of halogen and nitrogen modified halogen glasses prepared in Poland. At that time I was a co-author of one patent [IIC1]. In September 1995 I started working at the Faculty of Nuclear Physics and Technology, AGH University of Science and Technology, Krakow, which influence the change of my research focus. I concentrated on environmental analysis - the main research instrument was and still is an Energy Dispersive X-ray Fluorescence analyzer. I dealt with environmental sampling preparation (peat, soil and sediments) for the purpose of elemental analysis with the use of X-ray fluorescence method. I performed elemental concentration analysis of environmental materials together with optimization of working conditions for the spectrometer. This research work was presented in publications [IIA5, IIA6, IIA8, IIE7, IIE8, IIE9].

A bilateral Polish - Austrian collaboration project was realized under the supervision of Professor Barbara Holynska. The Polish and Austrian parties were represented by AGH University of Science and Technology and Vienna University respectively. Peat samples were collected near a highway both in Poland and in Austria and analyzed for the presence of Pb and Br [IIA6]. Chemical speciation of heavy metals in peat was performed. The TXRF method was used for elemental analysis. The collected peat samples were divided into

layers. For each layer elemental concentration analysis was performed with the use of X-ray fluorescence method. Correlations between particular layers and time were observed. Sections from different layers served as indicators of deposition of various metals, both of mineral and anthropogenic origin. This was followed by ^{210}Pb dating.

Later, my research concerned the dust pollution of the air. During my stay at the postdoc internship at the Micro- and Traces Research Center at the University of Antwerp, Belgium, five scientific papers were created [IIA9, IIA10, IIA11 and reports [IIF1, IIF2]. The first work involved the testing of the MiniPal spectrometer for the analysis of airborne dust pollutants. Subsequent works included the results of the elemental analysis of air pollutants, together with their wider characteristics collected in Antwerp in the years 2000-2002. The next stage of my work concerned research carried out within the framework of bilateral cooperation between Poland and Belgium in 2004-2006. AGH University of Science and Technology and the Institute of Catalysis and Surface Chemistry PAS in Krakow participated from the Polish side and University of Antwerp from Belgium. As part of this cooperation, we conducted a comprehensive study of air pollution in two selected churches: one wooden in Szalowa, the second bricked Saint Catherine in Krakow. These churches were equipped with the same modern system for heating the church in the winter. Namely, infrared radiators. The wood reactions to turning on the heating system in the wooden church in Szalowa were also checked. In addition, analysis of air transport inside and outside the churches was done. During the implementation of these tasks, the following works appeared: [IIA12, IIA13, IIA14, IIA15, IIA16, IIE11]. One of the most interesting studies was the work carried out at the Wawel Royal Castle Museum in Krakow in 2006 and 2010. Winter and summer campaigns for collecting air pollution samples in 2006 were carried out. They were subjected to elemental analysis. With the Berner's impactor, samples were also taken to analyze the composition of individual grains on an XRF transmission microscope. The origin of air pollutants was estimated using statistical methods. The work was carried out in cooperation with the art conservator who, based on the report prepared by us, made recommendations for the museum. After the modifications, the museum management asked us to repeat the research. The summer and winter 2010 sampling campaigns were again carried out, this time with PM₁₀, PM_{2.5}, PM₁ and Berner's impactor. The analyzes confirmed that the modifications made to the museum contributed to the improvement of the exhibits' storage conditions. The following works have been published in this regard [IIA17, IIA18, IIA19, IIA21, IIE16, IIE19, IIF3, IIF5]. Published studies in the field of Wawel research



were taken into account by the Faculty of Physics and Applied Computer Science, AGH in order to apply for the A + category with a positive result.

During the implementation of the project conducted by the Institute of Nuclear Chemistry and Technique in Warsaw within which I had to carry out research on air pollution in Otwock and Świder in the Mazowieckie Voivodship, the works [IIE13, IIE17, IIE18, IIF4] were published.

The implementation of regional IAEA projects with its headquarters in Vienna resulted in works included in the habilitation achievements [IB3- IB10] and other articles [IIA22, IIA24, IIE20, IIE21, IIE24].

In addition, I use the fluorescence method to study the elemental composition of other materials such as archaeological glass, hematites. I have carried out and continue to carry out these works in cooperation with the Department of Archeology, University of Rzeszów. Cooperation resulted in works [IIE12, IIE14]. In the field of air pollution, I cooperate with the Wrocław University of Technology [IIA22, IIA24, IIE20, IIE21] and the Department of Fuels and Energy, AGH University of Science and Technology [IIA23, IIA26, IIE22, IIE23], as well as the Jagiellonian University and the Pedagogical University in Kraków [IIE25].

To sum up, during the period after obtaining PhD degree in 1991 I have completed the following achievements: I am a co-author of one patent and an author or co-author of 60 reviewed publications including 42 positions which can be found in Journal Citation Reports (JCR). Total impact factor is 63,367(all publications) with the number of citations including auto-citations reaching 305. Number of citations without auto-citations 265. I have participated in 9 research projects 7 of which were lead or coordinated by me. On several occasions I have been awarded the AGH Chancellor prize for outstanding scientific and didactic achievement.

