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Receptor modeling source apportionment of PM10 and benzo(a)pyrene in Krakow, Poland

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The main energy source in Krakow, Poland is coal combustion, which is believed to be the reason for frequent winter episodes of extremely high ambient air concentrations of particulate matter (PM10) and associated benzo(a)pyrene B(a)P. Results are presented on the source apportionment of PM10 and B(a)P during two episodes of thermal inversion (14/1 – 2/3, 2005) at four different air monitoring stations and four apartments (indoor) in the city of Krakow, The results are compared to the Zakopane mountain site selected due to its prominent domestic coal heating and little traffic. The source apportionment was based on receptor modeling of the total of 72 ambient PM samples and 21 individual PM sources, chemically characterised for a high number of organic and inorganic compounds including polyaromatics (15 PAH and 18 azaarenes) heavy metals and trace elements (28 compounds), major ions, soot and organic carbon. An array of multivariate receptor models was used $i.e.$ chemical mass balance (CMB), constrained matrix factorisation (CMF), constrained physical receptor modelling (COPREM) positive matrix factorization (PMF), principle component analysis with multi-linear regression analysis (PCA-MLRA), edge analysis (UNMIX), cluster

analysis (CA), and self organizing maps SOM).

The variation in the receptor dataset (55 compounds, 60 outdoor and 12 indoor PM samples) allowed the models of the "pure factor analysis" type (PMF, UNMIX, PCA-MLRA) to identify 3-5 factors of mixed sources. The interpretation of the factors was not straightforward, but pointed to a dominating primary source contribution from coal combustion ($>$60%) and a minor contribution from traffic ($<$10%). The secondary PM sources (20-30%) comprised industry and traffic. The results of cluster analysis and self organizing maps supported these indications. PMF was able to disaggregate the coal combustion into three factors i.e. $\sim$10% related to industrial activities, $\sim$20% related to home heating by stoves (coal) and $\sim$30% related to boilers.

The chemical fingerprints of the receptor samples and the main PM sources in Krakow and Zakopane allowed the pure "chemical mass balance" type model (EPA-CMB8.2) to estimate the major contributions from two primary source types i.e. residential heating by coal combustion in small stoves and low efficiency boilers ($\sim$45%) and boilers with rudimentary PM reductions techniques such as cyclones ($\sim$15%), one major secondary source deriving from industrial and traffic emissions of SO_2 + NOx + possibly HCl ($\sim$20%). Five minor primary sources were also identified i.e. traffic 5%, biomass burning $\sim$5%, coke/fuel combustion $\sim$5%, industrial high efficiency coal combustion 3%, and road/salt/rock re-suspension $\sim$2%. The indoor PM10 and B(a)P were found to have the same sources as outdoor PM10 and B(a)P

The results obtained by the models CMF and COPREM - which are hybrids of factor analysis and chemical mass balance – generally agreed with the CMB results. However, their source contribution estimates are slightly different: residential heating $\sim$30%, boilers with rudimentary PM reductions techniques such as cyclones $\sim$30%, industrial high efficiency coal combustion $\sim$15% traffic 3-7%, secondary 13-21%, road/salt/rock re-suspension 2-8%.

All receptor models calculated residential heating to be the principal PM source in Zakopane (70-80%).