Integrated air quality assessment – A synthesis of elemental and organic air pollution indicators

L. SCHWARK AND E. LEHNDORFF

Department for Geology and Mineralogy, University of Cologne, Germany; (lorenz.schwark@uni-koeln.de)

In a multidisciplinary approach atmospheric quality in the Greater Cologne Area (GCA) was studied using pine needles as bioreceptors. This contribution describes accumulation behaviour, transport fractionation, source allocation, and the spatial distribution of major and trace elements including platinum group elements. Special emphasis is placed on synthesizing the inorganic and organic pollutant load on pine needles for improved differentiation of traffic, industrial and power plant emissions. The interpretation is corroborated by $\delta^{13}C$ and $\delta^{15}N$ isotopes and environmental magnetic data.

The GCA comprises various element emission sources, mainly lignite fueled power plants, urban regions of high traffic density and reduced air mixing, domestic heating and large industrial complexes along the Rhine Valley. We will first demonstrate that element accumulation on pine needles occurs in a systematic and predictable manner by analyses of 3 to 50 month old needles taken separately in summer and winter at six key locations. This allows for interpretation of spatial distribution maps constructed from 71 locations covering 3000 km² in the GCA. Absolute concentrations of elements and element enrichment factors were used for spatial analyses. Normalization to average dust composition was achieved using the sum of REE, as Ti was regionally enriched in the volcanic province of the "Siebengebirge".

Source characterization based on element concentrations revealed that Mo was best suited to identify petrochemical emissions. Cu enrichment results from petrochemial emission and traffic sourcs. PGE showed a predominantly traffic origin for Pt and Pd, the latter also affected by fertilizer application in agricultural areas. Ru and Re were less traffic dependent, the former being associated with industrial the latter with agricultural emission. Traffic pollution was clearly depicted by enhanced Sb and Ba concentrations, whereby Ba showed a higher degree of dispersal. Fe and V were shown also to be related to traffic emissions in urban areas but as well originate from power plant emissions. Verificaton of emission sources was achieved by polycyclic aromatic hydrocarbon (PAH) pollution indicators. Lignite-fueled power plants emit preferentially phenanthrene, cyclopentenophenanthrene, and dibenzothiophene; urban traffic is characterized by higher load of alkylated phenanthrenes and different isomer patterns of e.g. methylphenanthrenes. Correlation of element and PAH pollution indicators was excellent although certain pollutant sources were depicted by one group only. For example Pb/Zn mining activity in the Rhenish Massif was only detected by elevated Cd concentration.

Inorganic and organic multiproxy air quality analyses allows for very reliable and independent source allocation even in areas with multiple emission sources.

Constraints on the revision of the K decay constants

WINFRIED H. SCHWARZ AND MARIO TRIELOFF

Universität Heidelberg, Im Neuenheimer Feld 236, D-69120 Heidelberg (winfried.schwarz@min.uni-heidelberg.de)

As the accuracy of current K-Ar age calculations is seriously limited by the uncertainties of the ^{40}K decay constants [1,2], a reevaluation is required. ^{40}K has a dual decay to ^{40}Ar and ^{40}Ca with a branching ratio of 10.48/89.52 [1,3] and a total decay constant of $5.543 \cdot 10^{-10}$ a^{-1} (calculated with data from [3] and a $^{40}K/K$ ratio of 0.01167% [4]). Thus for conventional K-Ar and Ar-Ar dating (where the age calculation depend on mineral standards dated by conv. K-Ar technique) all three values are needed in the age equation.

To revise the decay parameters for ^{40}K, the systematic offset of Ar-Ar and U/Pb mineral ages of rapidly cooled rocks were determined [e.g. 5]. Using the H chondrite parent body cooling history [6,7] it is possible to calculate the age offset of U/Pb and Ar-Ar ages for c. 4.6 Ga old rocks – it is c. 30 Ma [8], significantly smaller than 1% which is noted in [5] or [9]. A biotite from the Great Dyke Intrusion in Zimbabwe/Africa with an age of c. 2.5 Ga, lead to an age discrepancy of c. 20 Ma. The age data for the c. 2.0 Ga old Vredefort impact structure from [10] recalculated for a new NL25 standard age [11] lead to a difference of c. 17 Ma.

These new age data lead to a decay constant of c. $5.520 \cdot 10^{-10}$ a^{-1}, only a little smaller than that defined by [1] - this result will not change including the available literature data [e.g. 5,9]. It is slightly different from the determination of the total decay constant of $5.554 \cdot 10^{-10}$ a^{-1} via LSC by [12] and [13], but different $^{40}K/K$ and branching ratios were used for these calculations. Using the geochronological data and the age equation for K-Ar dating it is not possible (though not important for calculating ages) to decide whether the branching or the $^{40}K/K$ ratio is wrong by about 1%. Assuming a $^{40}K/K$ ratio of 0.01167% would lead to the decay constant to ^{40}Ar of c. $0.575 \cdot 10^{-10}$ a^{-1} and thus a branching ratio of c. 10.42/89.58. Nevertheless an independent redetermination of the $^{40}K/K$ and the branching ratio is desirable.

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