Carbon isotopic analyses of individual Murchison amino acids

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A key insight into the origin of meteorite organics is offered by their stable isotopic composition which, when paired with molecular distribution and properly deciphered, may serve as a tracer of their physico-chemical history. Carbon isotopic analyses of various classes of meteorite organics have shown them to be all enriched in the heavy ^{13}C isotope compared to their terrestrial counterparts, to various degrees. This has been interpreted as to indicate an origin from interstellar precursors, reflecting also the heterogeneities of the interstellar clouds (1). The $\delta^{13}C$ values of individual compounds within these groups, however, may or may not vary, e.g., it was found that the $\delta^{13}C$ enrichments of meteoritic carboxylic acids and lower hydrocarbons decline with increasing chain length (2) while those of dicarboxylic acids do not appear to do so (3).

New carbon isotopic analyses of individual Murchison amino acids (aa) were carried out by gas chromatography-combustion-isotope ratio mass spectroscopy and will be reported. We obtained $\delta^{13}C$ values for a total of 30 aa, to represent homologous series of the various subclasses of these compounds in the meteorite. Two pyridine carboxylic acids were also analyzed. The results show interesting differnces in isotopic distributions: 1) The α-aa, both α-H and α-alkyl isomers, show declining $\delta^{13}C$ values with increasing carbon chain length. Values are higher for the α-alkyl series and decline, overall, from + 43.7 (α-amino isobutyric acid) to +15.2 ‰ (norvaline). 2) The β-, γ-, and δ- aa $\delta^{13}C$ values seem to show a reversed trend, and are as high as +35.5‰ for 6C aa. It is possible that these represent three distinct groups of compounds. 3) The dicarboxylic (di)-aa all have high $\delta^{13}C$ values. Given that the series start in meteorites with 4C aspartic acid (subjected to contamination even in the D-form) and is not represented in large enough amounts beyond 6C, it is difficult to establish trends beyond statistical fluctuation. Certainly, there is not a down trend with increased molecular weight. E.g., the $\delta^{13}C$ value found for glutamic acid was +38.0 and those for 6C di-aa as high as + 40.6‰.
4) The highest $\delta^{13}C$ value, 52.8‰, was found for sarcosine.

The differences in ^{13}C enrichment for the various sub-groups of Murchison aa likely represent different synthetic histories and the implications of these findings will be discussed in relation to those previously determined for other soluble metorite organics.

References

1. Cronin J.R. and Chang S. In: *The Chemistry of Life's Origins* , eds. J.M. Greenberg et al., 209-258. Kluwer, 1993. 2. Yuen G. et al. (1984) *Nature* **307**, 252-254. 3. Pizzarello S. and Huang Y. (2002). *Meteorit. Planet. Sci.* **37**, 687-696.

Modelling PCB pollution dynamics in the karstic environment

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The new method for modelling pollution dynamic for the karstified aquifers based on non-linear feed-forward artificial neural network models is presented. The results are shown in the figure below.

Over the period 1962 - 1984 a capacitors factory at Semic, Slovenia has polluted the relatively large karstic environment of the Krupa river source in Bela Krajina (a 100-km^2 region in Southeast Slovenia) with PCBs. The last state of PCBs pollution and their fate and exposure in the polluted environment of the Krupa river after remedial measures was researched in the period 1995 to 2003.

The pollution problems are related to sinking surface streams that mix with the regional groundwater supply, thus endangering the quality of the groundwater reservoirs. Due to the more dynamic nature of water flow in karstic aquifers, identifying pollution trends means integrating, in time, chemical measurements with hydrologic data, and developing models which can relate changing hydrologic conditions to vulnerability of aquifers to persistent pollutants. The key issue is the application of representative data to the model of flow and transport in karstic fractured media.

In order to try to reproduce the PCB concentrations in Krupa river water, the modelling procedure involved the correlation between the atmospheric precipitation, river flow rate and PCB concentration. With such model the evaluation of mass balance of PCB in the hinterland karstic underground and in the Krupa river is determined.

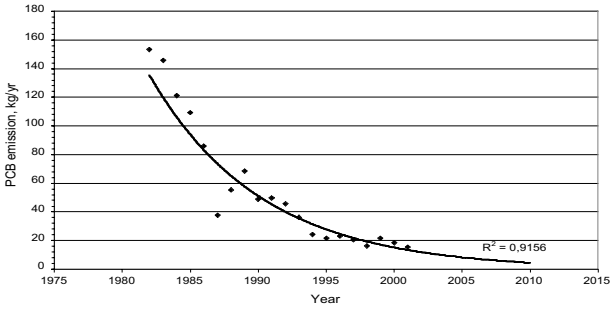

Figure 1: Modelled amount of emitted PCBs from 1983 to 2002 and logarithmic regression curve extrapolated to 2010.

References

Kocjancic R. and Zupan J., (2000). Modelling of the river flow rate: the influence of the training set selection. *Chemom. Intell. Lab. Sys.*, **54**, 21-34.
Polic S., Leskovsek H and Horvat M. (2000). PCB Pollution of Karstic Environment (Krupa River, Slovenia). *Acta Carsologica*, **29,** 141-151.