

Investigation for evaluating the sources and diagenesis of groundwater humic substances using ^{15}N and Carbon Isotopes

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Introduction

Recent investigations of dissolved organic matter in groundwater have shown that humic substances comprise a major proportion of the dissolved organic carbon (DOC) load. Information regarding the origin and geochemical stability of fulvic and humic acids (FA, HA) in the subsurface are still inadequately understood, yet are crucial to investigations concerning migration of non-polar organic pollutants, heavy metals, radionuclides, and the interpretation of isotopic groundwater ages. Here we present ^{14}C , d^{13}C results and, d^{15}N data of aquatic humic substances from contrasting shallow and up to 200 m deep aquifer systems in Germany, where FA is the dominant compound in DOC (Fig.1). The combination of three different isotopes at the same time give complementary information about the origin (^{13}C), age (^{14}C) and evolution (^{15}N) of dissolved fulvic acids [3, 4].



Fig 1. Sample sites

Dissolved fulvic acids (FA) were sampled from 20 to 2000 L groundwater dependent on DOC concentration by reverse osmosis and from cold water saturation extracts of topsoils

Methods

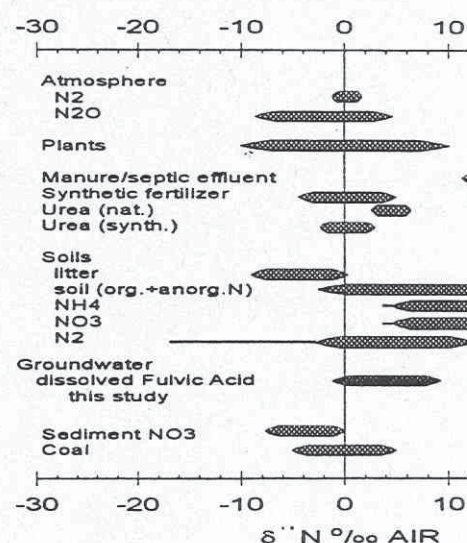
(Drömling samples) and extracted by XAD-8 resin chromatography. For most of the samples N_2 preparation was made by sealed quartz tube combustion [7]. Samples of the Drömling site were measured by new the technique of combined Gas Chromatography and Continuous Flow Isotope Ratio Mass Spectrometer (GC/CF-IRMS). Isotope measurements were performed on a Finnigan Mat Delta-S mass spectrometer, with reproducibility of 0.1 ‰ for $d^{15}N$ and 0.1 ‰ for $d^{13}C$, respectively. ^{14}C was prepared using conventional combustion techniques. Samples were analyzed by Accelerated Mass Spectrometry (AMS, Isotrace, University of Toronto), with a detection limit of 0.05 pmC.

Fig 2. Ranges for ^{15}N in natural materials and dissolved fulvic acids from ground water (this study) [1, 2, 5, 8]

Results and Discussion

During humification Nitrogen of organic matter (amino acids, amino sugars, NH_3 from hydrolysis of organic amino compounds) is incorporated into structures of water soluble humic and fulvic acids. This N is not readily available to plants. Mainly soil derived FA is transported by seepage to the groundwater whereas Humic Acids (HA) are strongly adsorbed to the soil matrix and do normally not reach groundwater. In organic rich aquifer sediments (e.g. „black water“ aquifers in Gorleben) FA and HA from the sediment matrix is a second source for dissolved humic substances [2]. No distinction can be made between these two sources by $d^{15}N$ and $d^{13}C$ because of range for sediment derived FA and HA and soil derived FA is the same. $d^{15}N$ of FA in shallow and deep groundwater from this study lie between 0 and 8 ‰ and is within the range of soil derived ^{15}N (Fig. 2).

A clear correlation exists between ^{15}N , ^{14}C and C/N ratio. $d^{13}C$ data has no correlation to the other parameters. $d^{13}C$ and ^{14}C data indicate that fulvic acid is principally soil derived by plants with C_3 Calvin-Benson photosynthetic cycle. Fulvic acid $d^{15}N$ values become enriched with increasing depth and age, indicating diagenetic loss of light nitrogen. The same effect but to a



smaller degree can be seen during evolution of FA in the unsaturated soil zone (Drömling area), where ^{14}C and d^{15}N is influenced by the state and evolution of the soil and with that from microbial activity as well from residence time of FA, FA storage capacity of soil and seepage water [4, 6]. A changing landuse from arable land to an extensive grassland results in a large increase of microbial activity indicated by an enrichment of d^{15}N in FA in seepage and groundwater [3].

Conclusions

FA in groundwater is not completely refractory but is changing as a function of activity of micro-organisms. Any factor that affects microbial activity can affect d^{15}N as well as C/N ratios. But as microbial activity in groundwater is minor in comparison to soil, the speed of response of transfer reactions in groundwater FA is much slower and lies in the range of 10^3 years.

Literature

- Clark, I.D., Fritz, P.**, Environmental Isotopes in Hydrogeology, 328 p., Lewis Publishers, New York (1997).
- Geyer, S.**, Isotopengeochemische Untersuchungen an Fraktionen von gelöstem organischem Kohlenstoff (DOC) zur Bestimmung der Herkunft und Evolution im Hinblick auf die Datierung von Grundwasser, GSF-Bericht 4/94, Neuherberg (1994).
- Geyer, S., Kalbitz, K., Geyer, W.**, The influence of changing land use (intensive to extensive) on the isotopic (^{14}C) and chemical signature of DOC - conclusions for the initial ^{14}C content of DOC for groundwater dating, IAEA-SM-349, IAEA, Vienna (1997), (in print).
- Kendall, C., Grimm, E.**, Combustion tube method for measurement of nitrogen isotope ratios using calcium oxide for total removal of carbon, Anal. Chem. 62, 526-529 (1990).
- Voerkelius, S.**, Isotopendiskriminierung bei der Nitrifikation und Denitrifikation, Grundlagen und Anwendungen der Herkunfts-Zuordnung von Nitrat und Distickstoffmonoxid, PhDiss, Tech. Univ. Munich (1990).
- Kalbitz, K., Geyer, S., Geyer, W., Rupp, H., Knappe, S., Meißner, R. & F. Braumann**, Land use effects on dissolved organic matter in the unsaturated and saturated zone of a fen area.- In F. Frimmel und G. Abbt-Braun (Hrsg.), Symposium on Refractory Organic Substances in the Environment - ROSE, Veröffentlichungen des Lehrstuhls für Wasserchemie und der DVGW-Forschungsstelle am Engler-Bunte-Institut der Universität Karlsruhe, H. 35, 156-158, Karlsruhe (1997).
- Geyer, S., Kalbitz, K., Artinger, R. & G. Buckau**, Contribution from ^{14}C in dissolved organic carbon for the evaluation of geochemical processes in groundwater systems.- In F. Frimmel und G. Abbt-Braun (Hrsg.), Symposium on Refractory Organic Substances in the Environment - ROSE, Veröffentlichungen des Lehrstuhls für Wasserchemie und der DVGW-Forschungsstelle am Engler-Bunte-Institut der Universität Karlsruhe, H. 35, 176-177, Karlsruhe (1997).
- Kalbitz, K., Rupp, H., Geyer, S., Geyer, W., Knappe, S., Meißner, R. & F. Braumann**, Auswirkungen der Landnutzung und von Landnutzungsänderungen auf die gelöste organische Substanz im Boden und Wasser eines Niedermoorgebietes.- Mitteil. Dt. Bodenk. Gesellsch. (1997), (im Druck).

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