The origin of nitrogen in aquifer systems in the Great Plain, Hungary

I. Varsány

L.Ó. Kovács

Institute of Mineralogy, Geochemistry and Petrology, Attila
József University, H6701 Szeged, Pf. 651., Hungary.
Hungarian Geological Survey, H1442 Budapest, Pf. 106.,
Stefánia út 14., Hungary

Introduction

Although N_2 is a dominant nonhydrocarbon component in the natural gases (Barker and Pollock, 1984) only few studies demonstrate its occurrence and origin in groundwater. Thorstenson et al. (1979) found in Dakota that N_2 concentrations in groundwaters were considerably higher than expected on the basis of saturation with atmospheric N_2. Reactions that affect the N_2 concentrations could not be identified.

In the southern part of the Great Hungarian Plain three groundwater systems in fluvialüsediments of Pleistocene age and 22 water samples from Pliocene aquifers (indicated as unclassified) were studied (Fig.1). These aquifer systems distinguished on the basis of majorüion chemistry are described elsewhere (Varsányi and Kovács, 1994).

The aim of this work is to establish the processes controlling the distribution of nitrogen in the different aquifer systems.

Methods

Chemical analyses and gas content data of 133 water samples are available. Routine analyses of dissolved and separable gases were performed using gas chromatography. Major ion chemistry, chemical oxygen demand (COD) and ammonium ion analyses were carried out using standard techniques.

Oxygen gas was considered as a contamination by the atmosphere during the sampling process. Where more than trace amounts of oxygen were found nitrogen gas analysis was corrected by subtracting nitrogen proportional to the measured oxygen.

Results and discussion

Chemical composition of the groundwater from the three aquifer systems of the Pleistocene sediments is summarized in Table 1.

The inverse relationship between the two forms suggests that both NH_4^+ and N_2 derive from a common source. This source may be the nitrogen content of organic material. Where this relationship differs from their stoichiometric proportion it is assumed that one part of NH_4^+ formed from organic matter is absent in this groundwater. A possible sink of NH_4^+ may be its adsorption on

FIG. 1. Location of the studied wells. 1) River Körös basin, 2) River Maros alluvial fan, 3) River Danube deposits, 4) unclassified samples.
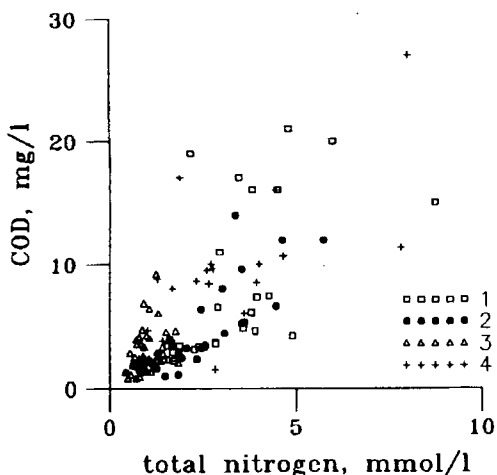

FIG. 2. COD vs. total nitrogen.

TABLE 1. Average chemical compositions in the studied aquifers

Aquifer	No. of samples		Na	Ca	Mg	NH_4^+ mmol/l	Cl	alk.	$N_2(g)$	total nitr.	COD mg/l
River Körös	x		11.90	0.83	0.50	0.15	0.63	14.53	1.17	3.42	9.83
basin	s	24	2.20	0.58	0.33	0.11	0.03	1.72	0.64	1.65	7.00
River Maros	x		3.70	0.93	0.37	0.16	0.39	5.96	0.67	2.66	5.19
alluvial fan	s	23	1.46	0.45	0.21	0.12	0.09	1.77	0.26	1.20	3.58
River Danube	x		2.56	1.06	0.67	0.07	0.13	6.14	0.21	1.01	2.12
deposits	s	64	2.36	0.54	0.34	0.04	0.06	1.19	0.10	0.37	1.48

(NO_3^- and NO_2^- are below detection limit, x = mean value, s = standard deviation)

clay minerals. The total nitrogen content released from organic matter can be calculated by summation of N_2, NH_4^+ dissolved and NH_4^+ adsorbed.

In studying the connection between total nitrogen and organic matter chemical oxygen demand (COD) was used to characterize the dissolved organic matter. Cation concentration equivalent with the bicarbonate anion was considered proportional to the organic matter mineralized to CO_2. The good correlation between COD and calculated total nitrogen (Fig. 2) suggests a common parent material for the dissolved organic matter and total nitrogen.

Fig. 3 shows that the aquifers are separated on the basis of the CO_2 production and that there is a linear correlation between the total nitrogen and cations within each aquifer. The relationship between COD and cations is perfectly similar. Figs. 2 and 3 suggest two consecutive steps in the

transformation of organic material. The first step is the oxidation of solid organic matter to CO_2. The degrees of this CO_2 production are different in the aquifers causing different cation concentrations. It may be the result of their different environments. The high mineralization of organic matter to CO_2 in the Pliocene samples and in the Körös basin indicates similar environments for the decay of organic matter. Thus, the subaquatic sedimentation typical of the Pliocene can be assumed to prevail here in the Pleistocene, maybe in shallower water. The lower mineralization in the two other aquifers rather suggests a subaerial environment. During the second step, the CO_2 production proceeds together with formation of dissolved organic matter and nitrogen species.

In accordance with the experimental results of Brons et al. (1991), the first step can be considered to be an aerobic CO_2 production, the second one an anaerobic transformation of organic material. Due to the lack of dissolved oxygen and electron acceptors, the disproportioning of the organic matter results in CO_2 and an increased COD. At around 30°C these processes are predominantly microbially mediated. Together with dissolved organic matter nitrogen is also released.

FIG. 3. HCO_3^- vs. total nitrogen.

References

Barker, J.F. and Pollock, S.J. (1984) Bull. Can. Petr. Geol., 32, 313–26.
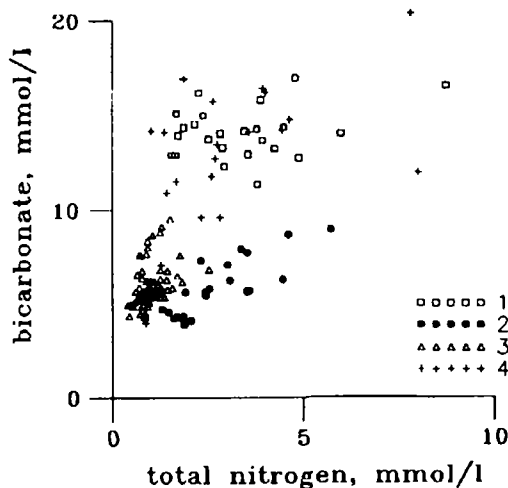Brons, H.J., Griffioen, J., Appelo, A.J. and Zehnder, A.J.B. (1991) Wat. Res. 25, 729–36.