

## **The influence of oil-derived substances on groundwater in the light of isotopic analyses of carbon, oxygen and sulphur**

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This abstract is focused on applying isotopic analysis of carbon, oxygen and sulphur as a tool to assess the influence of, covering the first groundwater system, oil-slick of petroleum hydrocarbons. During mineralization of hydrocarbons, both in aerobic and anaerobic conditions (when  $\text{SO}_4^{2-}$  is reduced), microorganisms produce  $\text{CO}_2$ . Thus, an increase of dissolved  $\text{CO}_2$  concentration, and in consequence of DIC, in groundwater, may indicate progressing biodegradation of hydrocarbons (Coates et al. 1996, Grishchenkov 2000). On the other hand, the DIC originated from decomposition of hydrocarbons, shows relatively low  $^{13}\text{C}/^{12}\text{C}$  ratios as compared to DIC of natural origin (Bolliger et al. 1999, Conrad et al. 1999). Likewise, when microorganisms utilize the sulphate (the terminal acceptor of electrons), its concentration in groundwater decreases, hence the residual sulphate ion becomes  $^{34}\text{S}$ -enriched. Based on the isotopic analyses of sulphur and oxygen in the sulphate ion, the dominating mechanisms of decomposition of hydrocarbons polluting the aquifer in particular zones of the oil-slick were tentatively determined. Traditional methods, based solely on chemical analysis are not sufficient enough to identify particular sources of DIC in groundwater, as well as processes regulating the mineralization of hydrocarbons.

Isotopic and chemical analysis indicated, that the zone with a dominating aerobic process of hydrocarbon decomposition is the northern margin of the oil-slick. This zone is characterized by easier oxygen and sulphate ion supply by groundwater, which is indispensable for hydrocarbon mineralization process. The region with the dominating anaerobic hydrocarbon decomposition process is the central part of the oil-slick, where much higher thickness of the oil product was observed. These zones were determined on the basis of DIC and sulphate ion concentrations, as well as their isotopic composition.

Moreover, seasonal variations within the oil-slick were observed. The mean concentration of DIC in groundwater, varied from 228.90 mg/dm<sup>3</sup> for the winter season to 519.47 mg/dm<sup>3</sup> in the summer season. Likewise,  $\delta^{13}\text{C}_{\text{DIC}}$  variations were also observed: the mean value of  $\delta^{13}\text{C}_{\text{DIC}}$  for the summer season was  $-16.16\text{‰}$ , and that in the winter season was  $-19.92\text{‰}$ . The increase of  $\delta^{13}\text{C}_{\text{DIC}}$  values is resulted from hydrocarbon decomposition. It is rather possible that the rate of biodegradation can probably be described by mean of the Rayleigh distillation model. Slight seasonal changes were also observed for  $\delta^{34}\text{S}$  in the sulphate ion. These differences are probably caused by various intensity of sulphate reduction.

Carbon isotope mass balance allowed calculating the percentage of DIC of anthropogenic origin (from hydrocarbon decomposition) in the groundwater within the oil-slick. During the summer season, when biodegradation of oil-derived substances is the most intense, ca. 50 to 54% DIC in groundwater within the oil-slick originates from microbiological decomposition of hydrocarbons. In the winter season, when biodegradation processes are considerably restricted, the percentage of DIC from hydrocarbon decomposition in the groundwater is about 16-31%. Zones with the most intense mineralization of oil-derived substances are areas of the oil-slick with easier oxygen supply (mainly the northern margin). In these areas the content of anthropogenic DIC oscillates from 68 to 72% in the summer season, to 24-33% in the winter season. In the central part of the stain, where anaerobic processes dominates, the content of DIC from the decomposition of oil-derived substances is much lower, in the summer season reaches 41-50%, and in the winter season from 9 to 15%.

This research indicates that isotopic analysis of carbon, oxygen and sulphur consist a useful tool for the quantitative evaluation of the hydrocarbon mineralization.

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