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Infiltration of Organic Pollutants into Groundwater: Field Studies in the Alluvial Aquifer of the Sava River

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Groundwater represents one of the most important sources of potable water for many public water supplies in the world. The benefits of these valuable water reservoirs are being reduced however, due to the increasing infiltration of both inorganic and organic pollutants from different sources such as wastewaters, polluted freshwaters, contaminated soils, sanitary landfills, and industrial dumping sites (Ward et al. 1985; Schwarzenbach et al. 1983; Barker et al. 1986). Therefore, investigations of pollutant migration and persistence in groundwaters are of great significance for groundwater protection strategies. The study of organic pollutants is perhaps the most complex issue in groundwater pollution chemistry. The extremely high number of possible organic pollutants as well as the severe ecotoxicological effects of specific organic compounds make the assessment of water quality and long term pollution trends in the aquifer very difficult. The application of the computer-assisted high-resolution gas chromatography/mass spectrometry in the last decade has extended our knowledge about the occurrence of specific organic pollutants in groundwaters and processes that determine their transport and transformation (Reinhard et al. 1984; Schwarzenbach et al. 1985; Murray and Beck 1990).

MATERIALS AND METHODS

This report describes a part of several comprehensive studies conducted between 1986-1989, designed to investigate groundwater quality and behaviour of pollutants in the alluvial aquifer of the Sava River. All field sites were located in the area around the city of Zagreb (Northern Croatia, Yugoslavia). This densely populated area (approximately 1 million inhabitants) is also one of the most industrialised regions of Yugoslavia. The Sava River is the major reservoir of

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freshwater in study area (average flow of 200 m^3/s) and consequently its infiltration into the subsurface is the major source of groundwaters. The municipal and industrial wastewaters discharged into the Sava River are for the most part not treated and the river is therefore heavily polluted (Ahel and Giger 1985a).
Field site I was situated near the Sava River at the point where the direction of the groundwater flow is almost perpendicular to the direction of the river flow. Field site II was located at the edge of the main municipal landfill of the city of Zagreb. Field site III was situated adjacent to a wastewater canal which receives untreated wastewater from the pharmaceutical industry and a baker's yeast production plant. The sampling wells were always positioned at increasing distances from the presumed dominant source of pollution along the direction of groundwater flow (Table 1). The depth of the wells varied from 25 m (field site III) to 40 m (field sites I and II). The groundwater table was found to exist between 3 and 6 m. Sampling of groundwaters at each well was performed at the depth of maximum velocity of the groundwater flow. These were 14 m for field site I, 11 m for field site II, and 10.5 m for field site III. Groundwater samples were collected using a small underwater plunger type pump suitable for the determination of trace concentrations of organic compounds (Schwarzenbach et al. 1983).

Highly-specific techniques, including high-performance liquid chromatography (HPLC), high-resolution gas chromatography (HRGC) and mass spectrometry (HRGC/MS) were applied for the analysis of samples. Several complementary enrichment and fractionation techniques were used to increase the volatility and polarity range for which organic compounds could be determined. Volatile organic compounds were concentrated from the water samples by a closed-loop gaseous stripping procedure (Grob and Zuercher 1976) Additional samples for HRGC/MS analysis were obtained by extracting acidified (pH<2) 10 L water samples with chloroform and separating the extracts into 3 fractions by chromatography on a column of partially deactivated silica gel (15 % water). The details of the analytical procedure are given elsewhere (Ahel and Giger 1985a). In addition to mostly qualitative or semiquantitative determinations using HRGC/MS, several specific methods for quantitative determination of selected compound classes were employed. The determination of nitrilotriacetate (NTA) and ethylenediaminetetraacetate (EDTA) was performed by HRGC after enrichment on an anion-exchanger (Schaffner and Giger 1984). The metabolites of alkylphenol polyethoxylate surfactants, including nonylphenol (NP), lipophilic nonylphenol ethoxylates (NP1EO and NP2EO) and nonylphenoxy carboxylic acids (NPEC), were determined by HPLC as described elsewhere (Ahel and Giger 1985b; Ahel et al. 1987).

RESULTS AND DISCUSSION

The concentrations of dissolved organic carbon (DOC) at pollution sources and in groundwaters from the three field sites are presented in Table 1. It can be seen that, despite different DOC in the particular pollutant sources, relatively similar DOC concentrations are found at all of the field sites at the distances of more than 30 m from the source.

Table 1. Dissolved organic carbon in groundwaters from three field sites near Zagreb (mg/L)

Field site I		Field site II			Field site III		
Sava River	well* MP-4	well* JP-1	well* JP-8	well* JP-9	waste water	well* KP-5	well* KP-6
5-10	1.6	2.9	2.2	1.8	460	2.9	1.8

*distance of the well from the pollution source: MP-4: 120 m; JP-1 0 m; JP-8: 25 m; JP-9: 30 m; KP-5: 3 m; KP-6: 15 m.

In contrast, a very complex picture is obtained for specific organic compounds. More than 300 single compounds were identified during this study using HRGC/MS technique. Table 2 gives a simplified overview of the major classes of organic compounds identified in the pollutant sources and in groundwaters.

Hydrocarbons were the most common pollutant class found in the groundwaters. A very complex hydrocarbon composition, which included all characteristic marker compounds (normal and branched alkanes, monoaromatic and polyaromatic hydrocarbons, steranes, and hopanes) as well as a "hump" of unresolved complex mixture indicated a significant oil pollution. The presence of petroleum hydrocarbons was very pronounced in the groundwaters near the Sava River (field site I) and near the sanitary landfill (field site II). The composition of petroleum hydrocarbons in the groundwaters at field site I was similar to the composition of these compounds in the Sava River (Ahel and Giger 1985a). However, an increase of the relative abundance of lower aromatic hydrocarbons in groundwaters was observed. The groundwaters from the wastewater infiltration site (III), showed strong predominance of volatile alkylbenzenes (most probably deriving from their use as industrial solvents), while the petroleum hydrocarbons occured at very low concentrations in both, wastewater and groundwater. Higher PAH's were present at very low concentrations at all investigated locations suggesting that input from pyrolytic sources was relatively in-

Table 2. Major classes of the specific organic compounds identified in groundwaters from three field sites near Zagreb

	Site I		Site II		Site III		
Compounds	Sava River	well MP-4	well JP-1	well JP-9	waste water	well KP-5	well KP-6
n-alkanes	++++	+++	++++	++++	++++	++	++
b. alkanes	++++	+++	++++	++++	+++	++	++
hopanes	++	+	++	++	+	-	-
steranes	++	+	+	+	-	-	-
alkylbenz.	++++	+++	++++	+++	++++	+++	+++
C_{10}-C_{14} alkylbenz.	++	+	++	+	-	-	-
tetralin	++	+	+++	+++	-	-	-
naphthalene	+++	++	++	++	++	+	+
biphenyl	+	+	++	++	-	-	-
fluorene	+	+	+	+	-	-	-
phenanthrene	++	++	++	++	++	+	+
anthracene	+	-	-	-	+	-	-
pyrene	+	+	+	++	+	+	-
fluoranthene	+	+	+	++	+	-	-
chrysene	+	+	-	+	+	-	-
higher PAH	+	-	-	+	-	-	-
trichloroethane	+++	+++	+++	+++	-	-	-
trichloroethylene	++++	+++	++++	++++	++	++	++
tetrachloroethylene	+++	+++	+++	+++	++	++	++
chlorobenzene	+	-	++	+	+	+	-
p-dichlorobenzene	+	-	-	+	++	++	-
fatty acids	++++	++	++++	++++	+++	++	+
phthalates	++++	+++	++++	++++	++++	++	++
phenol	+	-	-	-	++++	++	++
cresols	+	-	-	-	++++	++	++
NP	+++	-	-	-	++++	+++	+++
NPEO	++++	-	-	-	++++	++	++
NPEC	++++	+++	++	++	+++	+	+
benzophenone	-	-	-	-	+++	++	-
skatole	-	-	-	-	++++	-	-
NTA	+++	-	-	-	-	-	-
EDTA	++++	++++	++++	++++	-	-	-
dialkyl sulphides	++	+	+	+	++++	++	++

Legend: ++++: >1000 ng/L; +++: 100-1000 ng/L; ++: 10-100 ng/L; +: 1-10 ng/L; -: not identified.

significant and/or that they were efficiently eliminated during infiltration. Long-chain alkylbenzenes (C_{10}-C_{14}) derived from detergents (Eganhouse and Kaplan 1983) were detected at field sites I and II. Apart from hydrocarbons which clearly derived from anthropogenic sources, the contribution of biogenic hydrocarbons, such as higher odd-numbered n-alkanes, monoterpenes and diterpenes has also been recognised.

Among the polar organic compounds, the most abundant constituents were common fatty acids, predominantly palmitic and stearic acid. The composition and origin of phenolic compounds for each field site were different. Phenol and cresol were found at the riverwater infiltration site in rather low concentrations. These could be of either industrial or biogenic origin. However, at the wastewater infiltration site, the biogenic contribution from anaerobic degradation of proteinaceous matter, originating from baker's yeast production, was assumed to be the main source of phenol and cresol. The occurrence of alkylsulphides and indoles was also interpreted as being a consequence of anaerobic degradation of organic matter. Their concentration in the wastewater was rather high, but only traces of these compounds were detected in groundwaters indicating an efficient elimination during infiltration had occurred. Benzophenone, an important intermediate in the pharmaceutical industry, was detected only at the field site III. The results, however, indicated its rapid elimination during subsurface water movement.

Biodegradation was very probably the most important elimination process for the majority of investigated compounds during their infiltration from the polluted surface waters into groundwaters. However, the role of the abiotic processes such as adsorption on aquifer material must be taken into account. The compounds found to have the greatest mobility in the aquifers were comparatively more water soluble (and therefore less adsorbable) organic compounds such as alkylbenzenes, volatile chlorinated hydrocarbons, and EDTA. The elimination of alkylbenzenes (Table 3) in the first several meters of the aquifer was very rapid, but further concentration decrease was rather slow. Even greater mobility was observed for trichloroethylene and tetrachloroethylene which are well known for their high persistence and low retardation factors in groundwaters (Schwarzenbach et al. 1983).

Detergent derived organic compounds were found to be among the most abundant compounds in investigated groundwaters. Biodegradation products of nonylphenol polyethoxylate surfactants have been detected in all investigated groundwaters (Table 4). Results reported in the Table 4 indicate relatively efficient elimination of these compounds during infiltration, most probably by biotransformation (Ahel 1987). Residual concentrations, however, could be found in groundwaters distant from the presumed pollution sources. Another two compounds that derive from detergents, NTA and EDTA, showed completely different behaviours (Table 5). The absence of NTA in groundwater was most probably due to biological elimination (Kuhn et al. 1987). In contrast, the very similar concentrations of EDTA in river- and groundwaters suggested that this compound was not significantly eliminated during infiltration.

Table 3. Volatile organic compounds from three field sites near Zagreb (ng/L)

	Site I		Site II		Site III		
Compounds	Sava River	well MP-4	well JP-1	well JP-9	waste water	well KP-5	well KP-6
benzene	250	40	-	-	28	31	33
toluene	460	50	80	50	9200	150	92
ethylbenz.	220	58	3400	130	560	11	6
m+p-xylene	660	170	60	50	38000	230	135
o-xylene	110	51	60	20	3300	18	7
tetralin	31	13	560	300	-	-	-
$CHCl_2=CHCl$	1500	2300	1200	1400	40	49	53
$CHCl_2=CHCl_2$	900	300	300	200	58	53	60

-: not determined

Table 4. Nonylphenol (NP), nonylphenol ethoxylates (NP1EO and NP2EO), and nonylphenoxy carboxylic acids (NPEC) in groundwaters from three field sites near Zagreb (ng/L)

	Site I		Site II		Site III		
Compounds	Sava River	well MP-4	well JP-1	well JP-9	waste water	well KP-5	well KP-6
NP	700	<100	<100	-	10300	120	280
NP1EO	400	<100	<100	-	34000	78	31
NP2EO	200	<100	<100	-	1900	10	10
NPEC	5000	200	50	50	290	5	4

-: not determined

Table 5. Nitrilotriacetate (NTA) and ethylenediaminetetraacetate (EDTA) in groundwaters from three field sites near Zagreb (ng/L)

	Site I		Site II		Site III		
Compounds	Sava River	well MP-4	well JP-1	well JP-9	waste water	well KP-5	well KP-6
NTA	800	<100	<100	<100	<100	<100	<100
EDTA	5300	2000	3400	5000	<100	<100	<100

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