Bull. Environ. Contam. Toxicol. (2006) 76:458–462

DOI: 10.1007/s00128-006-0943-9

Bulletin of Environmental Contamination and Toxicology

Benzene, Toluene, Ethylbenzene, and Isomeric Xylenes in Various Water Samples in Croatia

B. Karačonji, L. Skender, V. Karačić

Clinical Toxicological Chemistry Unit, Institute for Medical Research and Occupational Health, Ksaverska c. 2, Post Office Box 291, HR 10001 Zagreb, Croatia

Received: 12 October 2005/Accepted: 17 January 2006

Benzene, toluene, ethylbenzene, and isomeric xylenes (BTEX) are ubiquitous environmental pollutants and main sources of these compounds are vehicular traffic and tobacco smoking. BTEX also occur in numerous products including paints, rubber, fuels, solvents, and in production of agricultural chemicals and chemical intermediates. The occurrence of BTEX in the environment is a great concern because of their toxicity. Among them, the most dangerous is benzene; it is classified as a human carcinogen by the International Agency for Research on Cancer (IARC 1982). BTEX, released to the atmosphere by industrial emissions and vehicle exhaust, can be removed from air by rain, leading to the contamination of water. Their volatility is the reason why they are not often found in concentrations above a few µg/L in surface waters, but in ground water their concentrations can be much higher (Golfinopoulos et al. 2001).

A number of analytical methods have been reported for the analysis of BTEX in water such as direct aqueous injection (Golfinopoulos et al. 2001), liquid-liquid extraction (Golfinopoulos et al. 2001), static headspace (Menendéz et al. 2000), purge and trap (Kuo et al. 1997; Bianchi and Varney 1998; Nikolaou et al. 2002; Huybrechts et al. 2005), and headspace solid-phase microextraction (HS-SPME) (Menendéz et al. 2000; Arambarri et al. 2004) followed by gas chromatography. Because of low concentration levels found in natural waters (ng/L to µg/L) a preconcentration step is necessary prior to analysis.

Despite the potential hazard to the environment, there are no data on BTEX concentrations in water samples in Croatia. In this paper, HS-SPME, a variation of static headspace sampling, followed by gas chromatography/mass spectrometry has been applied to the analysis of BTEX in river, marine, municipal, thermal, well and lake water samples.

MATERIALS AND METHODS

Sampling was performed in April 2005, at nine rivers, four wells, two lakes, six seawater areas, six municipal water areas and six thermal water areas in Croatia. The samples were collected in dark brown glass bottles (volume 20 mL), which were filled completely to avoid headspace. All samples were placed in the

---

Correspondence to: I. B. Karačonji

portable freezer for transfer to the laboratory where they were stored at 4 °C and analyzed within two days.

BTEX for standard solutions were analytical-grade-purity products of Merck (Darmstadt, Germany). Standard reference material for BTEX was purchased from Supelco (Bellefonte, USA) and used for estimating recovery and reproducibility of method. SPME holder and fiber (10 mm long, coated with a 100 μm thick polydimethylsiloxane (PDMS) film) were also obtained from Supelco (Bellefonte, USA).

Water samples (1 mL) were placed in 6 mL-clear glass vials with stir bar and sealed with PTFE septum and holed aluminum caps. The vials were thoroughly mixed and left for 30 minutes at room temperature (21 °C). The SPME fiber was exposed to the headspace above the sample for 15 minutes at room temperature while the sample was stirred at 300 rpm. After that, fiber was inserted into the septum-equipped programmable injector (SPI) and held for 3 minutes at 200 °C.

The GC analysis of BTEX was carried out on Varian 3400 CX gas chromatograph equipped with Saturn ion trap mass spectrometer operating in the electron impact (EI) mode. Compounds were separated on Rtx-5 (Restek, Bellefonte, USA) capillary column (30 m x 0.25 mm I. D., 0.25 μm film thickness). The oven temperature was kept at 35 °C for 2 minutes, and then increased at 90 °C at rate of 5 °C/min. Late-eluating compounds were removed by increasing the temperature to 300 °C at rate of 50 °C/min. Helium was used as a carrier gas. The analysis was performed using external standard method. *M*- and *p*-xylene could not be separated, and were reported as a single value (*m/p*-xylene).

RESULTS AND DISCUSSION

Prior to water samples analyses, the method recovery and reproducibility were estimated by six replicate analyses of water samples fortified with 100 and 600 ng/L of BTEX. Recoveries and RSDs ranged between 91-100 % and 2-11 %, respectively. Detection limits were calculated by a signal-to-noise ratio of 3 and ranged from 25 ng/L (for *o*-xylene) to 44 ng/L (for benzene).

The optimized method was applied for analysis of 33 water samples. The range of BTEX concentrations in water samples is shown in Table 1. The most frequently measured compound in this study was *m/p*-xylene (in 100 % of samples analyzed), followed by toluene (94 %), and ethylbenzene (73 %). Benzene was found in only three samples (9 %), and *o*-xylene in only one sample (3 %), respectively. BTEX were present in concentrations less than 800 ng/L in all samples if we exclude thermal water sample closed to the oil-wells. The exception is toluene, which occurred at concentration of 1.073 and 41.736 μg/L in one municipal water and one thermal water sample near the oil-wells, respectively.

Table 1. BTEX concentrations (ng/L) in water samples.

	Rivers (N=9)	Sea water (N=6)	Municipal water (N=6)	Thermal water (N=6)	Wells (N=4)	Lakes (N=2)
Benzene	nd	nd	nd	nd-60 38518*	nd	nd
Toluene	nd-495	138-795	99-1073	48-294 41736*	91-342	304-409
Ethylbenzene	nd-154	88-133	92-181	nd-176 16155*	95-128	106-133
m/p-Xylene	47-393	142-376	130-483	89-321 20409*	118-478	458-472
o-Xylene	nd	nd	nd	nd 16097*	nd	nd

* sampling site close to the oil-wells

Concentrations of BTEX in the Croatian rivers were comparable to those measured in rivers in Greece (Nikolaou et al. 2002) and Spain (Arambarri et al. 2004). They were, however, much lower than BTEX concentrations in Osaka River, Japan, found at level of 10 μg/L or even more, probably due to much larger population and wide range of industrial activities (Yamamoto et al. 1997). BTEX concentrations in well water samples and lakes were less than 500 ng/L, what is in accordance with results obtained by Dunemann and Hajimiragha (1993) who published BTEX concentrations in well water less than 600 ng/L and Nikolaou et al. (2002) who reported similar concentrations in lakes in Greece. In sea water samples, concentrations of BTEX ranged from <25 to 795 ng/L. Similar levels of BTEX were determined in the North Sea (Huybrechts et al. 2005). Arambarri et al. (2004) reported six to eight times higher concentrations of BTEX in seawater samples in Spain. In five thermal water samples, BTEX concentrations ranged from not detected to 321 ng/L. Markedly higher BTEX concentrations were measured in one thermal water sample, probably due to the presence of oil-wells close to the sampling site.

In order to check drinking water quality considering BTEX, samples from six public drinking water sources were analyzed. In these samples, benzene and toluene were not found at all. Concentrations of ethylbenzene and *m/p*-xylene did not exceed value of 500 ng/L. In only one sample toluene exceeded a value of 1 μg/L (1.073 μg/L). These concentrations are significantly lower than the maximum contaminant level (MCL) for BTEX proposed by the US Environmental Protection Agency who established MCL of 5.0 μg/L for benzene and values over the range 0.7-10 mg/L for toluene, ethylbenzene, and isomeric xylenes in drinking water (US EPA 2003). Review of literature data showed higher concentrations of BTEX in drinking water in other countries compared with our results. In Taiwan, drinking water concentrations for benzene, toluene, and ethylbenzene were found to be in range nd-4.09 µg/L, nd-63.12 µg/L, and nd-11.05 µg/L, respectively (Kuo et al. 1997). In California, only benzene was found at levels that exceed federal drinking water standard; of those drinking water sources found to contain benzene over the period 1998-2002, about 58 % had measured benzene concentrations above the USEPA's MCL of 5 µg/L (Williams et al. 2004).

BTEX in various waters from different areas in Croatia were in similar and low concentrations in the most samples analyzed in this work. It can be concluded that BTEX level in water samples from rivers, sea, municipal sources, wells and lakes do not represent a risk for environmental pollution.

REFERENCES

Arambarri I, Lasa M, Garcia R, Millán E (2004) Determination of fuel dialkyl ethers and BTEX in water using headspace solid-phase microextraction and gas chromatography-flane ionisation detection. J Chromatogr A 1033:193-203

Bianchi AP, Varney MS (1998) Volatile organic compounds in the surface waters of a British estuary. Part I. Occurrence, distribution and variation (1998) Wat Res 32:352-370

Golfinopoulos SK, Lekkas TD, Nikolaou AD (2001) Comparison of methods for determination of volatile organic compounds in drinking water. Chemosphere 45:275-284

Huybrechts T, Dewulf J, Van Lagenhove H (2005) Priority volatile organic compounds in surface waters of the southern North Sea. Environ Pollut 133:255-264

IARC (1987) Benzene. Monographs on the evaluation of the carcinogenic risk of chemicals to humans, suppl. 7. International Agency for Research on Cancer, Lyon, France

Kuo HW, Chiang TF, Lo II, Lai JS, Chan CC, Wang JD (1997) VOC concentration in Taiwan's household drinking water. Sci Total Environ 208:41-47

Menendéz JCF, Sánchez MLF, Uría JES, Martínez EF, Sanz-Medel A (2000) Static headspace, solid-phase microextraction and headspace solid-phase microextraction for BTEX determination in aqueous samples by gas chromatography. Anal Chim Acta 415:9-20

Nikolaou AD, Golfinopoulos SK, Kostopoulou MN, Kolokythas GA, Lekkas TD (2002) Determination of volatile organic compounds in surface waters and treated wastewater in Greece. Water Res 36:2883-2890

United States Environmental Protection Agency (USEPA) (2002) Current Drinking Water Standards. Office of Ground Water and Drinking Water. Washington, DC, USA

Williams PRD, Benton L, Sheehan PJ (2004) The risk of MTBE relative to other VOCs in public drinking water in California. Risk Anal 24:621-634

Yamamoto K, Fukushima M, Kakutani N, Kuroda K (1997) Volatile organic compounds in urban rivers and their estuaries in Osaka, Japan. Environ Poll 95:135-143