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Environmental impact of flood: The study of arsenic speciation in exchangeable fraction of flood deposits of Warta river (Poland) in determination of “finger prints” of the pollutants origin and the ways of the migration

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HIGHLIGHTS

- ▶ We determined of arsenic inorganic species in exchangeable fraction of flood sediments.
- ▶ We use the results of speciation analysis as markers of deposits origin.
- ▶ We defined of way and sources of contamination of the environment.

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ABSTRACT

The paper presents the application of the hyphenated technique – high-performance liquid chromatography with atomic absorption spectrometry detection with hydride generation (HPLC–HG–AAS) – in the determinations of inorganic forms of arsenic: As(III) and As(V) in the exchangeable fraction of flood deposits. The separation of analytical signals of the determined arsenic forms was obtained using an ion-exchange column in a chromatographic system with the atomic absorption spectrometer as a detector, at the determination limits of 5 ng g^{-1} for As(III) and 10 ng g^{-1} for As(V). Flood deposits were collected after big flood event in valley of the Warta river which took place in summer 2010. Samples of overbank deposits were taken in Poznań agglomeration and vicinity (NW Poland). The results of determinations of arsenic forms in the exchangeable fraction of flood deposits allowed indication of a hypothetical path of deposits migration transported by a river during flood and environmental threats posed by their deposition by flood.

1. Introduction

In the environmental studies, the significant information is not obtained by the determination of total content of elements, but by the determination of forms in which these elements occur in the environment. In the speciation analysis, a significant role is played by hyphenated techniques, by which the forms of determined elements are separated using chromatographic methods, with spectrometric techniques as detectors. Hyphenated systems, such as HPLC–HG–ICP–MS (Le et al., 1994), HPLC–ICP–MS (Xie et al., 2002), HPLC–HG–AFS (Suner et al., 2000) or HPLC–HG–AAS (Le et al., 1994; Gomez-Ariza et al., 1998) allowed determination of the content of arsenic forms, both inorganic As(III) and As(V) and organic. In the case of using hyphenated techniques in the speciation analysis, an important stage is the previous extraction of arsenic forms from a soil or deposit sample. Various extractants are used for this purpose: hydrochloric acid (Chappell et al., 1995), orthophosphoric acid (V) {H_2PO_4}, which can be used as the only extractant (Rattanachongkiat et al., 2004) or in combination with ascorbic acid (Garcia-Manyes et al., 2002), or hydroxylamine hydrochloride (Gong et al., 2002). Good results can be obtained by the extraction procedure using water and phosphate buffer with pH = 5.5–6.5 (Orero Iserte et al., 2004), or using only phosphate buffer (Kozak et al., 2008).

The flood in May and June 2010 afflict Poland, the Czech Republic and Slovakia, but it also caused damage in Hungary, Ukraine, Austria and Germany. In the region of Poznań, water levels recorded for the Warta river were highest since 1979. According to the Institute of Meteorology and Water Management, the flood started at the Poznań section of the Warta river with the water level increase from 270 cm (May 2010, discharge 115 m^3 s^{-1}) to maximum 668 cm (June 2010, discharge 682 m^3 s^{-1}) in the period of 3 weeks. The alarm water level (450 cm) dropped after the

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following 3 weeks. The major problem of the city agglomeration was flooding the areas of two water intakes with induced infiltration – Krajkowo and Debina. Apart from the immediate effects, the flood caused deposition of large amount of sandy deposits on the proximal flood plain (in study area average thickness amounts 10 cm). These deposits may become a source of environmental pollution, and toxic elements they contain can be a potential threat for ecosystems.

The study aimed at determining the content of inorganic forms of arsenic As(III) and As(V) in the exchangeable fraction of flood deposits. The study will allow for the estimation of potential possibility of arsenic migration from deposits to the environment as well as for defining which form of arsenic (differing, among others, in toxicity) potentially gets into the environment.

2. Experimental

2.1. Instrumental

An analytical system combining high-performance liquid chromatography with atomic absorption spectrometry detection with hydride generation HPLC–HG–AAS constructed in the laboratory (Niedzielski, 2005; Kozak et al., 2008) was used in the study. A liquid chromatograph LC-10A (Shimadzu) equipped with an LC-10AT pump with a GT-104 degassing device and an LC-SAX1 anion-exchangeable column (Supelco, 250 mm length and 4.6 mm internal diameter) thermostated in the module (CTO-10ASvp) was used in the analysis. The leads in the chromatographic system, the injection valve and the 200 μL loop were made of PEEK material. The chromatographic pump worked in the isocratic mode at the intensity of eluent flow amounting to 3 mL min^{-1}. The leak from the column was directed to the hydride generation system in the atomic absorption spectrometer. The detector was a SpectrAA 220FS atomic absorption spectrometer (Varian) equipped with a VGA-77 hydride generation add-on device (flow system, 100 cm polyethylene reaction loop with 0.8 mm internal diameter, glass gas/liquid separator, intensity of flow of hydrochloric acid and sodium borohydride amounted to 1 mL min^{-1}) with an ETC-60 quartz tube heated electrothermally to 900 °C as an atomizer and a SuperLamp lamp (Varian) with a hollow cathode, with an increased radiation intensity for arsenic determinations (lamp current 10 mA, wavelength 197.3 nm, slit 0.5 nm). Argon was used as carrier gas.

2.2. Reagents

Only analytically pure chemical reagents and deionized water obtained in a Milli-Q device (Millipore) were used in the analysis. Base standard solutions of arsenic patterns at various oxidation stages (As(III) and As(V)) with concentration of 1 g L^{-1} were made by weighing respectively: sodium arsenite ($NaAsO_2$) and disodium hydrogenarsenate ($Na_2HAsO_4 \cdot 7H_2O$) (Sigma–Aldrich)., calibration solutions characterized by lower concentration values were made by diluting standard solutions. For the purpose of performing determinations in the hyphenated system, model solutions were prepared, each of them containing both determined forms of a given element. The solution of sodium borohydride, with the concentration of 1% (w/v), was made on the day of the analysis by dissolving $NaBH_4$ in 1% (w/v) solution of sodium hydroxide. The solutions of hydrochloric acid were made of 10 mol L^{-1} acid (Suprapur, Merck). The solution of eluent and mobile phase – phosphate buffer with pH = 6.0 ± 0.2 – was made from 0.10 mol L^{-1} solution of disodium hydrophosphate (Na_2HPO_4) and potassium dihydrophosphate ($KH_2PO_4 \cdot 2H_2O$) (Merck). The prepared eluent was subjected to preliminary degassing in an ultrasound bath (ca. 30 min).

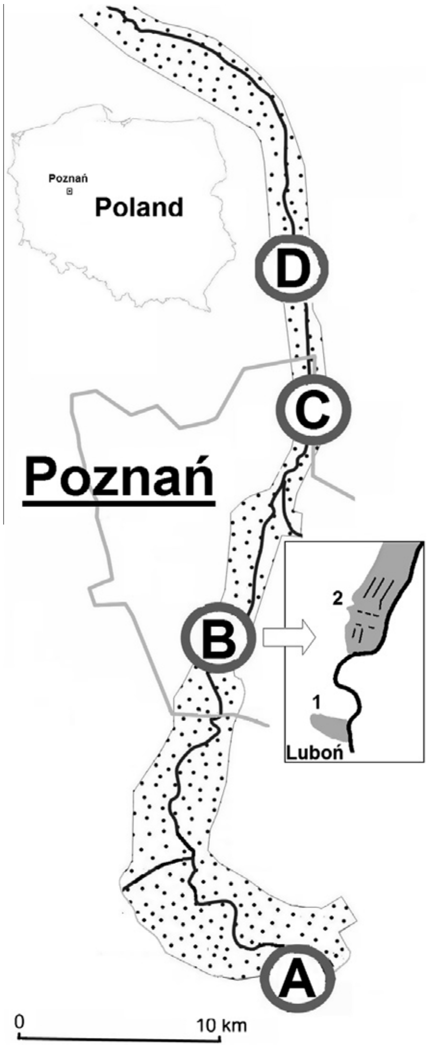

Fig. 1. The area of the studies, A–D sampling areas.

2.3. Sampling and samples preparation

Flood deposits samples were collected at four sites on flood plain in Warta valley (Fig. 1). The sites were located within and outside Poznań agglomeration as follows:

- A – water intake in Krajkowo located south of Poznań,
- B – water intake Dębina within the south part of the city agglomeration,
- C – the northern part of the city agglomeration (near Lech Bridge),
- D – the northernmost, forested area outside of the city agglomeration (the Naramowice Forest Inspectorate).

Each equalized sample was collected using plastic tools from the ~5 cm thick near-surface layer of sediment into polyethylene containers. There were sandy deposits accumulated during flood as well as soils within the flooding water influence.

The deposit samples were stored in the laboratory in the frozen state in the temperature of about −20 °C. A deposit fraction (after sieving) with grain size below 1 mm was used in the analysis. The moisture of deposit samples was determined by the weighing