Stable isotope deuterium as a natural tracer of mixing processes in rivers

Jacek Palige,
Sylwia Ptaszek,
Robert Zimnicki,
Andrzej G. Chmielewski,
Ryszard Wierzchnicki

Abstract. The possibility of application of naturally existing differences in isotope contents $^{18}O/^{16}O$, $^{2}H/^{1}H$ in waters for investigation of transport and mixing of various waters in the tributary-river system is presented. Experiments carried out on the Bug-Narew rivers-Zegrze Lake and the BugoNarew-Vistula rivers systems have indicated that the hydrogen isotope ratio $^{2}H/^{1}H$ can be used as an intrinsic tracer of natural mixing processes occurring in rivers. The IRMS methodology was used for isotope ratio measurement of water samples. The degrees of water mixing as a function of distance from the confluence point of rivers were determined. The obtained results indicate that in water systems where the natural differences in $\delta^{2}H$ are higher than 5‰ this technique can replace the time-consuming and expensive dye (or radiotracer) dispersion tests for evaluation of pollutant transport in rivers.

Key words: stable isotopes • tracer • deuterium • oxygen-18 • river • water flow

J. Palige✉, S. Ptaszek, R. Zimnicki, R. Wierzchnicki
Department of Nuclear Methods in Process
Engineering,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22 504 10 58, Fax: +48 22 811 15 32,
E-mail: jpalige@ichtj.waw.pl

A. G. Chmielewski
Department of Nuclear Methods in Process
Engineering,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland
and Faculty of Chemical and Process Engineering,
Warsaw University of Technology,
1 L. Waryńskiego Str., 00-645 Warsaw, Poland

Introduction

Continuous expansion of industrial activities and urban agglomerations results in increasing amount of pollutants being discharged into rivers. Successful protection of surface waters against excessive contamination requires sufficient knowledge of phenomena occurring during transport of pollutants in surface waters. This results in a growing interest in studies of interrelations between surface waters and wastes being discharged into these waters. Dispersion of pollutants and dynamics of mixing in natural water courses (rivers, channels, lakes and reservoirs, etc.), kinetics of self-purification processes as well as optimized design and appropriate location of sewage outfalls, are the areas of intensive research in this context. One of the research tools being used in solving the problems outlined above are tracer methods.

Radioactive and fluorescent tracers are widely used in investigation of dispersion and dilution of pollutants in surface waters [4, 5, 9, 10]. The choice of tracer is critical since it has to satisfy a number of requirements. The most important of them is that such processes as sorption of tracers on suspensions and bottom sediments, extraction by foreign phases and its precipitation have to be precluded. Numerous studies have shown that ^{82}Br in the aqueous solutions of KBr and rhodamine-WT (or B) and uranine fulfill most of the requirements of an ideal tracer in the context of studies of dispersion and mixing processes in surface water systems. Investigation of pollutant transport and mixing phenomena in surface water system with the aid of artificial tracers consists

of an injection of tracer of choice at a predetermined point of the water system under study and recording distribution of tracer concentration as a function of time and position within that system.

Ecological and sanitary regulations concerning limitations of maximum admissible concentrations of different substances in river water (including fluorescent dyes and radioactive materials) practically eliminated the possibility of artificial tracer application in surface water system where the water intake for local agglomeration are located.

This situation caused the need for new, intrinsic tracers of water phase which will satisfy the requirements for tracers and which are not controversial from the ecological point of view. Water temperature or heavy isotopes of hydrogen and oxygen are examples of such tracers. There are three isotope water molecules of interest here [6]; oxygen-18 ($^1H_2^{18}O$), deuterium ($^1H^2H^{16}O$) measured as isotopic ratios ($^{18}O/^{16}O$ and $^2H/^1H$) with mass-spectrometric techniques and tritium ($^1H^3H^{16}O$) measured by nuclear analytical techniques.

The different aspects of stable isotopes (^{18}O, ^2H) and ^3H applications for water systems investigations were disscused in the literature [8].

Presented work is an example of application of naturally existing differences in stable isotope composition ($^2H/^1H$ and $^{18}O/^{16}O$) of river waters as a tracer of mixing processes in main river-tributary systems. Two water systems in Poland have been investigated:
– the Narew and the Bug rivers and their mixing in Zegrze Lake,
– the BugoNarew and the Vistula rivers and their water mixing.

The differences in isotopic composition of the Bug, Narew and Vistula rivers results from the different "history" of water at river catchment area and depend on geographical, hydrological and regional climatic conditions. Water, during its natural circulation in nature, undergoes various processes (e.g. evaporation, condensation, rainfall etc.) resulting in modification of its isotopic composition. The investigations of water mixing in both the water systems were performed in 2004 and 2005.

Site description and methods

The methodology of the presented work was based on the measurements of $^{18}O/^{16}O$ and $^2H/^1H$ isotope ratios in water of tributaries and in the main river channel.

The isotope ratios $^{18}O/^{16}O$ and $^2H/^1H$ are expressed as per mille deviations from the internationally accepted standard:

$$\delta_{VSMOW} = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \cdot 1000$$

R_{sample} = $^2H/^1H$ or $^{18}O/^{16}O$ ratio in water samples; $R_{standard}$ = $^2H/^1H$ or $^{18}O/^{16}O$ ratio in standard VSMOW (Vienna Standard Mean Ocean Water).

The adopted methodologies of δ^2H and $\delta^{18}O$ measurements are presented in [1, 2, 7]. The isotope ratios, were measured by the IRMS (isotope ratio mass spectrometry) method.
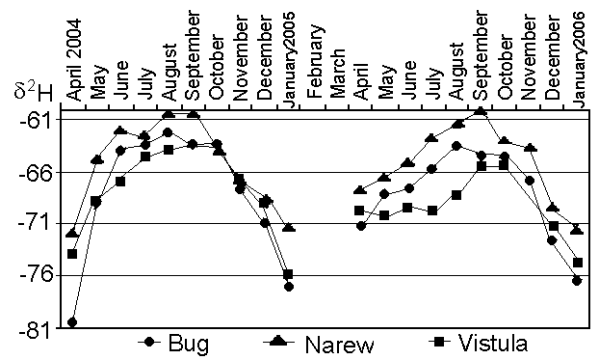

Fig. 1. The seasonal changing of δ^2H values in two year period of observations for the Bug, Narew and Vistula rivers.

During the initial phase of the study, a series of water samples from the Bug, Narew and Vistula rivers were collected at their respective cross sections to check the uniformity of isotopic composition of the river water.

The measured isotope ratios did not deviate more than 2% from their respective mean value characterizing the given river. Thus, the individual rivers could be considered well-mixed.

During the period April 2004 – January 2006 water samples were collected from each river on monthly basis.

The observed differences of isotope ratio between the studied rivers were 0.5 ± 0.1 for $\delta^{18}O$ and up to 6 ± 0.5 for δ^2H. Taking into account linear relationship between δ^2H and $\delta^{18}O$ for fresh waters [3] and the fact that the ratio deuterium measured value/precision of measurement is higher for δ^2H it was decided to use deuterium as a tracer of choice.

The time dependence of δ^2H for the two-year period of observations for the Bug, Narew and Vistula rivers is presented in Fig. 1. The presented data confirm that during summer period (May–October) the observed differences in hydrogen isotope composition are sufficient for application of this parameter as a tracer for studing mixing processes in rivers below their confluence point.

The maps of investigated regions with positions of sampled river profiles are presented in Fig. 2 for system the Bug-Narew rivers-Zegrze Lake, and in Fig. 3 for the BugoNarew, Vistula rivers.

To quantify the mixing processes in the investigated river systems several sections downstream of the confluence point were selected. Water samples (15 to 20) were collected along each section using a motor boat. The position of the boat was registered by GPS. For each water sample the δ^2H was measured. To quantify the degree of mixing along the river the parameter M, as defined by Eq. (1), has been introduced:

$$(1) \qquad M = 1 - \left[\frac{1}{N-1} \cdot \sum_{i=1}^{N}\left(1 - \frac{C_i}{\overline{\overline{C}}}\right)^2\right]^{1/2}$$

where: M – parameter describing degree of mixing (value of M equal to 1 corresponds to perfect mixing of river); $i = 1, 2, 3...$; N – number of samples; $\overline{C}$ – mean value of the measured isotope ratio ($^2H/^1H$) for a given profile; $\overline{C} = (C_1 \cdot Q_1 + C_2 \cdot Q_2)/(Q_1 + Q_2)$; $C_1 = (\delta^2H)_1$; $C_2 = (\delta^2H)_2$ for rivers 1 and 2; Q_1 and Q_2 – flow rates of
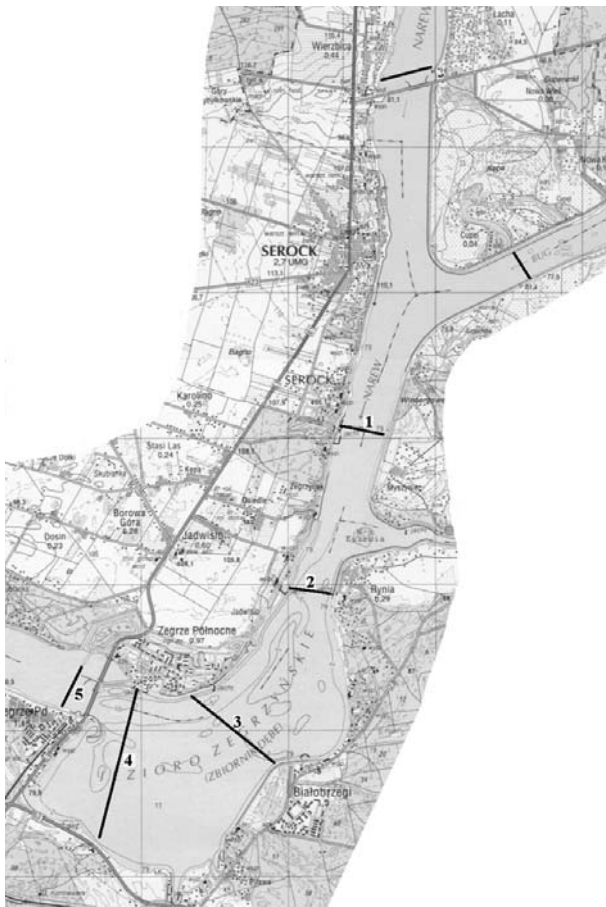
Fig. 2. The map of the Bug-Narew rivers-Zegrze Lake water system with indication of measuring profile positions.

Fig. 4. The distribution of hydrogen isotopes ratio δ^2H = in profiles during the consecutive measuring sessions 07.09.2004 (a) and 21.10.2004 (b) carried on Zegrze Lake.

river was 4 m. The distance between sampling points along the profile was 25 m. It has been assumed that the rivers are well-mixed in vertical [5].

All water samples were collected at the defined 0.5 m depth.

Results

The distribution of δ^2H in profiles during consecutive sampling compaigns carried out in Zegrze Lake is presented in Fig. 4. The calculated values of M parameter, the flow rates of rivers and distances of sampled profiles from the confluence point of the Narew and Bug are presented in Table 1. During sampling campaign on 7 September 2004, the flow rates of the Bug and Narew rivers were very similar ($Q_1 = 77.8$ m^3/s, $Q_2 = 75.5$ m^3/s), whereas during the second sampling campaign carried out on 21 October 2004, the Narew river revealed

river 1 and 2; $C_i = \Delta(\delta^2H)_0 - \Delta(\delta^2H)_i$; $\Delta(\delta^2H)_0 = |(\delta^2H)_1 - (\delta^2H)_2|$; $\Delta(\delta^2H)_i = |(\delta^2H)_1 - (\delta^2H)_i|$.

The M value describes properly the mixing processes for rivers with similar volumetric flow rates. For rivers with large differences in volumetric flow rates Q_i the M value can be used only as a qualitative parameter.

During the water sampling, in profiles in parallel the bathymetry and measurements of flow velocity distribution in river cross sections were carried out.

For Zegrze Lake, the width of the profiles varied between 700 and 1600 m. The mean depth was 3.6 m. The distance between sampling along the profile was ca. 50 m. For the Vistula river extension of the profiles was between 250–300 meters. The mean depth of the
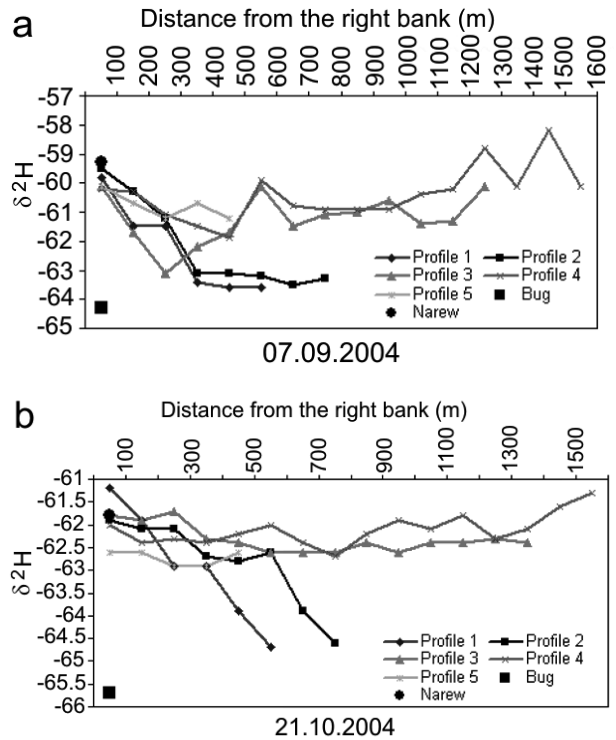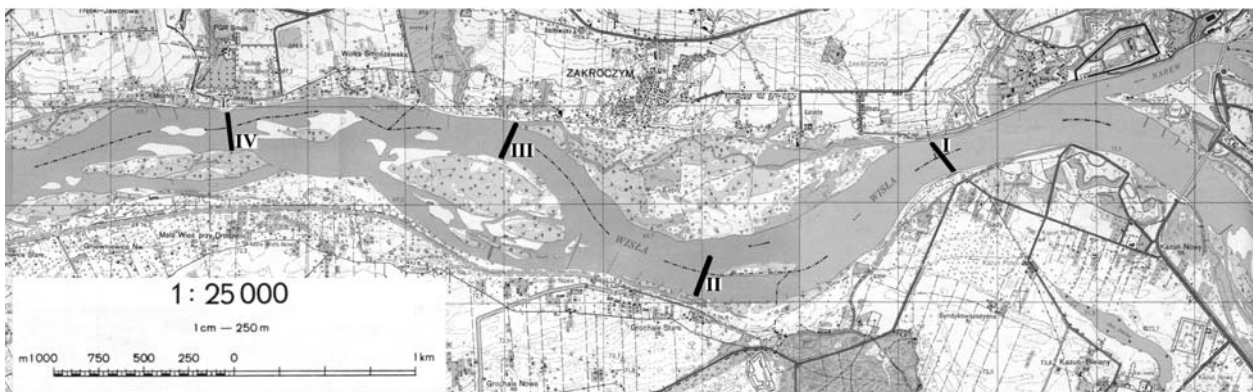

Fig. 3. The map of the BugoNarew, Vistula rivers water system with indication of measuring profile positions.

Table 1. Mixing degree (*M*) at selected river sections downstream from the confluence point for the Bug-Narew river system

Bug-Narew rivers	07.09.2004		21.10.2004	
Profiles	Distance from confluence (m)	*M*	Distance from confluence (m)	*M*
Profile 1	2738	0.25	2801	0.54
Profile 2	5130	0.27	5003	0.67
Profile 3	7809	0.71	7553	0.77
Profile 4	10124	0.76	9482	0.90
Profile 5	10800	0.87	11154	0.95

Table 2. Mixing degree (*M*) at selected river sections downstream from the confluence point for the Bug-Narew-Vistula river system

Narew-Vistula rivers	14.06.2005		13.07.2005	
Profiles	Distance from confluence (m)	*M*	Distance from confluence (m)	*M*
Profile I	497	0.19	673	0.26
Profile II	1515	0.50	1920	0.54
Profile III	2490	0.52	3875	0.56
Profile IV	3930	0.71	8765	0.76

ca. 30% higher flow rate ($Q_1 = 71.5$ m³/s and $Q_2 = 93.7$ m³/s).

In profile 4 (Figs. 4a and 4b), near the left bank of Zegrze Lake, the unexpected values of δ^2H (higher than the isotope ratios of constituent rivers) were registered.

This can be connected with the observed flow stagnation in this region (even small backflow) and the changing water evaporation conditions.

The same type of data for the BugoNarew-Vistula river system is presented in Fig. 5 and Table 2. For this river system, also two sampling campaigns were carried out (14 June 2005 and 13 July 2005). The Vistula and BugoNarew flow rates were respectively $Q_1 = 682$ m³/s, $Q_2 = 399$ m³/s during the 14 June 2005 compaign and $Q_1 = 361$ m³/s, $Q_2 = 126$ m³/s during the 13 July 2005 experiment. The Vistula river is characterized by ca. two times higher flow than the BugoNarew. Also, large differences in the measured flow rates were observed between consecutive sampling campaigns.

The data presented in Tables 1 and 2 indicate that for both studied river systems good mixing across the river channel was reached at a distance of 8–10 km from the confluence point.

It is worth of noting that the sampling campaign at the BugoNarew-Vistula river system, carried out on 14 June 2005, was preceded by several days of heavy rainfall. This resulted in significant intensifying water mixing processes and shortening complete mixing length up to 4 km.

Conclusion

The method of hydrogen isotopes ratio used in two confluated water systems can be successfully used for the evaluation of water mixing processes intensity in the observed region. The method of isotope ratio changing observations in profiles located across the river gives the possibility for global description of mixing processes, i.e. calculation of mixing degrees, the lenght

of complete mixing evaluation etc. The data obtained by this method can be applied for the verification of mathematical models and results of computer simulations for pollutant transport and mixing in river systems. They could also be a basis for forecasting a pollutant transport and for evaluation of ecological hazard, for example, for potable water intakes localized in the area under investigation.
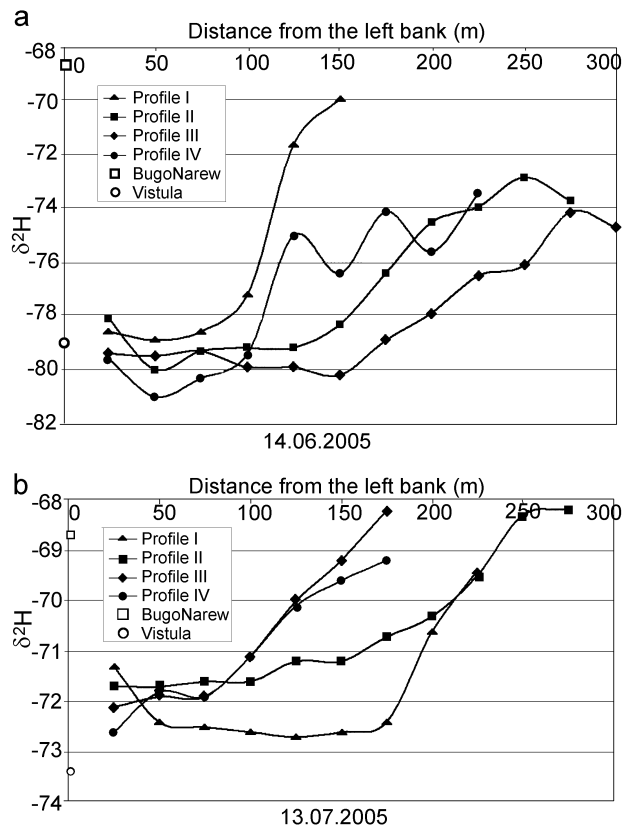
Fig. 5. The distribution of hydrogen isotope ratio δ^2H in profiles during the consecutive measuring sessions 14.06.2005 (a) and 13.07.2005 (b) carried on the system of the BugoNarew, Vistula rivers.

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