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The strontium isotope budget of the Warta River (Poland): Between silicate and carbonate weathering, and anthropogenic pressure

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ABSTRACT

The Sr isotope composition ($^{87}Sr/^{86}Sr$) and Sr content of waters of the Warta River (central-western Poland) and its tributaries were used to fingerprint water sources and their interactions in space and time. Dissolved Sr in river water of the Warta is characterized by a relatively narrow range of the $^{87}Sr/^{86}Sr$ values, from 0.7090 to 0.7105, which contrasts with a strong variation in isotopic signatures of the tributaries, from 0.7080 to 0.7121. With the exception of three streams, which include inputs of mine waters, the waters of tributaries are more enriched in ^{87}Sr than the master stream. The overall Sr budget of the Warta watershed is determined by the relative contributions of carbonate dissolution and silicate weathering. It can be accounted for by mixing between waters from three reservoirs: 1) groundwater charged with Sr through interaction with Sr-bearing clay minerals, 2) groundwater related to weathering (dissolution) of carbonate rocks, and 3) atmospheric waters charged with Sr from the near-surface weathering and wash-out of Quaternary glaciogenic deposits. Superimposed on the natural Sr isotope systematics is impact of mine waters and fertilizers. The former providing non-radiogenic Sr from the Permian/Mesozoic aquifers constitutes an important anthropogenic element of the Sr budget, whereas the impact of the latter is presumably common but of minor importance. The present-day Sr isotope systematics of the Warta is temporary and different from that of the pre-industrial times.

1. Introduction

Strontium isotopes ($^{87}Sr/^{86}Sr$) have proved to be useful tracers in various environmental studies, and especially, as indicators of interaction between the water and various rocks (e.g., Aberg, 1995; Bain and Bacon, 1994; Capo et al., 2014; Frost and Toner, 2004; Graustein and Armstrong, 1983; Shand et al., 2009). They are increasingly applied to study of weathering processes in catchments and to decipher climatic changes inferred from temporal shifts in composition of river water suspended and/or dissolved material (e.g., Blum et al., 1998; Bu et al., 2016; Jacobson et al., 2002; Krishnaswami et al., 1992; Poszwa et al., 2004; Rhodes et al., 2002). This is because weathering causes disintegration or alteration of minerals at the Earth's surface into products which tends towards equilibrium with conditions occurring in the environment. Weathering supplies strontium released from rocks of different age and composition to surface and ground waters. Strontium isotope ratios ($^{87}Sr/^{86}Sr$) depend primarily on Rb/Sr initial ratios of rocks and their ages (e.g., Faure, 1986; Faure and Powell, 1972) because radiogenic Sr isotopes ($^{87}Sr/^{86}Sr$) do not fractionate during natural processes (evaporation, precipitation, biological uptake) in the environment (e.g., Blum et al., 2000; Flockhart et al., 2015). Hence, variation in the Sr isotope composition of surface water results from mixing of Sr from various sources having different isotopic ratios. The $^{87}Sr/^{86}Sr$ values of surface water in a given area can, therefore, provide information about Sr sources and mixing processes involved (Andersson et al., 1992; Bain et al., 1998; Negrel et al., 1997; Negrel and Lachassagne, 2000; Shand et al., 2009; Siegel et al., 2000; Tripathy et al., 2010). In many cases, Sr isotopes are far more sensitive indicators of water sources than

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traditional geochemical analyses. If strontium in water is derived from the bedrock, its isotope composition reflects an average composition of rocks subjected to weathering and erosion within a given watershed (e.g., Négrel, 1999; Négrel and Pauwels, 2004; Palmer and Edmond, 1992; Semhi et al., 2000; Yang et al., 1996). Superimposed on natural processes is human activity which introduces usually various additions including mineral fertilizers, mine waters, road salt, combustion ash, and urban sewage (e.g., Aberg, 1995; Böhlke and Horan, 2000; Brinck and Frost, 2007; Négrel et al., 2004; Soler et al., 2002; Zieliński et al., 2016).

The present study reports Sr isotope fingerprints throughout the Warta River, a relatively large river in western Poland (Fig. 1), which drains an area characterized by a very diverse bedrock including carbonates and various siliciclastic rocks and sediments. Furthermore, the Warta River basin is known to be significantly influenced by mining and agricultural activities. The aim of the present study is to characterize in detail impact of natural and anthropogenic sources on the Sr budget of the Warta River and to define the main constraints on the respective contributions of these end-members in areas where water resources are under high anthropogenic pressure.

2. Hydrologic system

The Warta (German: Warthe), with its length of 808 km and watershed area of about 54 500 km^2, is the third-longest river in Poland (Fig. 1) and the largest tributary of the Oder River. Its fluvial system is visualized in Fig. 2A. The Warta River generally streams in a northwesterly direction but its course is characterized by several right-angled bends. This is because the river uses mostly a glacial and post-glacial drainage network, developed during the retreat of the Vistulian ice-sheet, which is composed of latitudinal ice-marginal and meridional proglacial valleys. The Warta River rises in the Cracow Upland, very close to Zawiercie. It flows northwest as a subsequent stream to Częstochowa, then turns northeast across the Polish Jura Chain and enters the Małopolska Upland. South of Radomsko the Warta turns west and flows within an obsequent valley for approximately 50 km, then turns again north and enters the Mid-Polish Lowland. Downstream of Sieradz, the discharge of the river is controlled by a dam of the Jeziorsko Reservoir to furnish irrigation and hydroelectric power supply. At Koło, where the river reaches the Warsaw-Berlin ice-marginal valley, it turns west and passing Konin flows west for about 100 km. South of Poznań the river turns again north and uses a former proglacial valley to reach the Toruń-Eberswalde ice-marginal valley, than flows west for approximately 200 km until it joins the Oder River at Kostrzyń. The Warta has several natural tributaries including Liswarta, Widawka, Ner, Prosna, Wełna, Obra and the Noteć (Fig. 2A). A summary of the Noteć River system, the largest tributary of the Warta, was recently presented by Zieliński et al. (2016). River regulation of the Warta began in the nineteenth century and was completed in the twentieth century. In 1850–1859, the Mosina Canal was constructed to redirect the upstream portion of the Obra River to the Warta and thus, to increase municipal water supply in Poznań. More recently, in 1949, the Warta was also connected with the Noteć by the Ślesin Canal to open a shipping route to the Vistula River. Today, however, this canal distributes only water from the Warta to compensate losses caused by energy industry and mining activity around Konin (Wachowiak et al., 2004).

Fig. 1. Schematic map showing the Warta River watershed (shaded area) and other major rivers of Poland.

In relation to the surface of its drainage area the Warta River is characterized by a low discharge and a moderate interannual variation. High water occurs from February to begin of May, whereas low water occurs from June to September. A long-term mean discharge with a SSQ value of 224 m^3/s (measured close to the mouth of the river near Gorzów Wielkopolski in the period from 1961 to 2000) is only about 2-fold higher than the mean minimum discharge (SNQ = 107 m^3/s) and about 2-fold smaller than the mean maximum discharge (SWQ = 498 m^3/s). Although land use is predominantly rural (about 55%) in the drainage area of the Warta, the river receives substantial anthropogenic pressure. Around Częstochowa, where iron ore mining was carried out until the eighties of the twentieth century, the river is subjected to contamination by leakage of mineralized waters from the flooded iron mines (Razowska, 2001). Downstream, northwest of Radomsko (Fig. 2A), a huge lignite mine located at Bełchatów supplies mine waters from a dewatering system into the Warta (via its tributary the Widawka). Before the mine opening in the mid-seventies the Widawka had a mean natural discharge of 13.6 m^3/s (Wachowiak et al., 2011). Due to input of mine waters the average discharge increased by about 15% in 2010. The Warta River is also recharged by mine waters from another, large lignite mine (Adamów open-pit mine) situated at Turek, southeast of Konin (Fig. 2A). Here, the mine waters are not released directly to the Warta but to its tributaries, the Teleszyna and the Kiełbaska. The former is additionally recharged by waters from the Jeziorsko Reservoir to compensate a significant water withdrawal for cooling systems of the Adamów power plant.

3. Geological background

Apart for its upstream part, where the Warta River is cutting over short distances into the Upper Triassic and Upper Jurassic rocks (Fig. 2C), it drains a post-glacial landscape originated during the retreat of the Vistulian ice-sheet (e.g., Galon, 1968; Kozarski, 1962). A continuous cover of glacial deposits commonly exceeds 200 m in thickness and consists of tills, glacial sands and gravels as well as outwash sands and gravels. This clastic material was transported within the ice-sheet from Scandinavia and is derived from Precambrian magmatic and metamorphic rocks as well as Paleozoic carbonates. The Neogene and Paleogene rocks are widely distributed in the Warta River basin but they do not crop on the surface along the river course. They underlay the Quaternary