



Application of isotopic and geochemical studies to explain the origin and formation of mineral waters of Staraya Russa Spa, NW Russia

Natalia Vinograd¹ · Adam Porowski²

Received: 20 October 2019 / Accepted: 26 March 2020 / Published online: 10 April 2020
© The Author(s) 2020

Abstract

There are two main types of mineral waters used in the Staraya Russa spa: (1) the saline waters of the Middle and Upper Devonian Arukjula–Shventoy aquifer with isotopic composition of $\delta^{18}\text{O}$ from -10.7 to -11.3‰ and $\delta^2\text{H}$ from -81.3 to -85‰ and (2) the brackish waters of the Upper Devonian Sargayev–Daugava aquifer with isotopic composition of $\delta^{18}\text{O}$ from -12.5 to -12.9‰ and $\delta^2\text{H}$ from -93.0 to -94.1‰ . Hydrogeological conditions within the spa and its vicinity are complex due to hydraulic contacts between artesian aquifers and the saline waters ascension into shallower fresh water aquifers. The studies revealed that saline waters of the Arukjula–Shventoy aquifer are mixtures of approximately equal fractions (0.5) of snow melt water of $\delta^{18}\text{O}$ around -21.7‰ and seawater-like end-member of isotopic composition similar to modern ocean water (i.e. VSMOW). The brackish waters of the Sargayev–Daugava aquifer are result of mixing between infiltration waters and saline waters ascending from deeper Arukjula–Shventoy aquifer, the fraction of saline water may reach from around 0.2 to 0.4. The sulfur ($\delta^{34}\text{S}$) and oxygen ($\delta^{18}\text{O}$) isotopic composition of sulfates dissolved in mineral waters indicate that their source is connected with marine sulfates. The ionic ratios of major chemical compounds corroborate the presence of the connate seawater-like component in the hydrogeological system, which is responsible for the observed chemical composition of mineral waters extracted in Staraya Russa spa.

Keywords Mineral water · Groundwater origin · Groundwater mixing · Saline water ascension · Isotopic composition · Dissimilatory sulfate reduction

Introduction

Staraya Russa, located on the Polist River, 99 km south of Veliky Novgorod, is known since ninth century and belongs to one of the oldest Russian towns. From the middle ages to the nineteenth century, the town was famous from the

production of salt from local saline waters (Ozerova and Shirokova 2017). The first dug wells built for the increase of saline water use for salt production are known from fourteenth century. The studies of the chemical composition of mineral waters directed on their therapeutic and healing properties began in eighteenth century. The first drilling well for extraction of mineral waters for balneological purposes was constructed in 1819 and the spa in Staraya Russa based on the curative mineral waters and muds was founded in 1828 when the first resort for eight bathing places was built (Kuklin and Shklovsky 2008; Ozerova and Shirokova 2017). Nowadays, the spa occupies the area of about 92 hectares and utilizes its mineral waters from ten intakes (springs and artesian wells) for bathing, drinking, and inhalations. The most famous artesian spring, the so-called Muraviov Fountain (well w-1, see Table 1, Fig. 1), was deepened in 1856 and reveals continuous artesian flow up to date with hydraulic pressure of about 10–14 m above ground surface. At present, for various balneological treatment, the spa uses

This article is a part of the Topical Collection in Environmental Earth Sciences on “Mineral and Thermal Waters” guest edited by Drs. Adam Porowski, Nina Rman and Istvan Forizs, with James LaMoreaux as the Editor-in-Chief.

✉ Adam Porowski
adamp@twarda.pan.pl

Natalia Vinograd
natalia_vinograd@yahoo.com

¹ Department of Hydrogeology, St. Petersburg State University, Universitetskaya nab. 7/9, 199034 St. Petersburg, Russia

² Institute of Geological Sciences Polish Academy of Sciences (ING PAN), Twarda 51/55, 00-818 Warsaw, Poland

Table 1 Chemical composition of mineral waters utilized in Staraya Russa spa

Intake	D [m]	S	pH	Eh [mV]	TDS [mg/L]	SC [μS/cm]	t [°C]	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Ba ²⁺	Fe	Sr ²⁺	B ⁻	Br ⁻	SiO ₂	Hydro-chemical type of water
Spring-2	3.8	D ₃ br	7.4	147	18,302.8	31,900	10.8	4997.0	78.1	1289.0	447.0	9950.0	1400.0	109.8	0.02	1.94	28.45	1.5	nd	6.1	Cl-Na-Ca
Spring-4	20.0	D ₃ br	7.4	157	17,313.0	31,200	11.7	4783.0	73.7	1317.0	447.0	9220.0	1318.0	122.0	0.03	2.16	28.66	1.4	nd	6.7	Cl-Na-Ca
Spring-8	1.0	D ₃ br	7.8	132	17,216.7	31,200	10.8	4697.0	75.3	1338.0	456.0	9200.0	1308.0	109.8	0.03	1.98	29.11	1.5	nd	6.1	Cl-Na-Ca
Well-11	78.4	D ₃ sr-dg	7.0	137	5869.3	11,190	10.3	880.0	79.0	669.0	365.0	3361.0	362.0	110.0	nd	nd	26.0	1.30	16.0	3.3	Cl-Na-Ca-Mg
Well-12	68.3	D ₃ sr-dg	7.1	102	3039.1	5940	9.7	235.0	54.0	363.0	298.0	1697.0	145.0	220.0	nd	nd	16.0	0.10	11.00	3.3	Cl-Mg-Ca
Artesian well-1	118.6	D ₂ ar-D ₃ sv	7.2	147	17,855.8	31,700	10.8	4833.0	74.6	1273.0	444.0	9700.0	1390.0	109.8	0.02	1.87	28.14	1.4	nd	6.0	Cl-Na-Ca
Artesian well-3	213.4	D ₂ ar-D ₃ sv	7.4	167	18,698.6	32,000	11.5	4881.0	76.9	1292.0	453.0	10,450.0	1398.0	115.9	0.03	1.88	28.31	1.5	nd	5.8	Cl-Na-Ca
Artesian well-6	80.5	D ₂ ar-D ₃ sv	7.5	177	16,397.1	29,800	12.9	4556.0	71.8	1263.0	421.0	8690.0	1255.0	109.8	0.11	1.93	27.11	1.4	nd	5.9	Cl-Na-Ca
Artesian well-7	248.0	D ₂ ar-D ₃ sv	7.4	167	16,416.3	29,900	13.2	4426.0	71.0	1329.0	445.0	8720.0	1283.0	109.8	0.01	2.11	29.13	1.3	nd	6.1	Cl-Na-Ca
Artesian well-9	131.5	D ₂ ar-D ₃ sv	6.5	147	19,265.8	32,100	11.1	5086.0	77.3	1254.0	437.0	10,850.0	1420.0	119.8	0.03	1.89	28.20	1.6	47.0	6.0	Cl-Na
River Pollist	-	-	8.0	312	143.5	160.9	16.8	2.8	3.1	24.2	4.7	7.1	<5	100.0	0.05	1.35	0.13	0.03	nd	6.5	HCO ₂ -Ca-Mg
River Porusia	-	-	8.0	310	155.7	159.7	17.4	7.3	2.6	21.9	4.8	12.5	<5	104.0	0.09	2.20	0.22	0.05	nd	6.4	HCO ₂ -Ca-Mg

Ion concentration in mg/dm³

Water from rivers Pollist and Porusia presented for reference. Hydrochemical type of water has shown major constituents in which concentration is more than 20 meq/dm³

D total depth of well or spring, S stratigraphy of exploited aquifer, D₃br Upper Devonian Buregi aquifer, D₃sr-dg Upper Devonian Sargatev-Daugava aquifer, D₂ar-D₃sv Middle and Upper Devonian Arukjula-Shventoy aquifer, TDS total dissolved solids, SC specific conductance, Eh redox potential, nd not determined in this study

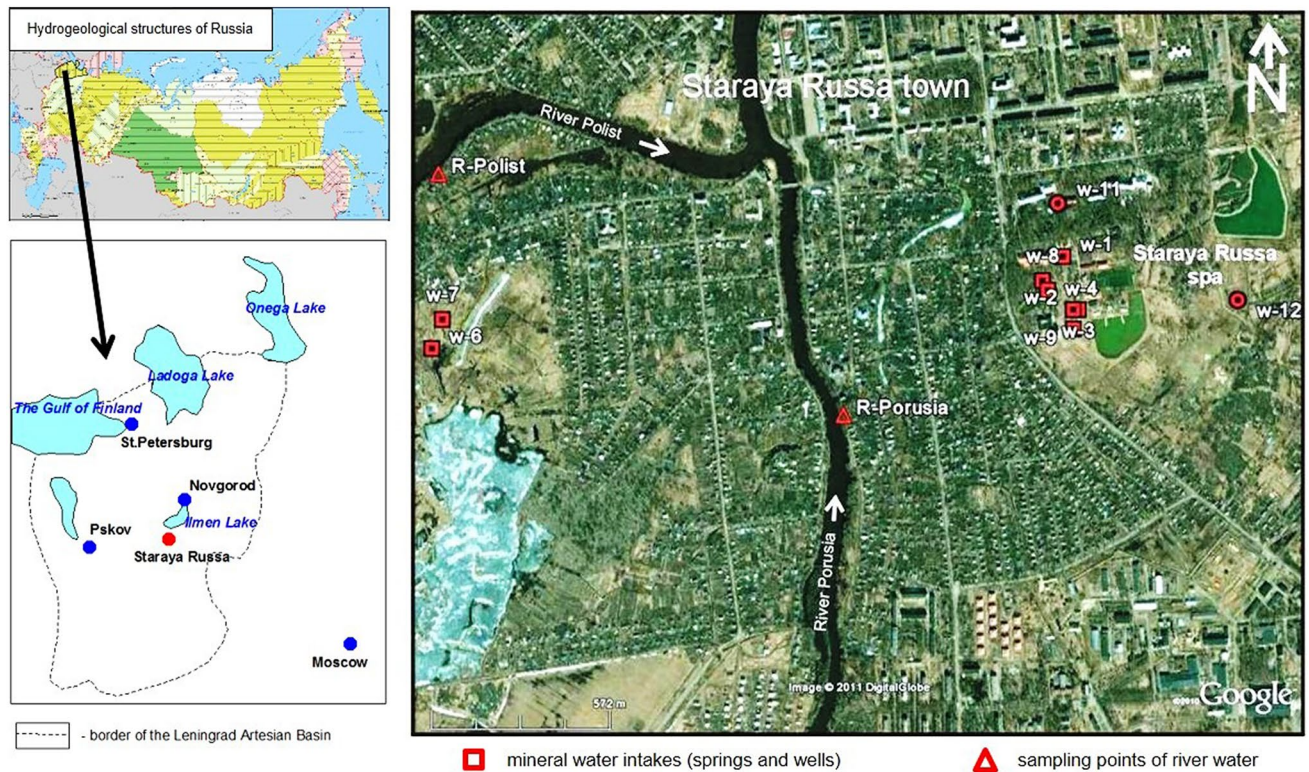


Fig. 1 The Leningrad Artesian Basin and location of the Staraya Russa spa with its mineral water intakes

also the medicinal silt muds from artificial lakes Verkhneye and Sredneye and muds from other local reservoirs.

Hydrogeologically this area belongs to the first-order Middle Russian (Srednerussky) Artesian Basin and the second-order Leningrad Artesian Basin (Fig. 1). Artesian basins occupy large areas in Russia and contain largest resources of mineralized waters and brines of various chemical composition and origin (Korotkov et al. 2013). Some of these waters are important resource for development of balneological treatment and curative drinking or extraction of valuable salts and minerals. However, in many cases, the origin of these waters as well as the origin of their chemical composition is not sufficiently recognized or understood to secure the sustainable development of the spa services. Usually, there is a traditional consideration of the sedimentary origin of such types of waters in Artesian Basins (Vinograd 2004; Korotkov et al. 2013; Ozerova and Shirokova 2017). The problems of the origin and ascension of deep saline waters in the vicinity of Staraya Russa spa were described in many reports documenting mineral water resources for the spa (e.g. Kuklin and Shklovsky 2008). The ecological problems in the vicinity of Staraya Russa connected with the saline waters discharge to the rivers and the influx of deep saline waters into fresh water aquifers have been gaining increasing interest in recent years (Kurilenko and Kirichenko 2016, 2017; Simonova and Rusakov 2018; Vinograd et al. 2019).

The influence of deep brines on the fresh water aquifers and soil salinization was discussed by Simonova and Rusakov (2018) on the example of uncontrolled artesian flow of the Caryinsky spring (well 7, Fig. 1). On the other hand, the important aspects of the origin, formation, and recharge of the fresh groundwaters in the main useful aquifers (up the Cambrian–Ordovician formations) of the northern part of the Leningrad Artesian Basin were discussed by Vinograd et al. (2019). However, too little attention has been paid up to date on the explanation of the origin and formation of saline waters or brines encountered in the deep parts of the Artesian Basin. The detailed recognition of groundwater origin and interactions between fresh and saline waters is a key issue for the spa managers and decision makers to apply appropriate strategies of protection of groundwater quality and management of mineral water resources especially when developing the local economy and increasing water demand.

This paper is focused exclusively on the isotopic characteristics of mineralized waters extracted for curative and drinking purposes in Staraya Russa spa. The study is the first one, which presents the results of determination of stable oxygen ($^{18}\text{O}/^{16}\text{O}$) and hydrogen ($^2\text{H}/^1\text{H}$) isotopic composition of mineralized waters, and stable oxygen ($^{18}\text{O}/^{16}\text{O}$) and sulfur ($^{34}\text{S}/^{32}\text{S}$) isotopic composition of dissolved sulfates. The application of isotopic methods and use of isotopic data are indispensable in modern hydrogeology to understand

vital problems concerning formation of groundwater resources, vulnerability assessment, and protection of their quality and their sustainable use.

A combined detailed interpretation of O and H isotopic composition of mineral waters and O and S isotopic composition of dissolved sulfates (e.g. sulfate is one of the major compounds of studied water) together with chemical composition of water allow (1) to explain the origin of mineral waters in geological formations, and (2) to identify the main biogeochemical processes in the aquifers responsible for the origin of water's chemical composition. A particular combination of isotopic and chemical data also helps to identify local or regional hydraulic contacts between different aquifers and the mixing processes between groundwaters.

Geological and hydrogeological settings of the study area

Geographically, Staraya Russa is located within the Baltic plain which extends from the Gulf of Finland in the north to the Valdai elevations in the south. Generally the Baltic plain is quite monotonic, with elevations around 20–50 m above sea level (a.s.l.) and slopes slightly northwards, to the

Baltic Sea (Kuklin and Shklovsky 2008). The Ilmen Lake, 17 km north from Staraya Russa, is located in the so-called Ilmen Lake Valley, which forms the local drainage base for surface and groundwater runoff. The watershed area of Ilmen Lake reaches about 67,300 km². Geologically, this area belongs to the north-western part of the Russian Platform which is composed of Archean crystalline basement (granites and gneisses) covered by thick sedimentary formations from Proterozoic to Devonian and Quaternary ages. The crystalline basement in the vicinity of Staraya Russa was found at depth range between 920 and 964 m (Fig. 2). Geological profile in the vicinity of Staraya Russa is quite well recognized by drillings and large scale groundwater prospecting conducted during the last decades (Fig. 2).

Hydrogeological settings in the study area are complex due to occurrence of several confined aquifers of variable thickness with local hydraulic contacts (Fig. 2). The main reservoir of mineral waters for the spa occurs in the Devonian formations. The regional tectonic dislocations continuing from crystalline basement as well a local fault zones or semipermeable strata play the crucial role in formation of hydraulic contacts with waters in different aquifers (Vinoograd 2004; Kuklin and Shklovsky 2008).

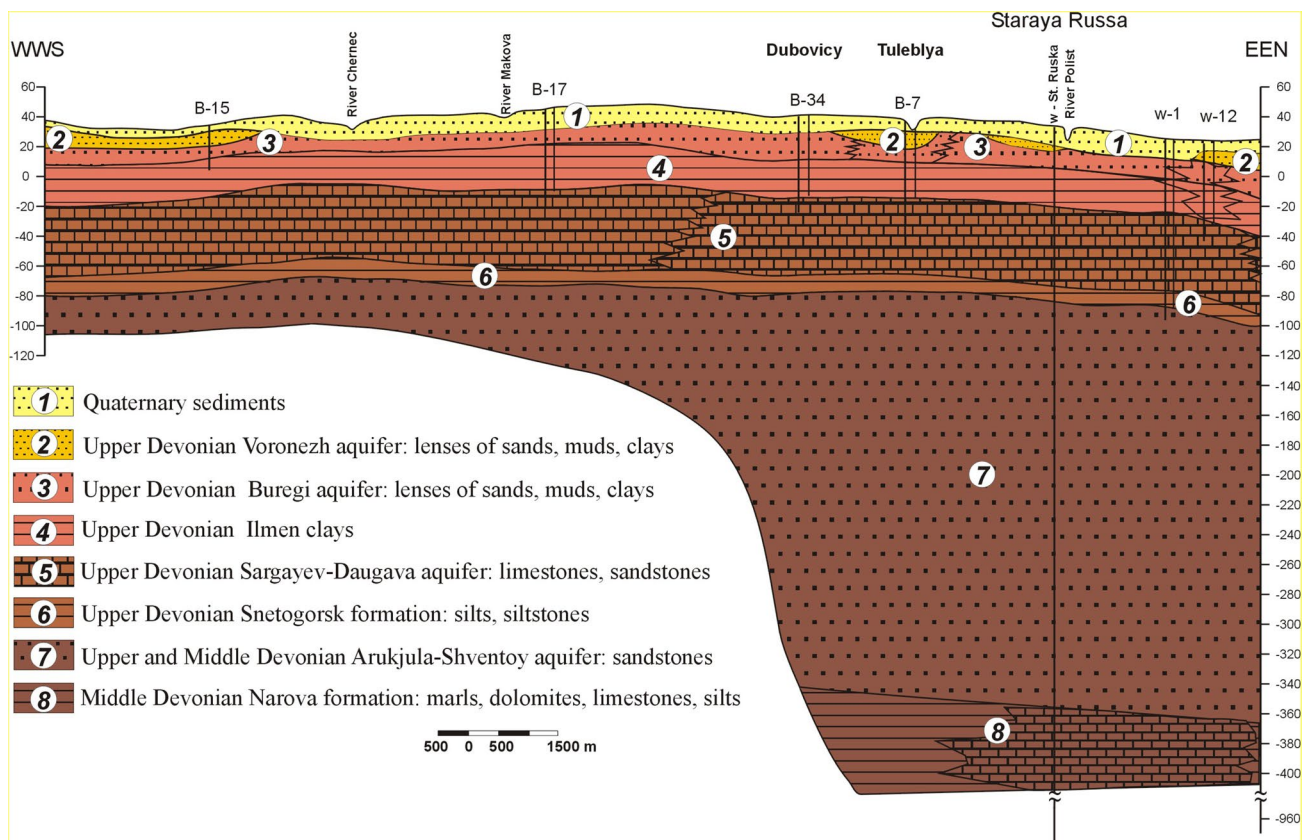


Fig. 2 Schematic geological cross section in the vicinity of Staraya Russa (after Kuklin and Shklovsky 2008)

The shallowest aquifer occurs in the Quaternary deposits of variable thickness (Fig. 2). Usually, groundwaters form discontinuous horizons connected with lenses of more permeable sediments. The highest water capacities, from 0.02 to 1.0 dm³/s, occur in fluvio-glacial and glaciolacustrine deposits of 2–5 m thick. Groundwater in permeable quaternary sediments is fresh and is formed by direct local infiltration of atmospheric precipitation. Bicarbonates, sodium, and calcium are dominant chemical compounds dissolved in these waters.

Below the Quaternary deposits, the Devonian formations occur, where several aquifers are distinguished.

The Voronezh aquifer (D_{3vr}) consists of thin layers and lenses of Upper Devonian sands formed between impermeable or low-permeable sediments dominated by muds and clays. The thickness of sands varies from 0.6 to 2.8 m and groundwaters form locally confined, discontinuous horizons (Fig. 2). The specific capacities of wells are very low and do not exceed 0.008 dm³/s. The Voronezh aquifer is practically unused due to low water capacity and discontinuous character.

The Upper Devonian-fractured dolomitic limestone of 12–16 m thick is the principal water-bearing unit of the Buregi aquifer (D_{3br}). In the vicinity of Staraya Russa, the Buregi aquifer is found at depths from 5 to 24 m. The limestone formation is heterogeneous and hydraulic properties of the aquifer change spatially. The resources of groundwater concentrate along preferred zones of fracture openings or deep tectonic dislocations. The groundwater forms confined aquifer with piezometric pressures varying from 3 to 30 m; the piezometric level decreases to north-west, in direction of the lake Ilmen, which is the main local drainage zone. In the vicinity of Staraya Russa, the specific capacities of wells discharging waters from Buregi aquifer reach 1–10 dm³/s, in average about 3–5 dm³/s (Kuklin and Shklovsky 2008).

Generally, the total dissolved solids (TDS) of the Buregi aquifer waters vary from about 300 to 700 mg/dm³ and they are the main reservoir of drinking water for the town of Staraya Russa and its suburbs. However, within the area of Staraya Russa spa, the ascension of saline waters from deeper layers into the Buregi aquifer has been documented. The influx of saline waters from strongly confined Arukjula–Shventoy aquifer occurs due to local geological settings (i.e. fault zone and fissured semipermeable limestones) as well as due to abandoned old boreholes and improperly insulated wells. This results in formation of specific “cone” of salinity which extends from the spa area to north-west to the lake Ilmen according to groundwater flow direction (Vinograd 2004; Kuklin and Shklovsky 2008). The mineralization of water

decreases along the flow path from the ascension zone in the spa to a local drainage base. The Buregi aquifer is separated from the deeper located Sargayev–Daugava (D_{3sr–dg}) aquifer complex by impermeable layer of Upper Devonian Ilmen clays of 18–20 m thick.

The Sargayev–Daugava (D_{3sr–dg}) aquifer complex is formed by the Upper Devonian slightly fractured limestones, rarely sandstones and marls, interbedded by thin layers of clays. The thickness of the whole formation reaches 45–55 m. The groundwater form confined aquifer with piezometric surface reaching elevations from about 0.6–14.0 m above land surface. Generally, the piezometric pressures rise to the south-west of Staraya Russa and decrease to the north-east, to the Ilmen Lake. The specific capacities of wells are usually in the range of 0.02–0.03 dm³/s, which indicates that the groundwater resources are small. In the vicinity of Staraya Russa, the TDS of water in the Sargayev–Daugava artesian aquifer varies from 2 to 10 g/dm³. The waters from this aquifer are used by the spa for curative drinking purpose. They are discharged by means of two wells: w-11 and w-12.

The aquifer is underlain by the low permeable Snetogorsk formation (D_{3sn}) composed mainly by silts and siltstones of thickness around 5–9 m.

In the vicinity of Staraya Russa hydraulic contacts are possible between the Sargayev–Daugava (D_{3sr–dg}) aquifer and the deeper Arukjula–Shventoy (D_{2ar–D_{3sv}}) aquifer. It is very likely that the ascension of highly mineralized waters from the Arukjula–Shventoy aquifer occurs due to significant hydraulic pressure advantage in the deeper aquifer.

The Arukjula–Shventoy (D_{2ar–D_{3sv}}) aquifer occurs in the red clayey sandstones of Upper and Middle Devonian age. The groundwaters form confined aquifer with potentiometric surface stabilized at 14–16 m above land surface, and decreases to the north-east to Lake Ilmen. The water resources in this aquifer are quite high: specific capacities of wells reach 100 dm³/s. The Arukjula–Shventoy aquifer is the main reservoir of mineral waters used by Staraya Russa spa for curative purposes. The average mineralization of water is in the range of 14–16 g/dm³, and reaches 19–20 g/dm³ in the vicinity of Staraya Russa. The Arukjula–Shventoy aquifer is underlain by the Middle Devonian Narova formation (D_{2nr}) composed of low fractured and low permeable marls, dolomites, limestone, and silts intercalated by small lenses of sands and sandstones. The thickness of the Narova formation reaches 20–25 m. This formation is an aquitard between the Arukjula–Shventoy aquifer and the Ordovician aquifer complex composed of well-fractured and permeable limestones and dolomites. The Ordovician aquifer in the Leningrad Artesian Basin has variable thickness from 5 to 130 m: the thickness of the carbonates increases eastwards and its fracturing decreases with depth.

Groundwater sampling and analysis

Samples of mineral waters were collected from ten intakes (seven wells and three springs) belonging to Staraya Russa spa. Eight wells extract water from Arukjula–Shventoy aquifer and only two from Sargayev–Daugava aquifer. Water samples for chemical analysis were filtered through 0.45- μm syringe filters and collected in polyethylene bottles of 150-mL capacity for anions, and 30 mL for cations; cationic samples were pre-acidified by 4% HNO_3 . A HPLC (high-performance liquid chromatography) method was applied for anion analysis and ICP-AES (inductively coupled plasma absorption emission spectrometry) method for cation analysis. Uncertainties in the determination of major ions, as reported by the laboratory, were in the range 5–10%. The chemical analyses were performed in the Institute of Environmental Protection in Warsaw, Poland. Field measurements of basic physicochemical water quality parameters such as pH, EC (electrical conductivity), ORP (oxygen/reduction potential), and temperature (T) were performed using portable multimeters Hach-Lange® HQ40D equipped with Intellical™ pH, EC and ORP electrodes with temperature sensor. The parameters such as EC and ORP were used to determine if formation-quality water is available for the sample collection (Nielsen and Nielsen 2007).

Water samples for stable isotopes of oxygen and hydrogen composition were collected to 30-mL amber-glass bottles and tightly sealed. The standard mass spectrometric techniques were applied for determination of isotopic composition of water, namely: (1) water– CO_2 gas equilibration using ThermoFisher Scientific's Gas Bench II system with online continuous flow $^{18}\text{O}/^{16}\text{O}$ isotope ratio determination on evolved CO_2 gas, and (2) water reduction on hot chromium using automated H-device system (by ThermoFisher Scientific) that enables dynamic water reduction on hot chromium and $^2\text{H}/^1\text{H}$ ratio determination in released H_2 gas. The results of analyses were reported using δ notation with respect to VSMOW international standard (Gehre et al. 1996, 2004; de Groot 2004).

The results of isotopic analyses were reported using δ notation as permil (‰) deviation from VSMOW international standard (Eq. 1):

$$\delta_{\text{sample}}[\text{‰}] = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000, \quad (1)$$

where R means the isotope ratio in the sample and in the internationally accepted reference standard. Measurement precision, based on the long-term repeated measurements of international reference materials was $\pm 0.1\text{‰}$ and $\pm 1.0\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The analyses were made at the Institute of Geological Sciences of Polish Academy of

Sciences (ING PAN) in Warsaw, Poland. The O and H isotopic compositions of studied water are shown in Table 3.

Water samples for stable isotopes of sulfur (ratio $^{34}\text{S}/^{32}\text{S}$) and oxygen (ratio $^{18}\text{O}/^{16}\text{O}$) composition of dissolved sulfates were collected in HDPE bottles of 1 L or 2 L volumes depending on SO_4^{2-} concentration which was determined in the field using portable spectrophotometer Hach® DR890. The water samples were acidified to pH 2–3 and appropriate amount of 10% BaCl solution was added to precipitate all dissolved sulfates as BaSO_4 (Carmody et al. 1998). The method based on the BaSO_4 reduction with graphite to CO_2 was applied for determination of $^{18}\text{O}/^{16}\text{O}$ ratio of sulfates (Mizutani 1971; Halas et al. 2007); for determination of $^{34}\text{S}/^{32}\text{S}$ ratio, the method of BaSO_4 conversion to SO_2 in 850 °C was applied (Halas and Szaran 2004). The results of analyses were reported using δ notation: $\delta^{18}\text{O}$ with respect to VSMOW, and $\delta^{34}\text{S}$ with respect to VCDT. Normalization of measured data was performed according to the international standards, namely: NBS-127 ($\delta^{34}\text{S} = +20.3\text{‰}$ VCDT, $\delta^{18}\text{O} = +9.3\text{‰}$ VSMOW) and IAEA-SO6 ($\delta^{34}\text{S} = -34.1\text{‰}$ VCDT, $\delta^{18}\text{O} = -11.35\text{‰}$ VSMOW). The precision of the measurements was $\pm 0.1\text{‰}$ for both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$. The analyses of the isotopic composition of sulfates were performed in the Laboratory of Mass Spectrometry at the Institute of Physics UMCS, Lublin, Poland. Isotopic compositions of dissolved sulfates are presented in Table 3.

The PHREEQC was used to calculate saturation indices (SI) for selected minerals.

Results and discussion

Chemical composition of studied waters

Chemical composition of mineral waters discharged in Staraya Russa spa belongs to four hydrochemical types (Table 1). The waters with the highest TDS are of Cl–Na and Cl–Na–Ca types and occur in the Arukjula–Shventoy ($\text{D}_{2\text{ar}}\text{--}\text{D}_{3\text{sv}}$) aquifer which is the main reservoir of mineral water for the spa. These waters are extracted from wide range of depths by means of five wells: w-1, w-3, w-6, w-7, and w-9 (Fig. 1). All waters from this aquifer, except wells w-6 and w-7, are utilized for bathing and balneological treatment (not for drinking purposes). The well w-9 is the main supply of highly mineralized water for the spa and is used continuously; wells w-6 and w-7, which are located outside the spa, are constantly discharged to maintain (or lower) the hydraulic pressure of mineral water in the Arukjula–Shventoy ($\text{D}_{2\text{ar}}\text{--}\text{D}_{3\text{sv}}$) aquifer to avoid the additional influx of highly mineralized waters into shallow aquifers within the Staraya Russa spa. The values of the total dissolved solids (TDS) vary from 16.4 to 19.2 g/dm^3 , which correspond with variation of electrical conductivity (EC) in the range

29.8–32.1 mS/cm. According to classification proposed by Davis (1964), which is based on the TDS values, these waters belong to saline waters. The pH values in the range of 6.5–7.8 show rather neutral character of these waters. The redox potential (Eh) in the range from 132 to 167 mV reveals moderately oxidizing conditions in the aquifer.

The same type of Cl–Na–Ca saline waters is discharged by means of three springs (w-2, w-4, and w-8, see Fig. 1) from the Upper Devonian Buregi aquifer (D₃br). Physico-chemical properties as well as the O and H isotopic composition (see Table 2) of these waters are identical with those of mineral waters from Arukjula–Shventoy aquifer, which means that groundwaters originate from the same reservoir. This fact corroborates previous hydrogeological observations of the extensive influx of saline waters from deeper, strongly confined Arukjula–Shventoy aquifer into the Buregi aquifer in the area of Staraya Russa spa. Such ascension of saline waters from deeper aquifer occurs first of all due to local geological settings connected with the fault zone and fissured semipermeable limestones where self-flowing springs are formed (Kuklin and Shklovsky 2008). On the other hand, there are also documented old, abandoned improperly insulated wells in the area of Staraya Russa spa and its vicinity, which additionally facilitate the ascension of saline waters into fresh water aquifers.

Waters of Cl–Na–Ca–Mg and Cl–Mg–Ca types are extracted from the Upper Devonian Sargayev–Daugava (D₃sr–dg) aquifer by means of two wells w-11 and w-12 from depths of 68.3 and 78.4 m, respectively (Table 1). These waters with the TDS values around 3.0 and 5.9 g/dm³ belong to brackish waters (Davis 1964) and, on average, are about four times less mineralized in relation to waters of

Arukjula–Shventoy aquifer. Taking into account the entire ionic structure, a characteristic feature of mineral waters from Sargayev–Daugava aquifer is the depletion in alkali metals (Na and K) and enrichment in divalent alkaline earth metals, first of all Ca (Fig. 3).

As can be seen on Piper diagram, there is a clear difference between the chemical composition of waters in both aquifers, especially in the structure of cations content; mineral waters of Sargayev–Daugava aquifer are located in the zone of mixed waters between bicarbonate–calcium fresh waters and chloride–sodium saline waters of Arukjula–Shventoy aquifer. This suggests that formation of brackish waters of Sargayev–Daugava aquifer might be connected with some dilution of saline waters; some variations of divalent cations and discrepancy from the straight two-component mixing line probably reflects water interaction with aquifer host rocks additionally affecting the chemical composition of mineral waters.

Shallow groundwaters and surface waters in the area of Staraya Russa are mainly of HCO₃–Ca–Mg type. They are represented in our study by waters from rivers Polist and Porusia which were sampled for comparison to mineral waters. Their TDS varies from 143.5 to 160.9 mg/L (Fig. 3).

Ionic ratios and the origin of major compounds dissolved in mineral waters

An analysis of selected ionic ratios has been performed to better understand the origin and formation of chemical composition of studied mineral waters and to identify the sources of the major constituents dissolved in water. The ionic ratio interpretation method is widely applied

Table 2 Selected ionic ratios for mineral water of Staraya Russa spa

Intake	Aquifer	$r \frac{Na^+ + K^+}{Cl^-}$	$w \frac{Br^- \cdot 1000}{Cl^-}$	$m \frac{HCO_3^-}{SiO_2}$	$m \frac{SiO_2}{Na^+ + K^+ - Cl^-}$	$r \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$	$r \frac{Ca^{2+}}{SO_4^{2-}}$	$r \frac{SO_4^{2-} \cdot 100}{Cl^-}$
Well-11	D ₃ sr–dg	0.43	4.7	32.8	<0.00	0.47	4.43	8.0
Well-12		0.24	6.5	65.7	<0.00	0.58	6.00	6.3
Spring-2	D ₂ ar–D ₃ sv	0.78	3.7	17.7	<0.00	0.36	2.21	10.4
Spring-4		0.81	3.8	17.9	<0.00	0.36	2.39	10.6
Spring-8		0.79	3.8	17.7	<0.00	0.36	2.45	10.5
Artesian well-1		0.78	3.7	18.0	<0.00	0.37	2.19	10.6
Artesian well-3		0.73	3.8	19.7	<0.00	0.37	2.21	9.9
Artesian well-6		0.82	3.9	18.3	<0.00	0.35	2.41	10.7
Artesian well-7		0.79	4.0	17.7	<0.00	0.36	2.48	10.9
Artesian well-9		0.73	3.6	18.0	<0.00	0.36	2.12	9.7
River Polist		1.00		18.2	110.951	0.24	–	–
River Porusia		1.09		15.8	3.440	0.27	–	–
Seawater		0.87	3.53	21.8	<0.00	0.84	0.36	10.5

River waters and seawater are presented for reference

Waters extracted by springs in Buregi aquifer represent ascension waters from Arukjula–Shventoy aquifer. Concentrations expressed in meq/dm³—*r*, mmol/dm³—*m*, mg/L—*w*. Values for *w* [Br × 1000/Cl] ratio after Kuklin and Shklovsky (2008)

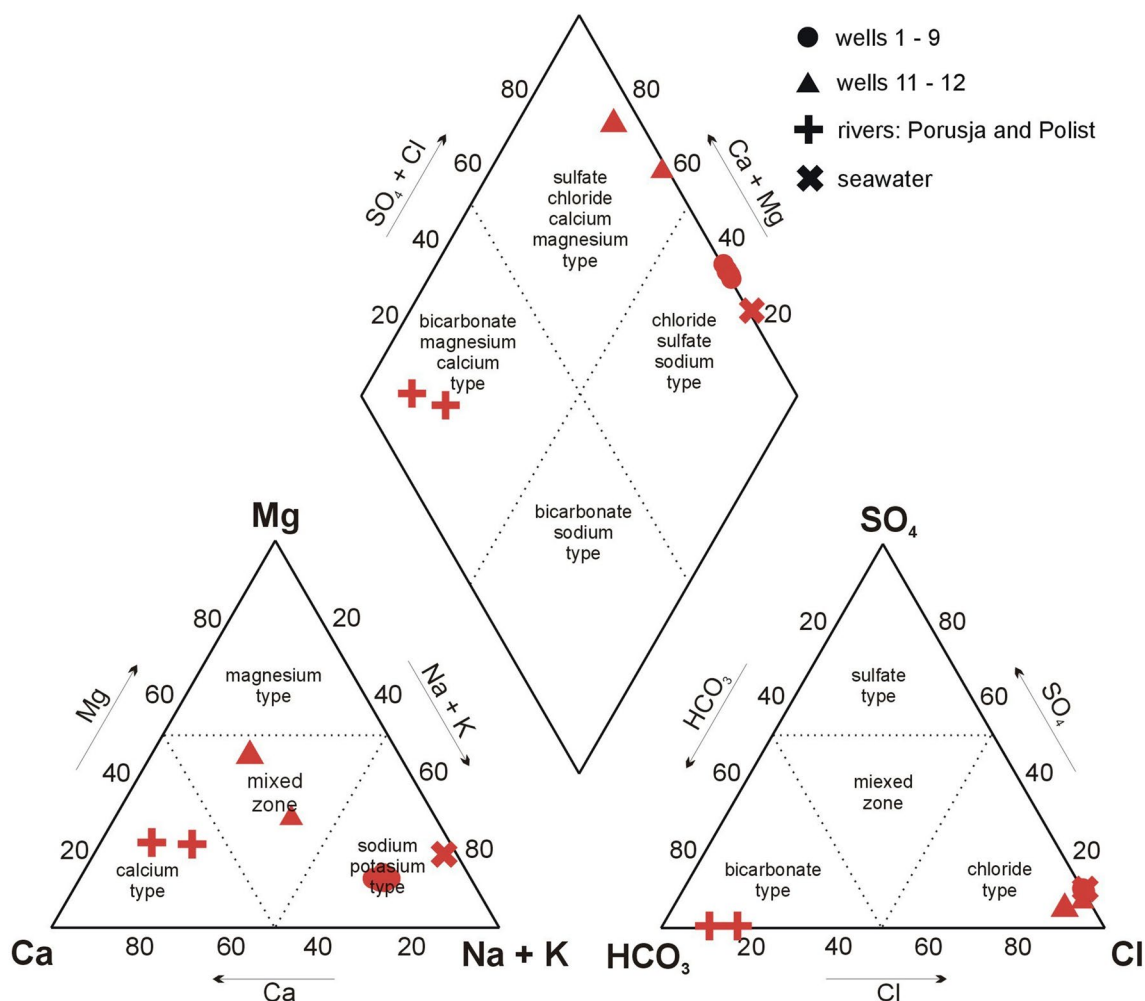


Fig. 3 Piper diagram showing chemical composition of groundwater in the Staraya Russa spa. The average composition of seawater and waters from Polist and Porusja Rivers were plotted for reference

to hydrogeochemical characterization of groundwater, to source rock deduction or mineral deposits prospecting (e.g. Hounslow 1995; Appelo and Postma 1996; Porowski 2001, 2006, 2015; Żaczek and Porowski 2017). The ratios of major ions first of all provide information about the type and character of water–rock interaction and help to distinguish between weathering of major source rocks like evaporites, carbonates, and silicates (Yingjie et al. 2016). Table 2 shows the selected ionic ratios applied in this study.

Chloride and sodium ions dominate in chemical composition of mineral waters of the Staraya Russa spa. Chlorides are one of the most conservative constituents of groundwaters and high chloride–sodium mineralization may be acquired by water in two ways: (1) directly—through dissolution of evaporite deposits and (2) indirectly—through mixing with seawater or seawater-like end-member, e.g. post-salinar fluids, evaporated seawater, connate water (Carpenter

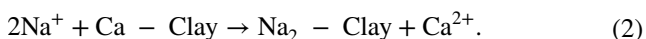
1978; Hem 1989; Hounslow 1995; Appelo and Postma 1996; Porowski 2001).

The r $[\text{Na}/\text{Cl}]$ ratio (r —expressed in meq/dm^3) can be used to identify the origin of chloride–sodium salinity in groundwater. The ratio that is typical for the average composition of the ocean water is around 0.87 (with assumption: $\text{Na}^+ = \text{Na}^+ + \text{K}^+$). It remains constant during simple dissolution of ocean water or its subaerial evaporation until halite starts to precipitate (Carpenter 1978). The values of this ratio close to 1.0 suggest that the chloride salinity originates first of all from dissolution of chloride evaporites, mainly halite. As can be seen from Table 2, mineral waters of the Arukjula–Shventoy aquifer reveal values of r $[(\text{Na}^+ + \text{K})/\text{Cl}^-]$ ratios between 0.73 and 0.82, which is very close to the values of this ratio typical of seawater—0.87. This suggests that the origin of Cl–Na salinity of waters in this horizon may be connected with admixture of seawater-like end-member. Presumably, this

end-member can be connate water–seawater-like fluids trapped in sediments in geological past.

The concentration of Br and Br/Cl ratio in these waters corroborate the seawater-like admixture. The main reservoirs of bromine are oceans and seas. During simple dilution or evaporation of seawater, the Br/Cl ratio remains constant around the typical value of 3.53 (i.e. for w [Br \times 1000/Cl], w —expressed in mg/L), until halite saturation is reached (Collins 1975; Carpenter 1978; Hounslow 1995). The values of this ratio for waters in Arukjula–Shventoy aquifer are in the range of 3.6–4.0 (Kuklin and Shklovsky 2008) which strongly suggest that studied saline water is oil-associated or originally was in contact with organic carbon-rich deposits, mainly of marine origin (Rittenhose 1967; Krasinceva 1968; Collins 1975).

On the other hand, the non-conservative behavior of Na^+ should be also taken into account. The Na^+ removal from water or incorporation into the water during different diagenetic or postdiagenetic processes can alter the Na/Cl ratio. Such processes can be for example, ionic exchange with clay minerals—the so-called natural softening (Na^+ incorporation into solution) or reverse softening (Na^+ removal from solution) or ultrafiltration through clay formations (Collins 1975; Hounslow 1995; Connolly et al. 1990). The mineral waters of the Sargayev–Daugava aquifer reveal much lower values of r [($\text{Na}^+ + \text{K}^+$)/ Cl^-] ratio in the range of 0.24–0.43 indicating considerable depletion in Na^+ . Presumably, the non-conservative behavior of alkali metals (i.e. Na^+ and K^+) during water–rock interaction is responsible for low Na/Cl ratio. The processes which are often responsible for alkali metal removal from the solution are known as reverse ion exchange or reverse softening and require the presence of clays with exchangeable calcium (e.g. usually montmorillonite) and a water higher in sodium than the clay-exchange equilibrium concentration (Hounslow 1995). The reverse softening can be written as follows:



Such process seems to be likely taking into account the fact that formation of brackish waters of Sargayev–Daugava aquifer may be connected with mixing with saline waters of Arukjula–Shventoy aquifer.

The distribution of major ion concentration in studied waters presented with application of Stiff diagrams clearly shows that waters of Arukjula–Shventoy aquifer are very similar to seawater, ionic ratios are not changed considerably, only dilution process have taken place (Fig. 4). On the other hand, the chemical composition of waters of Sargayev–Daugava aquifer is changed, especially with respect to cations and is similar with waters occurring in shale rich

deposits (Hounslow 1995) (Fig. 4). Chemical composition of water from rivers is typical for fresh water in contact with carbonates—limestones and dolomites.

Simple bicarbonate–silica ratio m [$\text{HCO}_3^-/\text{SiO}_2$] expressed in mmol/dm^3 , can be used to distinguish between carbonate and silicate weathering (Hounslow 1995). Bicarbonate is formed when CO_2 and water react with various minerals in the process of acid hydrolysis. Carbonates dissolve without releasing silica, whereas dissolution of silicates may release considerable amount of silica, e.g. dissolution of albite. The m [$\text{HCO}_3^-/\text{SiO}_2$] ratio greater than 10 is usually considered as the indicator of carbonate dissolution and less than 5—as the indicator of silicate dissolution. All mineral waters in Staraya Russa spa reveal the m [$\text{HCO}_3^-/\text{SiO}_2$] ratio greater than 10, namely from 17.7 to 22 in saline waters of Arukjula–Shventoy aquifer, and from 32.8 to 65.7 in brackish waters of Sargayev–Daugava aquifer (Table 2). This strongly suggests that dissolution of carbonates is a possible process of Ca and/or Mg incorporation into solution. In low temperature systems, the carbonates, mainly calcite, are known to be the most liable to dissolution and subsequent recrystallization. Moreover, as can be seen in Table 2, saline waters of Arukjula–Shventoy aquifer reveal this ratio very close to that in seawater—21.8.

The ratio r [$\text{Mg}^{2+}/(\text{Ca}^{2+} + \text{Mg}^{2+})$], expressed in meq/dm^3 , helps to understand which carbonate minerals undergo dissolution to greater extent. When m [$\text{HCO}_3^-/\text{SiO}_2$] $>$ 10, the values of the r [$\text{Mg}^{2+}/(\text{Ca}^{2+} + \text{Mg}^{2+})$] ratio around 0.5 indicate dolomite weathering, below 0.5—limestone dissolution, and above 0.5—dolomite dissolution or calcite precipitation (Table 2). Mineral waters of the Arukjula–Shventoy aquifer reveal this ratio below 0.5, which strongly suggests that limestone dissolution is the main process of water–rock interaction and may be responsible for Ca^{2+} incorporation into the water. On the other hand, the mineral waters of the Sargayev–Daugava aquifer reveal values of this ratio around and slightly above 0.5, which shows that limestone and dolomite weathering or calcite precipitation may occur depending on local geochemical conditions in the aquifer. Limestones are dominant rocks in the Sargayev–Daugava aquifer, whereas the Arukjula–Shventoy aquifer is composed by sandstones of which limestone, dolomite, and silicate grains are bounded by carbonate cement.

The ratio r [$\text{Ca}^{2+}/\text{SO}_4^{2-}$], expressed in meq/dm^3 , allows preliminary identification of sulfate sources dissolved in groundwater. In favorable hydrogeological conditions (i.e. the absence of intensive carbonate dissolution), gypsum or anhydrite dissolution is indicated by relatively equal concentrations of Ca^{2+} and SO_4^{2-} in water, which gives a value of r [$\text{Ca}^{2+}/\text{SO}_4^{2-}$] ratio around 1.0. The ratio is less than 1 when the Ca^{2+} concentration is clearly lower than SO_4^{2-} , which usually indicates pyrite oxidation or Ca^{2+} removal from solution in the process of calcite precipitation or ion

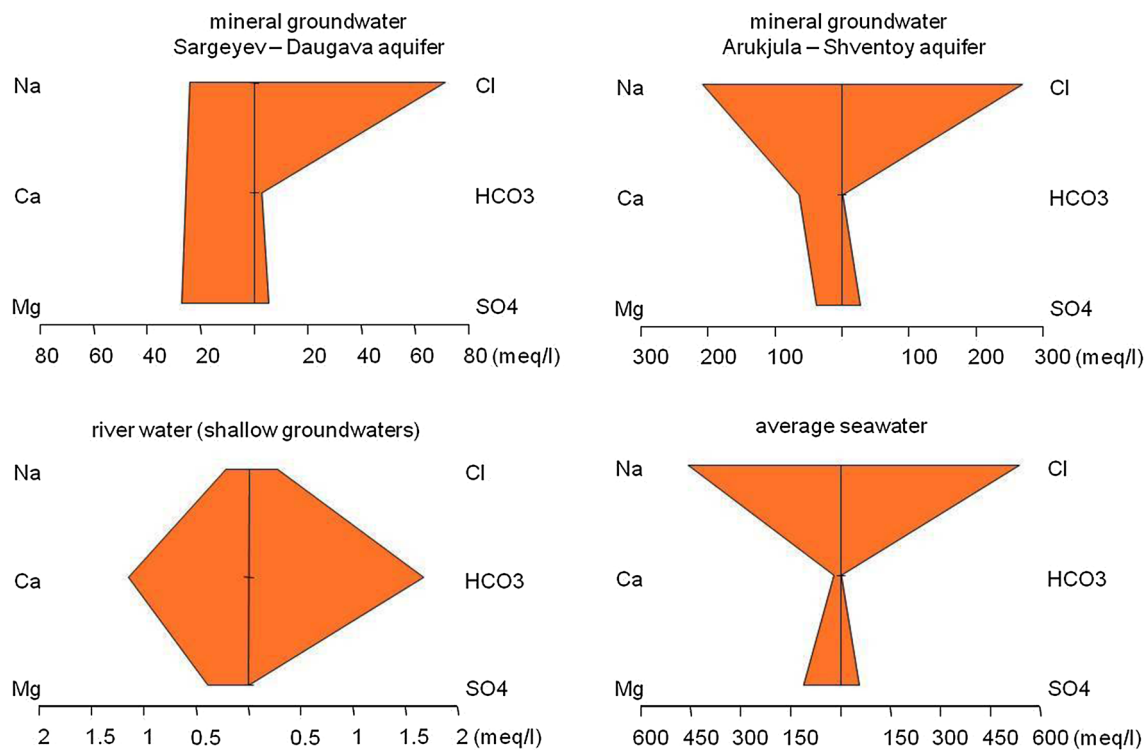


Fig. 4 Stiff diagrams showing average chemical composition of mineral waters in Staraya Russa spa. The average composition of seawater and river waters from Polist and Porusia are presented for reference

Table 3 Isotopic composition of mineral waters and dissolved sulfates

Mineral water intake	<i>S</i>	Hydrochemical type	TDS [mg/dm ³]	$\delta^{18}\text{O H}_2\text{O}$ [‰ vs VSMOW]	$\delta^2\text{H H}_2\text{O}$ [‰ vs VSMOW]	$\delta^{18}\text{O SO}_4^{2-}$ [‰ vs VSMOW]	$\delta^{34}\text{S SO}_4^{2-}$ [‰ vs VCDT]
Spring-2	D ₃ br	Cl–Na–Ca	18,302.8	– 11.1	– 84.1	+ 13.6	+ 13.1
Spring-4	D ₃ br	Cl–Na–Ca	17,313.0	– 10.7	– 81.3	+ 13.0	+ 13.5
Spring-8	D ₃ br	Cl–Na–Ca	16,898.1	– 11.2	– 84.4	+ 12.7	+ 13.8
Well-11	D ₃ sr–dg	Cl–Na–Ca–Mg	5869.3	– 12.5	– 94.1	+ 13.2	+ 17.8
Well-12	D ₃ sr–dg	Cl–Mg–Ca	3039.1	– 12.9	– 93.0	+ 13.4	+ 19.8
Well-1	D ₂ ar–D ₃ sv	Cl–Na–Ca	17,855.8	– 11.1	– 82.0	+ 14.7	+ 13.1
Well-3	D ₂ ar–D ₃ sv	Cl–Na–Ca	18,698.6	– 11.1	– 84.9	+ 13.2	+ 13.5
Well-6	D ₂ ar–D ₃ sv	Cl–Na–Ca	16,397.1	– 11.3	– 82.9	+ 13.5	+ 13.8
Well-7	D ₂ ar–D ₃ sv	Cl–Na–Ca	16,416.3	– 11.3	– 85.0	+ 12.8	+ 13.7
Well-9	D ₂ ar–D ₃ sv	Cl–Na	19,192.0	– 11.0	– 84.7	+ 13.3	+ 13.5
River Polist		HCO ₃ –Ca–Mg	143.5	– 7.6	– 58.1	<i>nd</i>	<i>nd</i>
River Porusia		HCO ₃ –Ca–Mg	155.7	– 8.3	– 59.7	<i>nd</i>	<i>nd</i>

TDS total dissolved solids, *nd* not determined due to concentration of SO_4^{2-} below the detection limit, *S* stratigraphy of aquifer rocks

exchange (i.e. natural softening). However, all groundwaters extracted in Staraya Russa spa have this ratio greater than 1.0 (i.e. meq Ca^{2+} exceeds that of SO_4^{2-} , Table 2), which

indicates an excess of Ca^{2+} ions and their additional source other than gypsum, presumably limestone, calcite and/or silicates.

The ionic ratio of m [$\text{SiO}_2/(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$], expressed in mmol/dm^3 , is considered to reflect ion exchange between water and clay minerals or the hydrolysis of alkali feldspars, mainly albite (Hem 1989; Hounslow 1995). In principle, this index shows the ratio of the so-called non-halite sodium to SiO_2 and helps to identify the sources of silica and sodium dissolved in the groundwater. All studied mineral waters show no sodium excess that could be considered as additional non-halite sodium. The depletion of alkali metal content may be connected with ion exchange reactions with clay minerals, especially reverse softening (Hounslow 1995).

The r [$(\text{SO}_4^{2-} \times 100)/\text{Cl}^-$], expressed in meq/dm^3 , usually indicates the character of the geologic environment of groundwater occurrence (Macioszczyk 1987; Hounslow 1995). Low values of this ratio, below 1.0–10.0 indicate a strongly reducing environment. Values within the range of several tens and more are characteristic for shallow meteoric waters in the active exchange zone in an oxidizing environment. The mineral waters in Staraya Russa spa reveal values of this ratio around 10 in saline waters of Arukjula–Shventoy aquifer (which is similar to seawater), and slightly less than 10 in brackish waters of Sargayev–Daugava aquifer, which seems to correspond with Eh measured in the field.

Stable O and H isotopic composition of mineral waters

The results of isotopic analysis of mineral waters of Staraya Russa spa are shown in Table 3.

The fundamental relationship between hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotopic composition of studied waters is shown in Fig. 5. All mineral waters of Staraya Russa spa are located along the Local Meteoric Water Line (LMWL) which is almost parallel to the Global Meteoric Water Line (GMWL): it has very similar slope of 7.86 but different deuterium excess factor (d) which results in its displacement to the right from the GMWL (Fig. 5).

The LMWL was derived from analyses of about 187 samples of atmospheric precipitation monitored in the research station of the University of Saint Petersburg in Peterhoff in the years 2012–2017. The observed isotopic composition of atmospheric precipitation revealed wide range of natural variations: from the most depleted values observed for snow, namely: $\delta^{18}\text{O} = -24.3\text{‰}$ and $\delta^2\text{H} = -183\text{‰}$, to the most enriched values observed for long lasting rainout in warm season: $\delta^{18}\text{O} = -6.1\text{‰}$ and $\delta^2\text{H} = -32\text{‰}$ (Voroniuk et al. 2016; Vinograd et al. 2019). The average weighted annual isotopic composition of atmospheric precipitation was estimated to have $\delta^{18}\text{O} = -9.7\text{‰}$ and $\delta^2\text{H} = -75\text{‰}$. As can be seen, the isotopic composition of mineral waters in Staraya

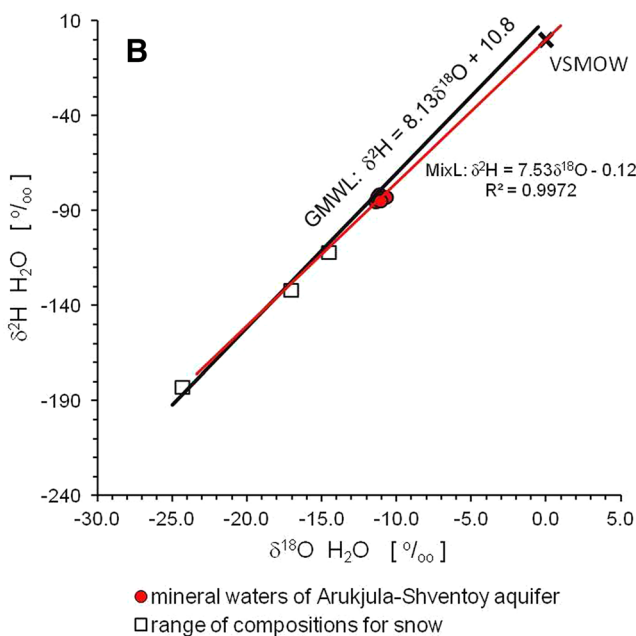
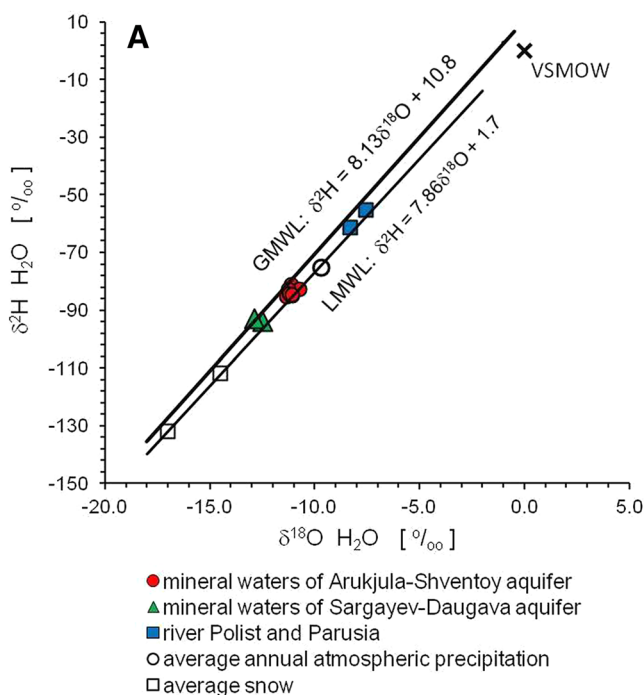


Fig. 5 The $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ relationship in mineral waters of Staraya Russa spa. Global Meteoric Water Line (GMWL) after Rozanski et al. (1993); Local Meteoric Water Line (LMWL) after Vinograd

et al. (2019), *MixL* potential mixing line between meteoric waters and seawater; average composition of ocean water (VSMOW) is plotted for reference. For more explanation see the text

Russa is within values typical for waters of atmospheric precipitation encountered in NW Russia and the region of the Leningrad Artesian Basin.

Position of mineral waters on the LMWL suggests their meteoric origin. The meteoric waters are defined as surface waters or groundwaters originating from atmospheric precipitation and taking part in the modern hydrological cycle. Such types of waters nowadays constitute the vast majority of fresh and potable water reservoirs. Mineral waters in Sargayev–Daugava and Arukjula–Shventoy aquifers differ in isotopic composition which is reflected in different position on the LMWL (Fig. 5). Such difference reaches about 1.5–2.0‰ on $\delta^{18}\text{O}$ and, respectively, around 10‰ on $\delta^2\text{H}$. The isotopic composition of waters from both aquifers are depleted in heavy isotopes of ^{18}O and ^2H in relation to the mean weighted isotopic composition of annual precipitation in the region, i.e. $\delta^{18}\text{O} = -9.7\text{‰}$ and $\delta^2\text{H} = -75\text{‰}$ (Voroniuk et al. 2016; Vinograd et al. 2019). This can be connected with very big seasonal biases in recharge. Infiltration of snowmelt and cool spring rains in cold seasons, when evapotranspiration losses are low (no leaves and reduced vegetation), replenishes aquifers by isotopically depleted waters. If recharge rates are greater than at other seasons of the year, then the groundwater will have less content of the heavy isotopes ^{18}O and ^2H than the weighted mean annual precipitation (Clark and Fritz 1997; Voroniuk et al. 2016). The mineral waters of Sargayev–Daugava aquifer have the lightest isotopic composition: $\delta^{18}\text{O}$ varying in narrow range from -12.5 to -12.9‰ and $\delta^2\text{H}$ from -93 to -94‰ . Such isotopic shift towards the average isotopic composition of snow (i.e. $\delta^{18}\text{O} \approx -14.5$ to 17.0‰ and $\delta^2\text{H} \approx -112$ to -132‰) indicates that the origin of mineral waters is undoubtedly associated with the infiltration recharge in cold seasons including water from thawing of snow cover and cold spring and autumn rains. The cold season is usually defined as the period when an average day temperature is not exceeding $+5\text{ °C}$, and when the influence of evapotranspiration on the isotopic composition of water is negligible, as no leaves or vegetation occur (Voroniuk et al. 2016). In the area of Staraya Russa, the long-term monitoring of the air temperature shows that monthly mean temperature less than $+5\text{ °C}$ occurs during 7 months from October to April (Kuklin and Shklovsky 2008). The Upper Devonian water-bearing limestone formations occur under the Quaternary sediments and the prevailing groundwater recharge undoubtedly takes place in colder seasons, mainly during thawing of snow cover in spring (Kuklin and Shklovsky 2008; Vinograd et al. 2019).

The observed isotopic and chemical composition of mineral waters extracted in Staraya Russa spa suggests two variants of their origin and formation: (1) they are mainly meteoric waters which acquired their chemical composition exclusively throughout the interaction with rock

environment along the flow paths from recharge zones to discharge points, or (2) they are mixtures of modern meteoric waters and seawater-like connate waters remained in the sediment from geological past; this refers especially to saline waters of Arukjula–Shventoy aquifer. The brackish waters of Sargayev–Daugava aquifer may be a result of direct infiltration of various components of atmospheric precipitation (e.g., water from snow melt as dominant component) and subsequent water–rock interaction in underground geological environment. In such case, the water–rock interaction would be the main process responsible for the formation of chemical composition of mineral waters in this aquifer. However, in hydrogeological settings of the Staraya Russa area, it is more likely that mineral waters of Sargayev–Daugava aquifer are formed as a result of mixing between infiltration waters (i.e. prevailing snow melt component) and saline waters ascending from deeper Arukjula–Shventoy aquifer (Fig. 6). Such two-component mixing process is corroborated by (1) the actual chemical composition and mineralization of water in Sargayev–Daugava aquifer, and (2) the linear relationship between $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) values of mineral waters and the concentration of chlorides Cl^- , which is the most conservative chemical compound of groundwater (Fig. 6) Mixing between two distinct groundwater types can be quantified by simple linear relationship using $\delta^{18}\text{O}$ and/or $\delta^2\text{H}$ values and Cl^- concentrations. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are conservative in mixing relationships and can preserve the mixing ratios. In such relationship, the proportion of mixing for a given sample will relate directly to its position on the mixing line, according to:

$$\delta_{\text{mixture}} = f \times \delta_A + (1 - f) \times \delta_B, \quad (3)$$

where, δ_{mixture} , δ_A and δ_B refer to $\delta^{18}\text{O}$ or $\delta^2\text{H}$ of the mixture formed by mixing of particular fraction f of water A and fraction $(1 - f)$ of water B (Fig. 6).

The application of two-component mixing model, using $\delta^{18}\text{O}$ isotopic composition of two end-members, shows that the portion of the saline water from Arukjula–Shventoy aquifer in the brackish waters of Sargayev–Daugava aquifer may reach values from around 0.2 (well-12) to 0.4 (well-11). The assumptions made for calculations are following: (1) the mean isotopic composition of mineral water of Arukjula–Shventoy aquifer has $\delta^{18}\text{O} = -11.1\text{‰}$ and $\delta^2\text{H} = -83.7\text{‰}$, and (2) the mean isotopic composition of the cold season local atmospheric precipitation recharging the Upper Devonian aquifer has $\delta^{18}\text{O} = -13.4\text{‰}$ and $\delta^2\text{H} = -100.0\text{‰}$ (values taken from mixing line near the intersection with x -axis on the plot Fig. 6).

The ascension of saline waters from Arukjula–Shventoy aquifer into the shallower aquifers are observed and documented in the area of Staraya Russa. As mentioned previously, the hydraulic contacts occur not only due to natural

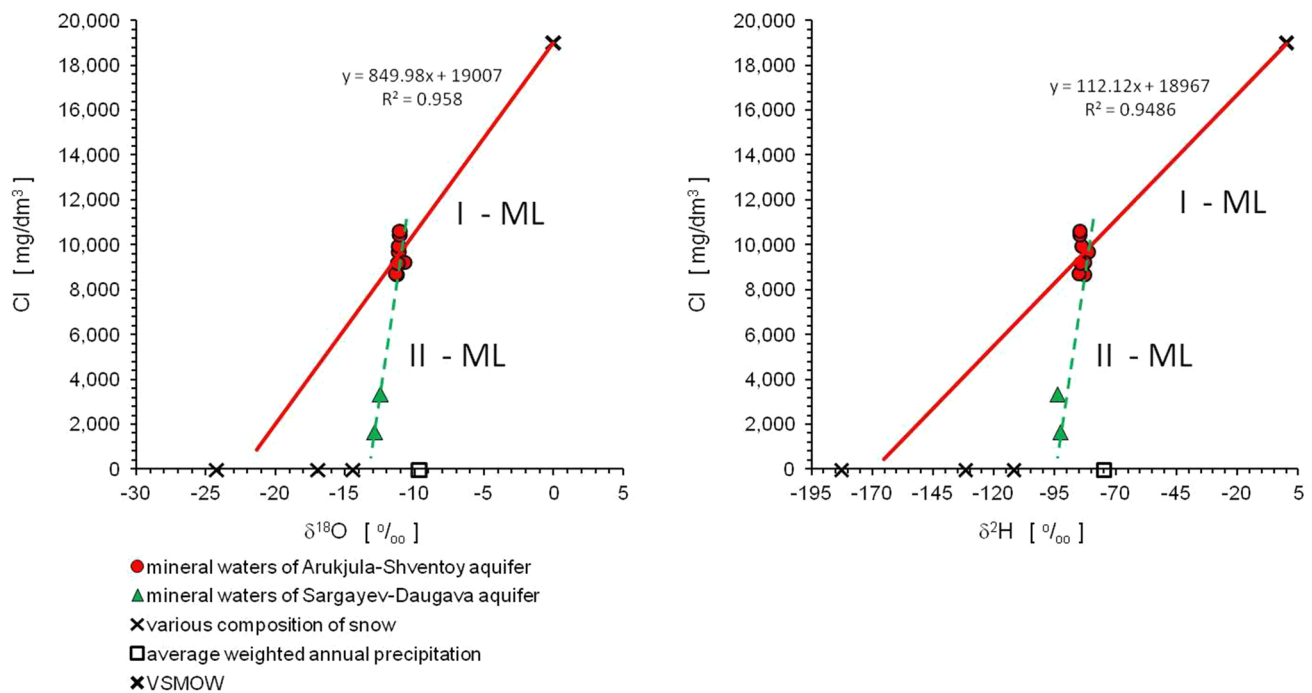


Fig. 6 Relationship between chloride [Cl^-] concentration and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in mineral waters from Staraya Russa spa. Straight mixing lines (ML) indicate possible two-component mixing trends: *I-ML* between connate seawater-like end-member and snow melt meteoric

waters recharging Arukjula–Shventoy aquifer, and *II-ML* between saline waters of Arukjula–Shventoy aquifer and meteoric waters recharging Sargayev–Daugava aquifer mainly in cold seasons. For more explanations see the text

tectonic and hydrogeological settings, but also due to drilling activity of man in the past which resulted in the appearance of abandoned, improperly insulated artesian wells. The Arukjula–Shventoy aquifer forms regional reservoir of saline (highly mineralized) groundwater which is recharged mainly in outcrops located far from discharge zone at the southern, south-eastern (Valday hills) and north-western parts of the Leningrad Artesian Basin. The hydraulic pressures in the vicinity of Staraya Russa (local discharge zone) are the highest among all studied aquifers: they reach about +20 to +22 m a.g.s. (above ground surface), which is about 4–5 m more than the hydraulic pressures found in Sargayev–Daugava aquifer, and several meters more than in the Buregi aquifer. The long groundwater flow paths allows better mixing of water in an aquifer profile, the attenuation of seasonal isotopic variation encountered in infiltration water, and the dissolution of more chemical compounds. As can be seen on Fig. 5b, the isotopic composition of saline waters locates them also directly along a line of possible two-component mixing between snow melt waters and seawater-like end-member of isotopic composition close to VSMOW: the slope of the mixing line of 7.53 is very close to that of the LMWL for this region (Fig. 5a). Again, the application of the simple two-component mixing model (see Eq. 3), using the $\delta^{18}\text{O}$ (or $\delta^2\text{H}$) isotopic composition of the end-members, allows to explain the formation of chemical and isotopic composition

of saline waters of Arukjula–Shventoy aquifer (Fig. 6). The mean isotopic composition of the Arukjula–Shventoy saline waters (i.e. $\delta^{18}\text{O} = -11.1\text{‰}$, $\delta^2\text{H} = -83.7\text{‰}$, and concentration of $\text{Cl}^- = 9.6 \text{ g/dm}^3$) can be obtained by mixing of approximately equal (0.5) portions of snow melt water of $\delta^{18}\text{O} = -21.7\text{‰}$ and Cl^- content of around 10 mg/dm^3 , with seawater-like end-member of assumed values of $\delta^{18}\text{O} = -0.5\text{‰}$ and Cl^- content of 19.0 g/dm^3 —similar to modern ocean water (Fig. 6). The calculations show that saline waters of Arukjula–Shventoy aquifer may contain admixture of connate seawater-like component, which is corroborated also by ionic ratios shown above in this section. The fraction of this potential seawater-like end-member in saline waters of Arukjula–Shventoy aquifer depends on its isotopic composition and concentration of chlorides, which may be slightly different from that assumed in our exemplary calculations:

O and S isotopic composition of dissolved sulfates

Dissolved sulfates (SO_4^{2-}) are the main species of sulfur in mineral waters discharged in Staraya Russa spa. The SO_4^{2-} belong to one of the major chemical compounds of groundwater and may be derived from various sources, such as atmospheric, pedospheric, lithospheric, and anthropogenic (Cook and Herczeg 2000). Various sources of

dissolved sulfates in groundwater can have a wide range of S and O isotopic compositions, i.e. expressed as $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values. The isotopic composition of dissolved sulfates measured in this study is presented in Table 3.

The isotopic composition of sulfates dissolved in groundwater is used first of all to identify the sulfate sources and biogeochemical processes controlling the distribution and isotopic transformation of sulfates in groundwater system that also helps to understand the origin of water and hydrogeochemical conditions in the aquifer.

The isotopic composition of groundwater sulfates is controlled first of all by (1) the isotopic composition of the primary and secondary sulfate sources and (2) the biogeochemical processes involving isotope exchange reactions (Cook and Herczeg 2000).

The local source of sulfate in groundwater can be estimated using the relationship between $\delta^{34}\text{S}$ values and the concentration of dissolved sulfates (Clark and Fritz 1997; Cook and Herczeg 2000; Knöller et al. 2004; Porowski 2014; Porowski et al. 2019). Plotting the $\delta^{34}\text{S}$ values of groundwater sulfate versus the inverse of sulfate concentration ($1/[\text{SO}_4^{2-}]$) for all mineral water samples yielded a straight line with very good correlation factor (R^2) of 0.89 and a y-axis intercept of $+12.8\text{‰}$ (Fig. 7a). The slope s of the line equals:

$$s = C_R \times (\delta^{34}\text{S}_R - \delta^{34}\text{S}_I), \quad (4)$$

where C_R refers to the concentration of the remaining (i.e., measured) sulfate, and δ_R and δ_I refer to the sulfur isotopic composition of the remaining (i.e., measured) and initial (i.e., source) sulfate, respectively. The y-axis intercept represents δ_I .

The y-axis intercept indicates the sulfur isotopic composition of the potential source of groundwater sulfates. Taking into account both aquifers separately, the y-axis intercept for sulfates of mineral waters of Sargayev–Daugava aquifer yielded a $\delta^{34}\text{S}_I$ value of $+16.5\text{‰}$ (Fig. 7b). On the other hand, isotopic composition of sulfates (both $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$) in saline waters of Arukjula–Shventoy aquifer demonstrates significant stability (variation of $\delta^{34}\text{S}$ is less than 1‰) and homogeneity regardless of the depth and location of the intake. In such case, the observed $\delta^{34}\text{S}$ values in the range $+13.1$ to $+13.8\text{‰}$ should be assumed as the sulfur isotopic composition of the source sulfates in the aquifer (Fig. 6b). Such values are closed to $+12.8\text{‰}$ obtained as the $\delta^{34}\text{S}_I$ of potential sulfate source for mixed waters of both aquifers considered as one hydrogeological system. Nevertheless, the range of estimated $\delta^{34}\text{S}_I$ values of source sulfates (i.e. from around $+13$ to 16.5‰) in mineral waters of both aquifers and the high concentration of dissolved SO_4^{2-} (i.e. $1.3\text{--}1.4 \text{ g/dm}^3$) indicate that the dominant sources of dissolved sulfate must be associated with the dissolution of

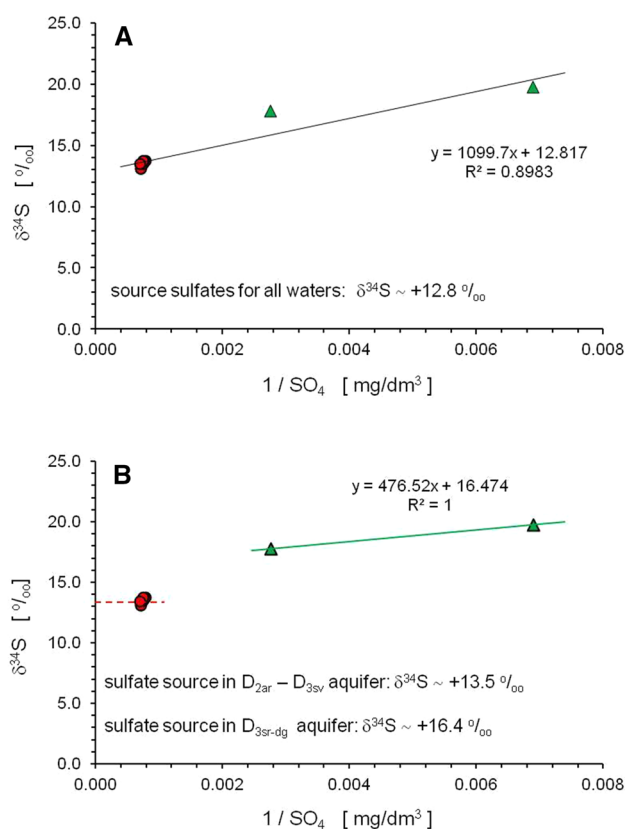


Fig. 7 The $\delta^{34}\text{S}$ values and concentrations of dissolved sulfates in mineral waters of Staraya Russa spa. For additional explanations, see the text

evaporitic sulfates of marine origin, mainly gypsum or anhydrite (i.e. lithogenic source). Saturation indices calculated based on our data show slight undersaturation with respect to gypsum, obtained SI are in the range from -0.18 to -0.23 . The isotopic composition of sulfates in marine evaporites deposited throughout the Earth's history varied and fluctuated considerably throughout the long-term trends; the maximum $\delta^{34}\text{S}$ values around $+35\text{‰}$ are characteristic for the Cambrian evaporites and the minimum values, less than $+10\text{‰}$, occur in the Permian. Modern marine sulfates have $\delta^{34}\text{S}$ values near $+21\text{‰}$. The respective $\delta^{18}\text{O}$ values of primary marine sulfate varied between $+20$ and $+7\text{‰}$ through the Earth's history with that of modern marine sulfate around $+9.5\text{‰}$ (Claypool et al. 1980; Krouse and Mayer 2000). The Sargayev–Daugava aquifer is composed mainly of Devonian carbonates, and the dissolution of associated evaporitic gypsum or anhydrite is very likely as primary source of dissolved sulfates with $\delta^{34}\text{S}_I$ value of $+16.5\text{‰}$ (Fig. 7). The dissolution of gypsum causes an increase in the sulfate concentration in groundwater, and occurs without measurable isotope fractionation, i.e., dissolved sulfates retain the original isotopic composition of gypsum (Clark and Fritz 1997; Krouse and Mayer 2000; Zuber 2007).

However, the observed $\delta^{34}\text{S}$ values of dissolved sulfates in waters of Sargayev–Daugava aquifer are at least about 1.3–3.3‰ higher than the predicted value of $\delta^{34}\text{S}_1$ of source sulfates, which suggests that the final isotopic composition of dissolved sulfates is controlled by additional sulfate sources and/or some overlapping geochemical processes. One of the most important processes responsible for the sulfur cycle in hydrogeological environments is the bacterial reduction of sulfates, which is characterized by considerable isotopic fractionation of sulfur and oxygen (Kaplan and Rittenberg 1964; Fritz et al. 1989; Rees 1973; Clark and Fritz 1997; Porowski 2014). During dissimilatory sulfate reduction, the heavy sulfur and oxygen isotopes are gradually accumulated in the residual sulfates, i.e., the residual aqueous sulfates are enriched in ^{34}S and ^{18}O isotopes relative to the original SO_4^{2-} (Rees 1973; Mayer 2007; Zuber 2007). This results in (1) a positive linear correlation between the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the residual sulfates as well as (2) in the increase of the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the dissolved sulfates with decreasing SO_4^{2-} concentrations (Fig. 8). Generally, the observed linear trend of $\delta^{34}\text{S}$ vs $\delta^{18}\text{O}$ for aqueous sulfates can be attributed to (1) the bacterial (dissimilatory) sulfate reduction, (2) the mixing process in the aquifer, and/or (3) the precipitation of sulfide minerals.

A positive linear correlation between the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of dissolved sulfates is observed only in brackish waters of Sargayev–Daugava aquifer (Fig. 8a). In these waters, a decrease of SO_4^{2-} concentration is associated with the increase of its $\delta^{34}\text{S}$ values which suggest the occurrence of dissimilatory sulfate reduction in the aquifer (Fig. 8b). It means, that the currently observed isotopic composition of dissolved sulfates in brackish waters of Sargayev–Daugava aquifer is modified by the imposition of the sulfate reduction process and mixing between saline waters and infiltration snow melt water. Due to relatively high SO_4^{2-} concentration in saline waters compared to rain water or snow, the contribution of sulfates originating directly from atmospheric precipitation is rather minor.

Such positive linear correlation between the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of dissolved sulfates is not observed in saline waters of Arukjula–Shventoy aquifer, where $\delta^{34}\text{S}$ values are stable within less than 1‰, and $\delta^{18}\text{O}$ reveals only small variation within 2‰ (Fig. 8a). Presumably, the observed isotopic composition of dissolved sulfates here reflects directly the isotopic composition of the source sulfates, which may be associated with dissolution of marine evaporates (mainly gypsum or anhydrite), and some small variations of isotopic composition may be connected with mixing processes in the aquifer. Also the dissolution of sulfides (e.g. pyrite), which may occur in the aquifer composed by sandstone, cannot be excluded.

A general summary of the sulfate sources in mineral waters of confined aquifers of Staraya Russa spa estimated

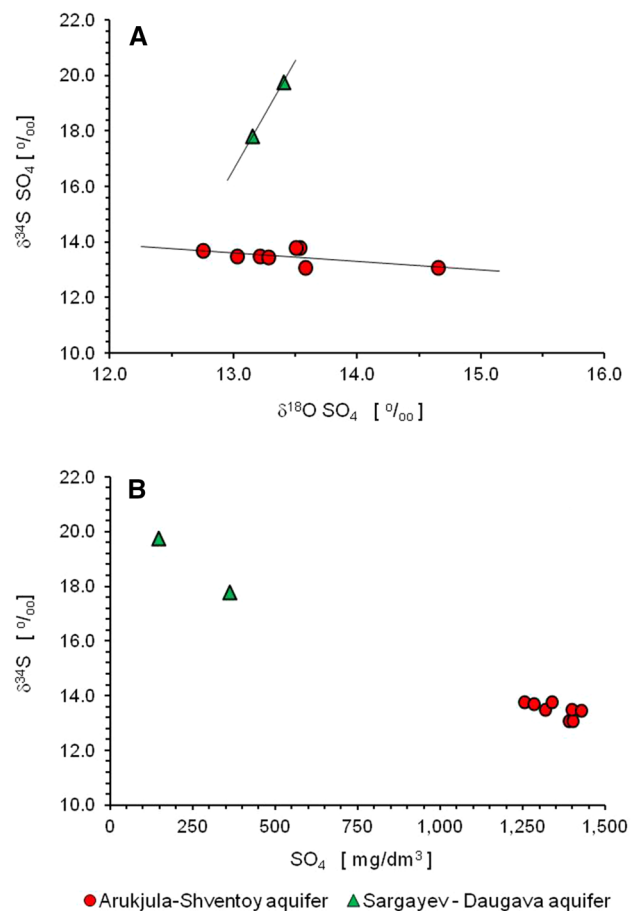


Fig. 8 Trends of the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for residual sulfates in mineral waters of Staraya Russa spa. A positive linear trend in waters of Sargayev–Daugava aquifer (a) and decrease of SO_4^{2-} concentration with $\delta^{34}\text{S}$ increase (b) suggest the occurrence of the dissimilatory sulfate reduction. For more explanation see the text

from distribution of dissolved sulfates and their O and S isotopic compositions is shown in Fig. 9.

As can be seen (Fig. 9), there is one most likely source of dissolved sulfates in mineral waters of Staraya Russa spa, namely: the evaporitic marine sulfates. Part of the dissolved SO_4^{2-} originates undoubtedly from dissolution of evaporitic sulfates present in the rocks forming particular aquifers. To directly corroborate this fact, the S and O isotopic composition of gypsum or anhydrite from Devonian formations in the study area should be determined; unfortunately, we did not take any aquifer rock samples during this study. On the other hand, the major part of dissolved sulfates in the studied mineral waters comes from the admixture of connate seawater-like end-member; nevertheless, the isotopic composition of such sulfates reflects the sulfates precipitated from this waters. The observed enrichment of sulfur isotopic composition of dissolved SO_4^{2-} in mineral waters of Sargayev–Daugava aquifer may reflect the occurrence of the bacterial sulfate reduction in the aquifer.

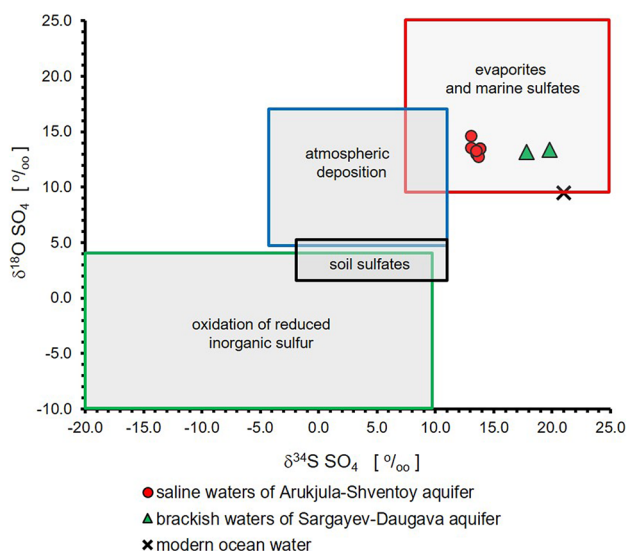


Fig. 9 The $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ of dissolved SO_4^{2-} in mineral waters of Staraya Russa spa against the background of typical sulfate sources (scheme after Clark and Fritz 1997; modified by the author)

Conclusions

There are two main types of mineral waters used in the Staraya Russa spa: (1) the saline waters of the Middle and Upper Devonian Arukjula–Shventoy (D_{2ar} – D_{3sv}) aquifer of Cl–Na and Cl–Na–Ca types with isotopic composition of $\delta^{18}\text{O}$ from -10.7 to -11.3‰ and $\delta^2\text{H}$ from -81.3 to -85‰ and (2) the brackish waters of the Upper Devonian Sargayev–Daugava (D_{3sr} – dg) aquifer of Cl–Na–Ca–Mg and Cl–Mg–Ca types with isotopic composition of $\delta^{18}\text{O}$ from -12.5 to -12.9‰ and $\delta^2\text{H}$ from -93.0 to -94.1‰ . Although, all mineral waters are located along the LMWL, their pure meteoric origin is not sufficiently corroborated by their chemical composition and ionic ratios. In hydrogeological settings of the Staraya Russa area, the brackish waters of the Sargayev–Daugava aquifer are result of mixing between infiltration waters (i.e. prevailing snow melt component) and saline waters ascending from deeper Arukjula–Shventoy aquifer. Such two-component mixing process is corroborated first all by the linear relationship between $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) and the concentration of chlorides Cl^- . The fraction of saline water of Arukjula–Shventoy aquifer in brackish waters of Sargayev–Daugava aquifer may reach values from around 0.2 (well-12) to 0.4 (well-11). On the other hand, the saline waters of the Arukjula–Shventoy aquifer are mixtures of approximately equal fractions (0.5) of snow melt water of $\delta^{18}\text{O} = -21.7\text{‰}$ and seawater-like end-member of isotopic composition similar to modern ocean water (i.e. VSMOW). Such mixing process is fully corroborated by the observed chemical composition and ionic ratios of saline waters in Arukjula–Shventoy aquifer. The sulfur ($\delta^{34}\text{S}$) and oxygen

($\delta^{18}\text{O}$) isotopic composition of sulfates dissolved in mineral waters indicate that the evaporitic marine sulfates are the main source of dissolved sulfates in mineral waters of Staraya Russa spa. Part of the dissolved SO_4^{2-} originates undoubtedly from dissolution of evaporitic sulfates present in the rocks forming the particular aquifers. Additional part of dissolved sulfates in the studied mineral waters comes from the admixture of connate seawater-like end-member: the isotopic composition of such sulfates reflects the isotopic composition of potential sulfates precipitated from this waters. The studies strongly suggest that one of the most important factors responsible for the observed chemical composition of mineral waters extracted in Staraya Russa spa is the presence of the connate seawater-like component in the hydrogeological system.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Appelo CAJ, Postma D (1996) *Geochemistry, groundwater and pollution*, 2nd edn. A.A. Balkema Publishers, Amsterdam, p 536
- Carmody RW, Plummer LN, Busenberg E, Coplen TB (1998) Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition. In: U.S. Geological Survey Open-File Report. Reston, Virginia, pp 97–234
- Carpenter AB (1978) Origin and chemical evolution of brines in sedimentary basin. *Okla Geol Surv Circ* 79:60–76
- Clark I, Fritz P (1997) *Environmental isotopes in hydrogeology*. CRC Press, Boca Raton, p 328
- Claypool GE, Holser WT, Kaplan IR, Sakai H, Zak I (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem Geol* 28:199–260
- Collins AG (1975) *Geochemistry of oil field waters*. Developments in petroleum science. American Elsevier Publishing Company, New York, p 4961
- Connolly CA, Walter LM, Baadsgaard H, Longstaffe FJ (1990) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. *Chemistry. Appl Geochem* 5:375–397
- Cook PG, Herczeg AL (2000) *Environmental tracers in subsurface hydrology*. Kluwer, Boston, p 529
- de Groot PA (2004) *Handbook of stable isotope analytical techniques*, vol 1. Elsevier, Amsterdam, p 1234
- Davis SN (1964) The chemistry of saline waters by R.A. Krieger—discussion. *Groundwater* 2(1):51–51
- Fritz P, Basharmal GM, Drimmie RJ, Isen J, Qureshi RM (1989) Oxygen isotope exchange between sulphate and water during bacterial sulfate reduction. *Chem Geol* 79:99–105

- Gehre M, Hoefling R, Kowski P et al (1996) Sample preparation device for quantitative hydrogen isotope analysis using chromium metal. *Anal Chem* 68:4414–4417
- Gehre M, Geilmann H, Richter J et al (2004) Continuous flow $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ analysis of water samples with dual inlet precision. *Rapid Commun Mass Spectrometer* 18:2650–2660
- Halas S, Szaran J (2004) Use of $\text{Cu}_2\text{O}-\text{NaPO}_3$ mixtures for SO_2 extraction from BaSO_4 for sulphur isotope analysis. *Isot Environ Health Stud* 40:229–231
- Halas S, Szaran J, Czarnacki M, Tanweer A (2007) Refinements in BaSO_4 to CO_2 preparation and $\delta^{18}\text{O}$ -calibration of the sulphate standards NBS-127, IAEA SO-5 and IAEA SO-6. *Geostand Geoenal Res* 31:61–68
- Hem JD (1989) Study and interpretation of the chemical characteristics of natural water. In: Water-supply paper 2254. Department of the Interior. U.S. Geological Survey, Alexandria. p 194
- Hounslow A (1995) Water quality data: analysis and interpretation. Lewis Publishers, Boca Raton, p 395
- Kaplan IR, Rittenberg SC (1964) Microbiological fractionation of sulfur isotopes. *J Gen Microbiol* 34:195–212
- Knöller K, Fauville A, Mayer B, Strauch G, Friese K, Veizer J (2004) Sulfur cycling in an acid mining lake and its vicinity in Lusatia, Germany. *Chem Geol* 204:303–323
- Korotkov AI, Potapov AA, Rumynin VG (2013) Rare types of mineral water of the Srednerussky Artesian Basin. *Nauka, St. Petersburg*, p 303 **(in Russian only)**
- Krasinceva VV (1968) *Gidrogeochimia chlora i broma* (Hydrogeochemistry of chlorine and bromine). Nauka, Moscow, p 194 **(in Russian only)**
- Krouse HR, Mayer B (2000) Sulphur and oxygen isotopes in sulphate. In: Cook PG, Herczeg AL (eds) *Environmental tracers in subsurface hydrology*. Kluwer, Boston, pp 195–231
- Kuklin DN, Shklovsky OA (2008) Technological scheme of mineral water extraction in Staraya Russa in Novgorod district, Staraya Russa Spa. The correction of the technological scheme. *GEOM-INVOD*, p 196 **(in Russian only)**
- Kurilenko VV, Kirichenko YA (2016) Characteristic of the environmental impact of the spa-resort of Staraya Russa on adjacent natural areas. In: *Environmental problems of subsoil use. Proceedings of the sixteenth international youth scientific conference*, pp 252–254 **(in Russian only)**
- Kurilenko VV, Kirichenko YA (2017) The assessment of the ecogeological condition of a town and spa-resort called Staraya Russa. In: *Environmental problems of subsoil use. Proceedings of the sixteenth international youth scientific conference*, pp 107–108 **(in Russian only)**
- Macioszczyk A (1987) *Hydrogeochemia*. Wydawnictwa Geologiczne, Warszawa, p 324 **(in Polish only)**
- Mayer B (2007) Assessing sources and transformations of sulphate and nitrate in the hydrosphere using isotope techniques. In: Aggarwal PK, Gat J, Froehlich KFO (eds) *Isotopes in the water cycle; past, present and future of a developing science*. Springer, Dordrecht, pp 67–90
- Mizutani Y (1971) An improvement in the carbon-reduction method for the oxygen isotopic analysis of sulphates. *Geochem J* 5:69–77
- Nielsen DM, Nielsen GL (2007) *The essential handbook of groundwater sampling*. CRC Press, Boca Raton, p 309723
- Ozerova NA, Shirokova VA (2017) Salt works and salt springs of Staraya Russa in the works of 18th- and 19th-centuries Russian scientists. *Vestnik Acad Sci Chechen Repub* 2(35):68–75 **(in Russian only, English abstract)**
- Porowski A (2001) Chemical composition and origin of ionic ratios in the Iwonicz Anticline mineralized groundwater. *Ann Soc Geol Pol* 71:125–134
- Porowski A (2006) Origin of mineralized waters in the Central Carpathian Synclinorium. *SE Stud Geol Pol* 125:5–66
- Porowski A (2014) Isotope hydrogeology. In: Eslamian S (ed) *Handbook of engineering hydrology. Fundamentals and applications*. CRC Press, Boca Raton, pp 345–3781
- Porowski A (2015) Geothermometric and isotopic studies of dehydration waters: implications for thermal conditions in the Central Carpathian Synclinorium, SE Poland. *Environ Earth Sci* 74:7539–7553
- Porowski A, Porowska D, Halas S (2019) Identification of sulfate sources and biogeochemical processes in an aquifer affected by Peatland: insights from monitoring the isotopic composition of groundwater sulfate in Kampinos National Park, Poland. *Water* 11:1388
- Rees CE (1973) A steady-state model for sulfur isotope fractionation in bacterial reduction process. *Geochim Cosmochim Acta* 37:1141–1162
- Rittenhouse G (1967) Bromine in oil-field waters and its use in determining possibilities of origin of these waters. *Am Assoc Petrol Geol Bull* 51:2430–2440
- Rozanski K, Araguas-Araguas L, Gonfiantini R (1993) Isotopic patterns in modern global precipitation. In: Stewart PK, Lohmann KC, McKenzie J, Savin S (eds) *Climate change in continental isotopic records*. Geophysical Monograph American Geophysical Union, Washington, DC, pp 1–36
- Simonova YV, Rusakov AV (2018) Features of the genesis of soil salinization in the Devonian lowlands on the example of the Starorussky district of the Novgorod region. In: *Materials of the international scientific and practical conference dedicated to the 85th anniversary of the Department of Soil Science of BSU and the 80th anniversary of the birth of V. S. Anoshko*, pp 289–294 **(in Russian only)**
- Vinograd NA (2004) Formation of mineral and thermal waters of some artesian basins in Russia. *Environ Geol* 46(5):675–679
- Vinograd NA, Tokarev IV, Stroganova TA (2019) Features of groundwater formation of the main aquifers of St. Petersburg and suburbs based on data of chemical and isotope composition. *Earth Sci* 64(4):575–597
- Voroniuk GJ, Borodulina GS, Krainyukova IA, Tokarev IV (2016) Groundwater exchange in the Baltic shield marginal areas and adjacent artesian basins based on isotope and hydrochemistry data. *Scientific problems and practical applications. Karelian Isthmus. Trudy Karelskogo Nauchnogo Centra RAN* 9:46–56 **(in Russian only, English abstract)**
- Yingjie C, Changyuan T, Gaoming C, Xingze W (2016) Hydrochemical zoning: natural and anthropogenic origins of the major elements in the surface water of Taizi River Basin. *Northeast China Environ Earth Sci* 75:811
- Żaczek J, Porowski A (2017) Hydrogeological settings and origin of groundwater composition in the southern part of the Gorce Mts., Kowaniec Maly catchment. *Ann Soc Geol Pol* 87:183–197
- Zuber A (2007) *Metody znacznikowe w badaniach hydrogeologicznych, poradnik metodyczny*. Wrocław, Oficyna Wydawnicza Politechniki Wrocławskiej, p 402 **(in Polish only)**

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.