

## PRELIMINARY HYDROCHEMICAL, ISOTOPE, AND NOBLE GAS INVESTIGATIONS ON THE ORIGIN OF SALINITY IN COASTAL AQUIFERS OF WESTERN POMERANIA, POLAND

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### ABSTRACT

Preliminary environmental tracer investigations performed in Western Pomerania revealed a complex origin of waters and the origin of their salinity. Nineteen samples were taken for hydrochemical and stable isotope analyses, and ten of them also for noble gas determinations. Samples represent different geological formations with waters of different salinity. Of nineteen samples, only three represent fresh Holocene water; four Holocene water with admixture of ascending pre-Quaternary water, and two Holocene water with salinity from indirect intrusion of the Baltic Sea water. Two samples represent evidently dominant component of glacial water with salinity most probably gained also by a small admixture of ascending saline water. Three samples represent glacial water mixed with Holocene and pre-Quaternary waters. Five samples (four deep wells and a spring) represent pre-Quaternary saline water as indicated both by the isotopic composition of water and noble gas data. In conclusion, the dominant source of salinity is not caused by Baltic water intrusions, but by ascending waters from Mesozoic formations, which in the central and northern Poland contain pre-Quaternary meteoric waters with high salinity gained from Zechstein salt structures.

The area of investigation extends along the Baltic Sea shore from Świnoujście in the west to Ustronie Morskie in the east (Fig. 1). In that region there are three health resorts (Świnoujście, Kamień Pomorski and Kołobrzeg) where saline waters are exploited for therapeutical purposes. Within the present study 19 samples were collected at 18 sites for chemical and isotopic analyses, in that ten for noble gas determinations (in some cases the technical conditions were unfavourable for noble gas sampling). Samples were taken

at different depths from formations of different stratigraphy and lithology.

Fresh groundwater reservoirs are scarce and of limited extend due to shallow occurrences of brackish and saline waters. Their exploitation often leads to the degradation of quality due to brackish water intrusions. Therefore, the origin of brackish and saline waters in Western Pomerania was a subject of a number of studies. Kolago (1964) and Dowgiałło (1965) showed that their occurrences in Jurassic, Cretaceous and

Cenozoic formations are mainly related to anticline structures and dislocation zones. Dowgiałło (1971, 1988) regarded the saline waters in Mesozoic formations of northern and central Poland to be mixtures of waters of different origin and age (calling them poligenetic waters). Similarly Dowgiałło and Tongiorgi (1972) on the basis of some isotope data regarded them to mixtures of connate marine waters with younger meteoric waters. A different opinion was expressed by Grabczak and Zuber (1983), Zuber and Grabczak (1991), and Krawiec (1999a, 1999b) who, on the basis of isotope and hydrochemical data, regard these saline waters to result mainly from pre-Quaternary infiltration, with salinity gained by leaching of Zechstein salt structures.

Main geological structures of the Pomeranian anticlinorium are shown in the insert of Fig. 1. In two main anticlines of Kamień Pomorski (AKP in Fig. 1A) and Kołobrzeg (AK), below Cenozoic sediments, usually lie Jurassic rocks. Trzebiatów (ST), Wiselka (SW) and other synclines, are formed by Cretaceous rocks (Figs. 1 and 2). Different water levels have hydraulic connections due to the presence of numerous dislocations.

Saline waters in Permian and Triassic formations are of the Na-Cl type with high TDS values, often above 180 g/L, which mainly result from leaching of Zechstein salt structures.

In Lower Jurassic formations the TDS values are usually from 0.4 to about 100 g/L, the highly saline waters being exploited for therapeutical purposes. For instance, deep wells in Kamień Pomorski (Edward II, No. 8 in Table 1) and in Dziwnówek (Józef, No. 7) exploit saline waters of the Na-Cl type from Lias formations. Similar waters are also exploited from Anastazja and B-2 deep wells in Kołobrzeg (not investigated within the present work), and discharged by several springs through Quaternary sediments (e.g., spring No. 11). Shallow Lias, Malm and Dogger anticline formations contain saline waters (e.g. in Kołobrzeg B-1 well, No. 3), brackish waters (e.g. in Dźwirzyno, No. 4; and Trzęsacz, No. 13) and fresh waters (e.g.

in Mrzeżyno, No. 5; Bagicz, No. 1; and Pobierowo, No. 14).

In Świnoujście saline waters are exploited from Quaternary and Upper Cretaceous formations for desanilisation (No. 17). Saline waters are exploited from Lower Cretaceous for therapeutical purposes too (No. 18).

Within Trzebiatów syncline (ST) a number of wells exploit fresh water from Upper Cretaceous marls (e.g. in Niechorze, No. 6), in some cases with Cl<sup>-</sup> content up to about 300 mg/L.

Waters in Quaternary aquifers are of the HCO<sub>3</sub>-Ca type, usually fresh (e.g., Nos. 10, 12 and 16) or brackish (e.g., Nos. 2, 9 and 15). As mentioned, the exploitation of fresh waters is hindered by intrusions of saline waters. Saline components in fresh and brackish waters may be caused either by admixture of ascending older water or by intrusion of Baltic water. Indirect intrusion of Baltic water is the result of bank filtration either from lagoons or from estuaries.

Due to complex geology and small dimensions of fresh groundwater bodies, there is no sufficient number of sampling sites, which would enable to observe space distributions of ages and salinity in particular systems. That limitation hinders seriously the identification of the origin of salinity. Due to that reason it was decided to use the stable isotope method, which is well known to be particularly useful at the initial stages of studies. That method when combined with chemical data has appeared to yield unique answers only for waters with distinct chemical and/or isotope signatures, i.e., for those representing pre-Quaternary or glacial infiltration. For Holocene meteoric waters, the determination of the origin of Cl<sup>-</sup> is rather difficult, if its concentration is low, say, below about 500 mg/L.

The noble gas methods, particularly the noble gas temperature (NGT) and the <sup>4</sup>He excess have appeared to be very useful in identification of the age and origin of old groundwaters in southern and central Poland (Ciężkowski et al., 1992; Zuber et al., 1995, 1997, 2000). On the other hand, for a large aquifer (Gdańsk Cretaceous) in the central

part of the Polish coast, the noble gas data have appeared to yield ambiguous results. Namely, in some cases too low NGT values, which supply information on the temperature of recharge, and too high  $^4\text{He}$  excess contents, which yield relative ages, were observed for waters which according to their  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values should be of Holocene origin (Zuber et al., these proceedings). Therefore, a caution is also needed when considering the noble gas data within this work.

Chosen chemical components with  $\text{mNa}/\text{mCl}$  and  $\text{Cl}/\text{Br}$  indicators, stable isotope and noble gas data (only for Nos. 1-10) are shown in Table 1. In the last column the origin of water is given, i.e., its "age" in terms of both the deduced climatic period in which the main component was recharged and the supposed origin of the salinity. That interpretation is also supported by Figs. 3 and 4 in which  $\delta^{18}\text{O}$ - $\delta\text{D}$  and  $\text{Cl}$ - $\delta\text{D}$  relationships are given, respectively.

Three samples with the lowest  $\text{Cl}$  contents can be regarded as representative for background Holocene water (Nos. 1, 10a and 14, see Table 1 and Figs. 3 and 4). Tritium has not been measured so far, and, therefore, it is impossible to say if these samples represent modern (i.e. with bomb-era tritium), or older Holocene ages. Their isotopic composition reasonably agrees with the values expected from the maps of the Holocene groundwaters in Poland, i.e., with  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values within  $-9.2$  to  $-9.4$  ‰ and  $-64$  to  $-66$  ‰, respectively (d'Obyrn et al., 1997). Noble gas data are known only for No. 1 sample with  $^4\text{He}$  excess suggesting rather early Holocene age, and with the NGT value somewhat lower than the yearly mean present air temperature ( $7.5$  to  $8.2$  °C, from the east to the west of the area).

A prolonged pumping at site No. 10 leads to increased salinity, which seems to be related to an admixture of glacial water as indicated by isotopic shift to more negative values and by adequate NGT and  $^4\text{He}$  excess values (No. 10b in Table 1). That result was rather unexpected because due to the small depth and close position of the well to the

shore, the intrusion of Baltic water was expected. As in other cases, the salinity of glacial water is most probably caused by admixture of pre-Quaternary water.

Two samples (Nos. 4 and 17) evidently represent water of glacial origin as shown by delta values distinctly more negative than those of the local Holocene water. In the case of No 4, a low NGT and adequately high  $^4\text{He}$  excess confirm its glacial origin. The position of No. 17 in Fig. 4 suggests that its salinity may result from direct leaching of a salt diapir. However, a shallow presence of such structures is not known close in that region. Therefore, the salinity of both No. 17 and No. 4 is thought to result probably from an admixture of pre-Quaternary water. Artesian outflow at site No. 4 additionally excludes an admixture of the Baltic water as the cause of increased salinity.

Two samples (Nos. 2 and 13) probably represent glacial water with a pre-Quaternary component, which is supposed to explain their position close to the Holocene waters in Figs. 3 and 4 as well as their salinity and a relatively high molar ratio of  $\text{Na}^+$  to  $\text{Cl}^-$ . For No. 2, a low NGT value and relatively high  $^4\text{He}$  excess seem to support the hypothesis of three-component mixing. In addition, the artesian character of No. 13 excludes the intrusion of Baltic water as an explanation of increased salinity. In conclusion, Nos. 2 and 13 are grouped in Figs. 3 and 4 with No. 10b, which was discussed above.

Five samples (Nos. 3, 7, 8, 11 and 18), which represent saline waters, have distinctly heavier isotope contents than those of the local Holocene water. Judging only from the position of these waters in Fig. 3, mixing of Quaternary waters with sedimentary waters of marine origin can wrongly be deduced. However, such mixing must be excluded due a number of reasons. Firstly, the presence of a Quaternary component is little probable at the depths much greater than the depths at which Quaternary waters commonly occur at the coast of Western Pomerania. Secondly, according to Fig. 4, the salinity of the hypothetical marine water should be much higher than that of unaltered marine water,

which is not justified by any evidence. Thirdly, though the values of  $m(\text{Na}^+/\text{Cl}^-)$  and  $\text{Cl}^-/\text{Br}^-$  indicators are known to decrease in old waters independently of their origin, in three cases, at least one of them is larger than the value typical for marine water (0.86 and 265, respectively), suggesting the origin of  $\text{Cl}^-$  to be related to leaching. Fourthly, for three samples with noble gas determinations (Nos. 3, 7 and 8), high NGT values, high concentrations of  $^4\text{He}$  excess, and high values of the argon isotope ratio ( $^{40}\text{Ar}/^{36}\text{Ar}$ ) also confirm their pre-Quaternary age (Table 1).

The origin of other investigated fresh and brackish waters (Nos. 5, 6, 9, 12, 15 and 16) is more difficult to deduce due to the lack of distinct isotope and  $\text{Cl}^-$  signatures, and the lack of noble gas determinations in three cases (12, 15 and 16). Their position in Fig. 4 suggests that some of them may result from mixing of Holocene water with the Baltic Sea water. However, considering high values of the  $m(\text{Na}^+/\text{Cl}^-)$  and  $\text{Cl}^-/\text{Br}^-$  indicators in the case of Nos. 5, 6, 9 and 12, and the artesian character of Nos. 5 and 12, the marine origin of  $\text{Cl}^-$  should be excluded and related to small admixtures of ascending older waters. High values of  $^4\text{He}$  excess (especially for No. 9) support the hypothesis on the contribution of pre-Quaternary water. Sample No. 6 is especially interesting. Its position in Fig. 4

strongly suggests mixing with Baltic water. However, as mentioned, the high values of the  $m(\text{Na}^+/\text{Cl}^-)$  and  $\text{Cl}^-/\text{Br}^-$  indicators (2.42 and about 1000, respectively) rather exclude Baltic water as a cause of increased salinity. Relatively high  $^4\text{He}$  excess indicates the presence of an admixture of older water whereas a relatively low NGT may result from an additional admixture of a glacial component. However, the presence of that third component seems to be little probable considering the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of that sample and its position in Figs. 3 and 4.

Samples Nos. 15 and 16 represent water exploited from shallow Quaternary sands. The salinity of these samples most probably results from an admixture of marine water, which enters aquifers indirectly by bank filtration from Dziwna river (No. 15) and Szczecin Lagoon (No. 16).

In spite of a preliminary character, the present study showed the salinity of coastal aquifers of Western Pomerania to be in most cases caused by ascension of pre-Quaternary saline waters. In some cases saline and brackish waters are of glacial origin with salinity also gained by ascension of older waters. Indirect intrusions of the Baltic Sea water are observed only for two wells in the Wolin (No. 15) and Uznam (No. 16) islands.

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