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Hydrogeochemical Settings of the Boryslav–Pokuttia Oil and Gas Bearing Area within the Carpathian Oil and Gas Bearing Province, Ukraine

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Гідрогеохімічні умови Бориславсько-Покутського нафтогазоносного району в межах Карпатської нафтогазоносної провінції, Україна

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Ключові слова: нафтогазоносна зона, водоносний горизонт, гідрогеохімічні характеристики, підземні води.

The objective of this study was to investigate the hydrogeochemical characteristics of aquifers within the Boryslav-Pokuttia oil and gas-bearing area, to examine the genesis of groundwater and its influence on the conditions of formation and preservation of hydrocarbon accumulations, and to identify hydrogeochemical criteria of hydrocarbon potential. The research methodology relied on the statistical and graphical processing of verified archival data and the subsequent interpretation of the results obtained. Paleohydrogeological analysis was also applied.

It was established that the principal factors controlling the hydrogeochemical parameters of aquifers in the area include the palaeohydrogeological evolution and the degree of hydrogeological isolation. Prolonged and intensive dynamo-elisional development, the fold-and-thrust structural pattern, numerous disjunctive faults, and the presence of evaporite deposits have resulted in the formation of a complex hydrogeochemical system lacking distinct zonation.

Genetically, most waters represent sedimentogenic residual brines of evaporitic basins or brines resulting from the leaching of salt-bearing molasse deposits, as well as their mixtures. At shallow depths, mineralised and saline waters enriched in bicarbonate and sulphate ions are occasionally encountered. Based on geochemical indicators, these waters are identified as mixtures of ancient or modern infiltration waters with sedimentogenic thalassogenic waters.

Indirect hydrogeochemical criteria for hydrocarbon potential in the Boryslav-Pokuttia area include: high Total Dissolved Solids (TDS) and waters metamorphization, their Na-Cl or Ca-Na-Cl composition, enrichment in trace elements and microcomponents, and low sulphate concentrations. Collectively, these features indicate a closed hydrodynamic system favourable for the formation and preservation of hydrocarbon accumulations.

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1. Introduction

The study of hydrogeochemical settings in oil and gas bearing regions is one of the areas of contemporary petroleum geology, as the chemical composition of groundwater directly reflects geological evolution, fluid-regime dynamics, and the conditions under which hydrocarbon reservoir form. Formation waters constitute sensitive indicators of migration processes, fluid systems type and evolutionary stage, as well as water-rock interaction. Hydrogeochemical parameters are widely used to determine water genesis, assess hydrocarbon potential, delineate prospective zones, evaluate trap isolation, and reconstruct hydrocarbon migration pathways.

The relevance of such studies is reinforced by the current demands of the petroleum industry, which require reliable methods for evaluating geological settings and improving field development efficiency. Hydrogeochemical analysis supports the assessment of hydrodynamic conditions, identification of anomalous zones, and prediction of fluid behaviour during drilling and reservoir exploring.

Beyond their applied significance, hydrogeochemical investigations are also fundamental to reconstructing the geological evolution of petroleum basins. The chemical and isotopic characteristics of groundwater enable reconstruction of water system genesis, the stages and mechanisms of their transformation, the link between tectonic and sedimentary processes, and the conditions of hydrocarbon generation and preservation.

Collectively, these factors highlight the need of a systematic and integrated approach to studying hydrogeochemical settings in oil and gas bearing areas, which is essential for advancing exploration methods, improving resource assessment, and ensuring the rational development of oil and gas fields.

The objective of this study was to determine the conditions for the formation and preservation of hydrocarbon accumulations and to identify specific hydrogeochemical criteria of oil and gas potential in the Boryslav–Pokuttia oil and gas bearing area (OGBA), based on the analysis of the geochemical characteristics of groundwater.

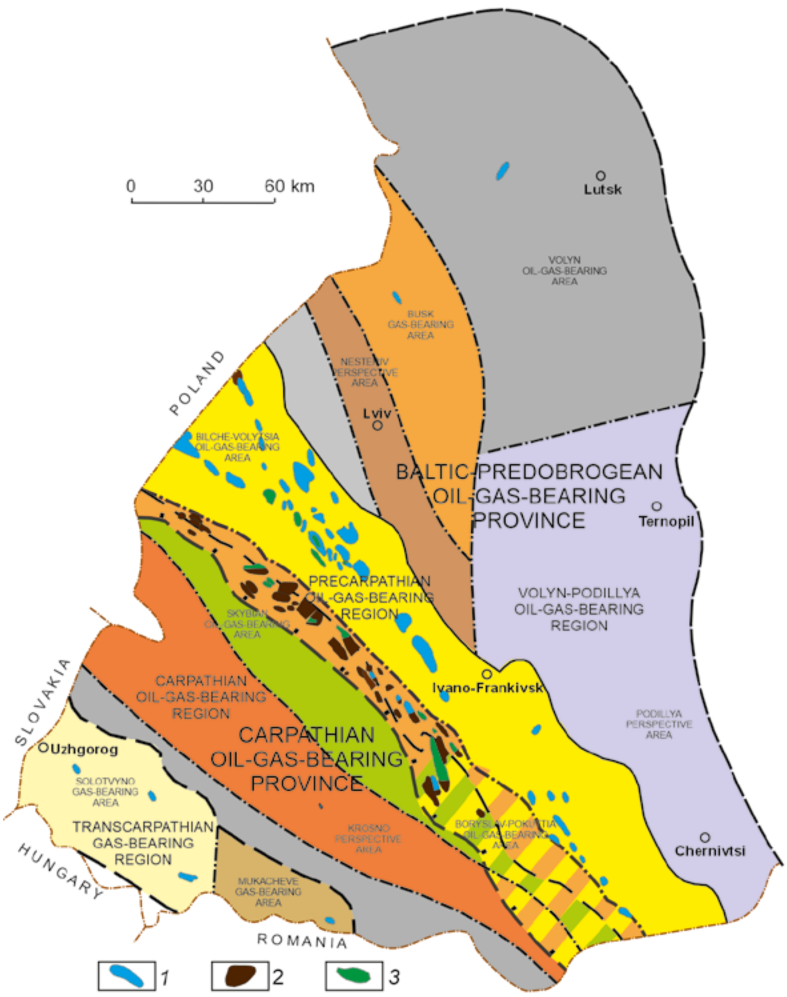


Fig. 1. Scheme of oil and gas geological zoning of the western region of Ukraine (Ivaniuta, 1998): *1* – gas fields; *2* – oil fields; *3* – gas-condensate fields

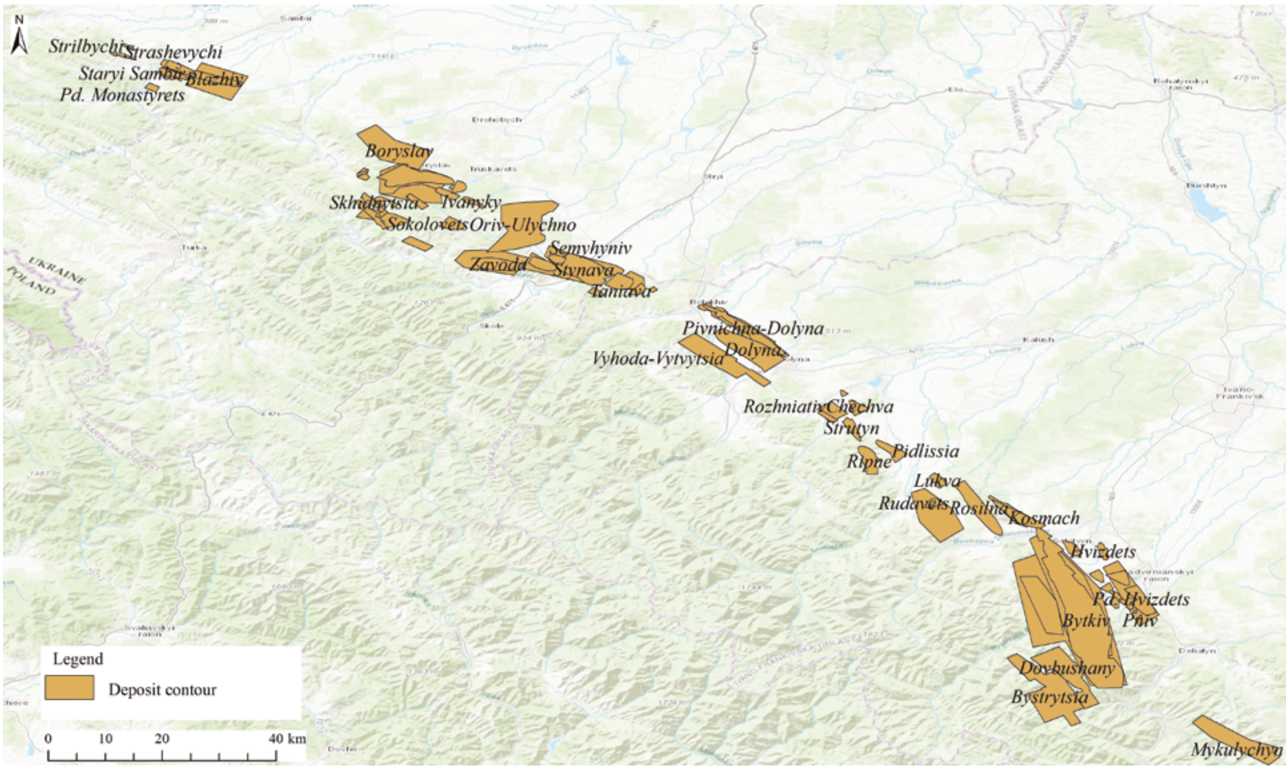


Fig. 2. Locations of hydrocarbon fields in the Boryslav-Pokuttia oil and gas-bearing area

According to the oil and gas geological zoning of Ukraine (Ivaniuta, 1998), the Boryslav-Pokuttia OGBA forms a part of the Precarpathian oil and gas bearing region within the Carpathian oil and gas province (Fig. 1). The region is predominantly oil-bearing. Within its boundaries a total of 37 oil fields, 7 oil-gas-condensate fields, 2 gas-oil fields, and 2 gas-condensate fields have been discovered (Fig. 2).

The Boryslav-Pokuttia OGBA is one of the oldest petroleum-producing regions in Europe and the most thoroughly explored one within Ukraine. It is associated with the Boryslav-Pokuttia Nappe of the Precarpathian Foredeep and encompasses the southwestern part of Lviv Region and the northwestern part of Ivano-Frankivsk Region. The area exhibits a complex system of linear folded and thrust structures. The productive strata include Oligocene and Miocene formations represented by sandstones, siltstones, and argillites, which form fractured-porous and fractured reservoirs. The main accumulations are associated with anticlinal and disrupted structures, often of the multi-storey and block-type.

Oil and gas accumulations occur at depths of 800–2500 m, increasing to 3000–3500 m in sub-thrust zones. Oils are predominantly light to medium, low-sulphur, and enriched in light fractions. Formation waters exhibit Na-Cl and Ca-Na-Cl composition with high TDS (40–120 g/dm^3) and elevated gas content.

Although substantially depleted by long-term development, the region retains exploration potential within deeper productive horizons and local structures in sub-thrust zones.

The research was conducted within the framework of the state-funded scientific project *"Hydrogeological Conditions of Hydrocarbon Accumulation in the Boryslav-Pokuttia Oil and Gas Bearing Area and the Impact of Petroleum Extraction on Surface and Groundwater Systems"* at the Institute of Geology and Geochemistry of Combustible Minerals of the National Academy of Sciences of Ukraine.

2. Materials and Methods

The research methodology involved statistical and graphical processing of archival data, followed by their validation, and interpretation of the results obtained. Empirical physical and chemical groundwater data (macro- and microcomponents) from the Boryslav-Pokuttia OGBA were sourced from well records ("Well Reports") archived at the State Geological Enterprise "Zakhidukrgeologia" of the National Joint Stock Company "Nadra Ukrainy". Water sampling was conducted during drilling and testing of exploratory and production wells at oil and gas fields during the 1960s–2000s. In the same years, analytical studies of formation water

Table 1. Changes in the chemical composition of seawater during evaporation (based on data adapted from (Carpenter, 1978; Holland, 1978) with the authors' additions)

Evaporation stage	TDS, g/L	Concentrations, mg/L							rNa/rCl	rCa/rMg	rSO_4-100/rCl	Cl/Br
		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	Cl^{-}	Br				
Black Sea water	18.76	233	679	5,820	193	1,460	10,340	35	0.86	0.21	10.30	295.43
World Ocean water	35.97	420	1,330	11,060	410	2,790	19,890	69	0.85	0.19	10.23	288.26
Onset of gypsum precipitation	143.63	1,700	5,200	44,000	1,460	11,000	80,000	269	0.84	0.20	10.03	297.40
Visible gypsum	192.05	1,040	7,590	59,700	2,220	13,300	107,800	396	0.84	0.08	9.00	272.22
Onset of halite precipitation	311.72	600	10,200	99,000	3,300	18,000	180,000	617	0.84	0.04	7.29	291.73
Visible halite	331.82	307	19,600	94,300	5,600	27,700	183,300	1,010	0.78	0.01	11.02	181.49
Halite	388.27		50,500	55,200	15,800	76,200	187,900	2,670	0.45	0.00	29.57	70.37
Onset of $MgSO_4$ precipitation	397.67		56,100	48,200	17,700	82,200	190,500	2,970	0.39	0.00	31.46	64.14
Onset of potassium salt precipitation	405.77		72,900	22,100	25,900	56,100	224,000	4,770	0.15	0.00	18.26	46.96
Potassium salts	434.62		92,600	8,960	18,800	54,200	254,000	6,060	0.05	0.00	15.56	41.91

samples were conducted in the laboratories of "Zakhidukrgeologia" using titrimetric, spectrophotometric and gravimetric methods.

To ensure the reliability of the dataset, analytical results were systematically verified, and unreliable records were excluded. The exclusion criteria were as follows:

- Where multiple samples had been collected from the same interval over a short period, only the sample with the highest mineralisation was retained, as the remaining samples likely reflected mixing of formation water with technical fluids (e.g. drilling muds and flushing waters).
- Samples representing injected waters used to maintain reservoir pressure during the late stages of field development were excluded.
- Samples exhibiting clear geochemical evidence of mixing with technical waters (as indicated by rNa/rCl, rCa/rMg, Cl/Br ratios) were removed.
- Samples containing evidently erroneous analytical values or recording errors were eliminated.

Following this filtering procedure, a total of 592 groundwater analyses were retained for further evaluation.

Statistical processing of groundwater geochemical parameters included correlation analysis (Pearson's correlation coefficient, presented as a correlation matrix), data distribution analysis, and descriptive statistics were applied. The software employed were Microsoft Excel and TIBCO Statistica. Graphical output was generated in CorelDRAW and ArcMap. Palaeohydrogeological analysis integrated palaeotectonic, palaeosedimentological, palaeohydrogeochemical, and palaeohydrodynamic investigations.

For the palaeohydrogeological analysis, data on the composition of seawater during evaporation (Table 1) were incorporated.

3. Review of Previous Studies

One of the earliest researchers of Carpathian groundwater was the renowned Austrian scholar and professor at Lviv University, Balthasar Hacquet (1739–1815), who initiated systematic investigations into groundwater chemistry associated with petroleum accumulations (Krushelnytska, Valo, 2000).

In the 19th century, groundwater Steller and Zakrzewskyi furthered these studies. Lviv scholar Torosiewych, while examining hydrogen-sulphide mineral springs, suggested that hydrogen sulphide originates from organic matter decomposition (Krushelnytska, Valo, 2000).

Significant data on saline formation waters of the Precarpathian petroleum province, particularly those in the Boryslav oil field, were published by Zuber, Tolwinskyi and Katz. Tolwinskyi concluded that the waters of the Boryslav field are hydrodynamically connected to deeper aquifers (Tolwinskyi, 1921).

K. S. Havrylenko and O. D. Shtohryn emphasized the role of endogenous factors in the formation of groundwater in the oil and gas bearing regions of the Precarpathian area (Shtohryn, Havrylenko, 1968; Havrylenko et al., 1971). Hydrogeochemical and hydrodynamic features, as well as criteria for hydrocarbon potential in the Carpathian province, are presented in the works of (Shchepak, 1971; Romaniuk et al., 1973; Sprynskyi , 1998; Kolodiy et al., 1996; Kolodiy, 2004; Pavlyuk et al., 2021) among others.

Issues of groundwater genesis and chemical evolution in sedimentary and petroleum basins worldwide are extensively discussed in the literature (Carpenter, 1978; Xinong et al., 2006; Birkle et al., 2009; Dresel, Rose, 2010; Cortes et al., 2016; Cai et al., 2022; Luan et al., 2022;).

4. Results and Discussion

4.1 Geochemical Characteristic and Genesis of Groundwater

Aquifers within the Boryslav-Pokuttia OGBA occur in the Upper Cretaceous (K_2st) Stryi Formation, the Paleocene (P_1jm) Yamna Formation, Eocene units (P_2), the Oligocene Menilite Formation (P_3ml), and the Miocene Polyanytsia (N_1pl) and Vorotyshcha (N_1vr) formations. Due to intense folding, fragmentation, and block-thrust tectonics, these aquifers occur at highly variable depths.

According to their main geochemical features (Table 2), water characteristics across all aquifers are similar: they are predominantly highly mineralised brines of Na-Cl or Ca-Na-Cl composition. Waters with lower TDS (<30 g/L) contain higher concentrations of bicarbonate and sulphate ions and lower amounts of trace elements.

Groundwater genesis in the region was evaluated using palaeohydrogeological analysis supported by statistical methods.

The lithological (flysch-type clayey rocks) and palaeontological (Inoceramid debris) features of the Stryi Formation indicate shallow-marine depositional conditions with the normal marine water circulation.

Paleogene sedimentation occurred in shallow to moderately deep open-marine settings under warm subtropical climate conditions (Temniuk et al., 1973), as evidenced by molluscan and nummulite faunas.

The greenish coloration and the presence of gypsum in the flysch-like deposits of the Polyanytsia Formation suggest shallow-water conditions of a restricted marine basin, with the inflow of highly

Table 2. Principal geochemical characteristics of the aquifers of the Boryslav-Pokuttia oil and gas bearing region

Aquifer		K_2st	P_1jm	P_2	P_3ml	N_1pl	N_1vr
Number of samples		37	24	208	297	13	13
Depth, м		330–4101	345–4825	726–5373	240–5439	564–4227	606–2774
TDS, g/L	from–to	12.12–298.44	39.88–312.27	11.03–381.11	5.14–366.60	20.27–335.00	19.79–319.77
	modal series	55-228	140–201	53–334	31–329	168–308	21–92
rNa/rCl	from–to	0.41–0.88	0.49–0.88	0.49–0.90	0.30–1.29	0.45–0.90	0.67–0.94
	modal series	0.62–0.84	0.59–0.75	0.66–0.88	0.66–0.90	0.62–0.86	0.69–0.84
rCa/rMg	from–to	0.09–22.74	1.29–17.92	0.11–459.75	1.18–57.14	0.25–7.19	1.27–89.77
	modal series	1.03–5.5	3.01–6.80	3.60–12.14	0.20–7.22	1.73–4.95	1.27–5.64
$rSO_4 \times 100/rCl$	from–to	0.02–3.48	0.008–1.49	0.001–4.22	0.001–13.08	0.04–2.04	0.01–2.73
	modal series	0.01–0.29	0.05–0.18	0.07–0.38	0.06–0.76	0.11–0.43	0.02–0.27
Cl/Br	from–to	110.46–1731.95	92.96–1410.85	87.09–33537.81	48.97–51425.23	84.39–2077.12	180.77–4067.83
	modal series	1) 113–145 2) 368–628	92.96–342.16	272.49–920.50	370.25–842.25	84.39–609.71	195.21–418.35
Br^-, mg/L	from–to	44.1–1517.7	16.7–1642.8	1.6–1803.6	2.1–1483.8	18.8–2,271.2	12.0–496.2
	modal series	64.0–174.2	132.8–645.8	248.1–460.6	101.5–306.3	182.2–460.0	59.8–79.8
J^-, mg/L	from–to	0.8–127.0	3.3–46.9	0.72–65.5	0.21–84.6	9.9–90.8	2.5–71.8
	modal series	25.3–46.5	9.14–16.4	12.0–36.9	11.0–21.6	23.7–37.7	2.5–71.8

saline marine water (160–180 g/L; see Table 1), corresponding to the gypsum stage of evaporation.

Potash and rock salt deposits, gypsum, and anhydrite of the Vorotyshcha Formation clearly indicate formation within a shallow restricted lagoonal basin. Periodic isolation and reopening of the connecting strait permitted episodic inflow of marine water, accounting for the rhythmic alternation of salt layers and grey lagoonal clays (Fedushchak, 1972). TDS of water entrapped during sedimentation exceeded 300 g/L.

The formation of highly mineralised groundwater is possible through two mechanisms:

- Preservation or accumulation of parent brines from which various saline deposits precipitated.
- Dissolution of readily soluble evaporite deposits and leaching of soluble salts from salt-bearing rocks (Carpenter, 1978).

To determine groundwater genesis and the degree of its metamorphism, indicators expressing quantitative relationship between individual macro- and microcomponents of groundwater are used. Most commonly, the ratios rNa/rCl and rCa/rMg are applied for marine sedimentary waters. In seawater, rNa/rCl is 0.85, and rCa/rMg is 0.19. As a result of the metamorphism of marine waters during prolonged interaction with water-bearing rocks, the content of Ca increases at the expense of decreasing Mg and Na concentrations.

It is considered that lower rNa/rCl values and higher rCa/rMg values in water indicate a higher degree of metamorphism. Elevated rNa/rCl values may indicate a certain proportion of continental infiltration waters. With an increasing degree of seawater evaporation, these ratios also decrease (see Table 1). High rNa/rCl values in groundwater may also result from the leaching of halite (Kolodiy et al., 2009).

The sulphate coefficient, calculated as $rSO_4 \times 100/rCl$, in shallow aquifers (zones of active and limited water exchange) ranges from 10 to 500. Higher values may result from the leaching of sulphate-bearing rocks. In seawater, this ratio is 10.2.

Table 3. Pearson's correlation coefficients of groundwater parameters of the Boryslav-Pokuttia oil and gas bearing region (calculated using Statistica software; sample size: 592 water samples)

Parameter	Depth	pH	TDS	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Cl^-	SO_4^{2-}	HCO_3^-	Br^-	J^-	rNa/rCl	rCa/rMg	rSO_4×100/rCl	Cl/Br
Depth	1.00	-0.12	0.24	0.14	0.36	0.19	0.14	0.24	0.03	-0.02	0.42	0.22	-0.29	0.08	0.02	-0.14
pH	-0.12	1.00	-0.50	-0.40	-0.53	-0.42	-0.18	-0.50	0.07	0.20	-0.34	-0.08	0.49	0.23	0.18	-0.07
TDS	0.24	-0.50	1.00	0.95	0.81	0.61	0.50	1.00	-0.14	-0.32	0.68	0.33	-0.61	0.00	-0.48	-0.14
Na^+	0.14	-0.40	0.95	1.00	0.58	0.48	0.56	0.95	-0.13	-0.35	0.49	0.28	-0.37	-0.03	-0.48	-0.14
Ca^{2+}	0.36	-0.53	0.81	0.58	1.00	0.59	0.25	0.81	-0.12	-0.17	0.83	0.32	-0.84	0.10	-0.34	-0.13
Mg^{2+}	0.19	-0.42	0.61	0.48	0.59	1.00	0.27	0.62	-0.19	-0.22	0.52	0.25	-0.75	-0.16	-0.39	-0.01
NH_4^+	0.14	-0.18	0.50	0.56	0.25	0.27	1.00	0.50	-0.06	-0.23	0.33	0.16	-0.16	-0.07	-0.24	-0.19
Cl^-	0.24	-0.50	1.00	0.95	0.81	0.62	0.50	1.00	-0.15	-0.33	0.67	0.32	-0.62	0.00	-0.49	-0.14
SO_4^{2-}	0.03	0.07	-0.14	-0.13	-0.12	-0.19	-0.06	-0.15	1.00	0.16	-0.05	0.10	0.22	0.07	0.80	0.08
HCO_3^-	-0.02	0.20	-0.32	-0.35	-0.17	-0.22	-0.23	-0.33	0.16	1.00	-0.22	-0.04	0.26	-0.10	0.30	0.18
Br^-	0.42	-0.34	0.68	0.49	0.83	0.52	0.33	0.67	-0.05	-0.22	1.00	0.46	-0.65	0.05	-0.25	-0.27
J^-	0.22	-0.08	0.33	0.28	0.32	0.25	0.16	0.32	0.10	-0.04	0.46	1.00	-0.27	0.00	-0.11	-0.26
rNa/rCl	-0.29	0.49	-0.61	-0.37	-0.84	-0.75	-0.16	-0.62	0.22	0.26	-0.65	-0.27	1.00	-0.06	0.40	0.05
rCa/rMg	0.08	0.23	0.00	-0.03	0.10	-0.16	-0.07	0.00	0.07	-0.10	0.05	0.00	-0.06	1.00	0.08	-0.04
rSO_4×100/rCl	0.02	0.18	-0.48	-0.48	-0.34	-0.39	-0.24	-0.49	0.80	0.30	-0.25	-0.11	0.40	0.08	1.00	0.10
Cl/Br	-0.14	-0.07	-0.14	-0.14	-0.13	-0.01	-0.19	-0.14	0.08	0.18	-0.27	-0.26	0.05	-0.04	0.10	1.00

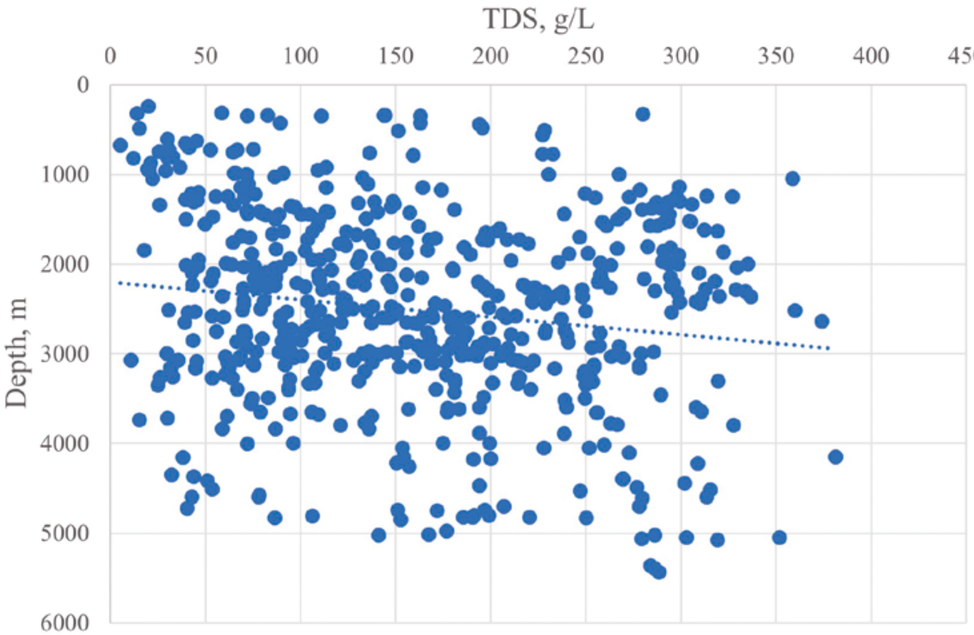


Fig. 3. Diagram of the relationship between groundwater mineralisation and aquifer depth within the Boryslav-Pokuttia oil and gas bearing region

Sulphate concentrations in waters are significantly lowered through bacterial sulphate reduction, a process occurring in anoxic conditions with the participation of organic matter following the below regime:

$$2SO_4^{2-} + 4C + 3H_2O \rightarrow H_2S + HS^- + 3HCO_3^-. \quad (1)$$

A clear indicator of water origin, regardless of its concentration, is the Chlorine-Bromine ratio (Cl/Br), since the metamorphic process does not affect Bromine; its content in metamorphosed solutions is primarily determined by its initial concentration (Kolodiy et al., 2009). In seawater, Cl/Br ratio is 288.26 decreasing significantly from the "visible halite" stage of seawater concentration (see Table 1). As a result of the metamorphism of marine sedimentary waters, this ratio decreases. High Cl/Br values (>1000) may result from leaching chloride salts from salt-bearing rocks or diluting sedimentary waters with freshwater.

Correlation analysis (assessing the strength and direction of linear relationships between two variables) of groundwater parameters in the Boryslav-Pokuttia OGBA revealed the following features (Table 3).

Aquifer depth. Its direct correlation with groundwater mineralisation (and with Ca, Mg, Cl, Br, I ion contentss – listed here in order of correlation coefficient increasing) reflects an intensifying level of system hydrodynamic confinement with depth, preserving primary sedimentary waters. The inverse correlation between aquifer depth and rNa/rCl indicates an increase in the intensity of water metamorphism processes (replacement of Na by Ca from water-bearing rocks).

The distribution of highly mineralised brines in shallow aquifers, as well as brackish and saline waters in deeper horizons (Fig. 3), may indicate different geneses of these waters.

Water mineralisation shows a direct correlation with the of Cl, Na, Ca, Mg, Br, NH_4, and I ion contents. Its inverse correlation with HCO_3 likely reflects enrichment of infiltrated waters in the active water exchange zone with these ions.

Studies on the genesis of highly mineralised groundwater in the Bilche-Volytsia oil and gas bearing region established a clear direct correlation between groundwater mineralisation and the Cl/Br ratio (most values reaching the low thousands). This is explained by leaching of clay-salt deposits of the Sambir-Rozhniativ formation and their subsequent expulsion into autochthonous reservoir rocks during the dynamo-elision cycle of hydrogeological history (Harasymchuk, Kolodiy, 2002; Harasymchuk et al., 2004).

In the Boryslav-Pokuttia OGBA, Cl/Br ratios in groundwater occasionally reach values in the low thousands, while most range between 84.39 and 920.5 (see Table 1), including the aquifer within clay-salt molasse deposits (N_1vr). No correlation was observed between water mineralisation and the Cl/Br ratio (see Table 3).

Na ion shows the strongest correlation with Cl (r = 0.95), reflecting the shared mechanism of concentration due to seawater evaporation. High correlations were also found with Ca, NH_4, Br, Mg, and I. Its inverse correlation with SO_4 and HCO_3 likely reflects the increasing contribution of low-mineralised infiltrated waters in the active water exchange zone.

NH_4 ion strongly correlates with Na, water mineralisation, Cl, B^-, Mg, Ca, and I. Ammonium genesis in groundwater of oil and gas regions is associated with diagenetic processes, during which ammonium can be released from clay minerals where it was adsorbed or replaced potassium in the crystal lattice. In organic-rich sedimentary rocks, anaerobic protein decomposition produces ammonia, which converts to ammonium ions in water. Ammonium remains stable in water under oxygen-deficient conditions, preventing oxidation to nitrites and nitrates (Kolodiy et al., 2009).

In this case, the inverse correlation of NH_4 with rSO_4×100/rCl, Cl/Br, and rNa/rCl reflects the hydrodynamically closed nature of deep aquifers in the Boryslav-Pokuttia region, favorable for its formation and preservation.

Inverse SO_4 correlation with rNa/rCl likely reflects sulphate-reduction processes characteristic of deep aquifers under hydrodynamically closed conditions.

4.2 Hydrogeochemical Features of Hydrocarbon Fields

To identify local characteristics, an analysis of the geochemical parameters of groundwater in contact with or in close proximity to hydrocarbon deposits in individual fields of the Boryslav-Pokuttia OGBA was conducted.

Blazhiv Oil Field. The field is located in the first structural fold tier in the northwestern part of the Boryslav-Pokuttia zone, 10 km away from the town of Staryi Sambir. Nine wells were drilled in the field, six of which penetrated the productive horizon of the Yamna Formation (Paleocene). Industrial oil inflows were obtained only from wells No. 3-BM and 3-Bl.

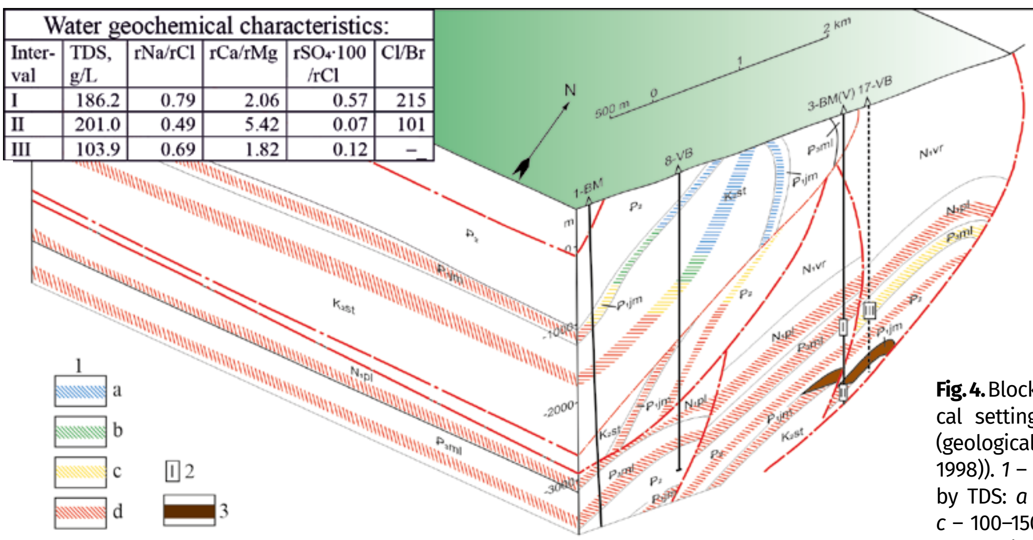
The geological structure of the field includes flysch deposits of the Stryi Formation (Upper Cretaceous), Paleocene (Yamna Formation), Eocene (Maniava, Vyhoda, Bystrytsia formations), Oligocene (Menilite Formation), and Miocene molasse deposits (Polianytsia and Vorotyshcha formations).

Industrial oil-bearing capacity is associated with thick massive sandstones of the Yamna Formation within the Blazhiv fold. In the southwestern part of the fold (well 3-BM) at 3,348–3,370 m depth, oil inflow was 3.8 m^3/day and gas 0.38 thousand m^3/day. Oil composition (% by weight): paraffins – 8.14, resins – 8.68, asphaltenes – 4.85, sulphur content – 2.0%. At 3,359 m depth, reservoir pressure was 43.29 MPa, temperature – 353 K (Ivaniuta, 1998).

Hydrogeochemical analysis of the field was based on 17 water samples. Some results were discarded as they reflected technical waters injected into lower horizons to maintain reservoir pressure at the final stages of development, showing significantly lower mineralisation and absence of metamorphosis compared to formation waters.

Natural waters composition in the field are predominantly Na-Cl, occasionally Ca-Na-Cl or Mg-Ca-Na-Cl. Depth-dependent increase in water TDS from 12.2 to 201.0 g/L indicates increasing hydrodynamic isolation with depth.

At depths exceeding 2,500 m, groundwater occurs under quasi-stagnant hydrodynamic conditions, resulting in high TDS (>150 g/l) and significant metamorphism. Low sulphate coefficient values reflect sulphate-reduction processes. Such hydrodynamic conditions with corresponding hydrogeochemical characteristics are associated with the distribution of oil deposits in the field (Fig. 4).



Water geochemical characteristics:

Interval	TDS, g/L	rNa/rCl	rCa/rMg	rSO_4·100/rCl	Cl/Br
I	186.2	0.79	2.06	0.57	215
II	201.0	0.49	5.42	0.07	101
III	103.9	0.69	1.82	0.12	–

Fig. 4. Block diagram of hydrogeochemical settings of the Blazhiv oil field (geological base according to (Ivaniuta, 1998)). *1* – distribution of groundwater by TDS: *a* – <50 g/L, *b* – 50–100 g/L, *c* – 100–150 g/L, *d* – >150 g/L; *2* – well perforation interval (penetration of the aquifer); *3* – oil reservoir

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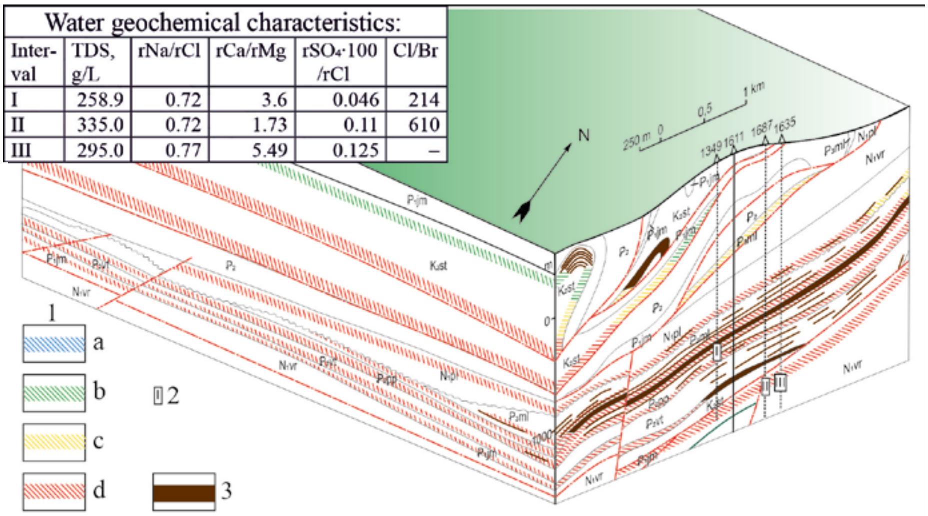


Water geochemical characteristics:

Interval	TDS, g/L	rNa/rCl	rCa/rMg	$rSO_4 \cdot 100$/rCl	Cl/Br
I	258.9	0.72	3.6	0.046	214
II	335.0	0.72	1.73	0.11	610
III	295.0	0.77	5.49	0.125	–

Fig. 5. Block diagram of the hydrogeochemical settings of the Boryslav oil and gas condensate field (geological base after (Ivaniuta, 1998)). *1* – distribution of groundwater by TDS: *a* – <50 g/L, *b* – 50–100 g/L, *c* – 100–150 g/L, *d* – >150 g/L; *2* – well perforation interval (aquifer penetration); *3* – oil reservoir

Boryslav Oil and Gas Condensate Field. The Boryslav field is located within the city of Boryslav and its surrounding areas in the southwestern part of the Boryslav-Pokuttia zone, encompassing the Oriv and Berehove nappes of the folded Carpathians.

The field comprises four distinct structural-tectonic elements, i.e. the Oriv and Berehove nappes, the Boryslav deep fold, and the Boryslav subthrust. These structures are imbricated in a lens-like arrangement from southwest to northeast. The field represents a complex of hydrocarbon reservoirs at various depths, distributed across different levels of the Boryslav Nappe (Fig. 5).

The geological structure of the field includes terrigenous flysch deposits from the Upper Cretaceous to the Oligocene, as well as Neogene molasse formations – the Polianytsia and Vorotyshcha suites. All of these formations are hydrocarbon-bearing (Ivaniuta, 1998).

The analysis of the field hydrogeochemical settings was based on the analysis of 62 water samples. Waters are predominantly Na-Cl and Ca-Na-Cl brines, except for shallow aquifers in the Oriv and Berehove nappes. Regardless of the depth of the aquifers, their lithological composition, stratigraphic complexes, or association with different structural-tectonic elements, formation waters are mostly medium to highly metamorphosed brines with TDS ranging from 49.9 to 374.0 g/L.

Oil and gas condensate reservoirs of the field are mainly located within zones of quasi-stagnant hydrodynamic conditions (characterized by highly mineralised and metamorphosed waters), which prevail at depths greater than 1,500 m (see Fig. 5).

Hydrocarbon reservoirs at shallower depths are less common, though locally hydrodynamically isolated structures may exist, providing favourable conditions for the formation and preservation of hydrocarbon accumulations. Additionally, waters in contact with oil reservoirs exhibit very low SO_4 contents, which, as noted above, result from ongoing sulphate reduction processes.

Oriv-Ulychno Oil Field. The field is located in the first structural fold tier in the northwestern part of the Boryslav-Pokuttia zone, 16 km away from the city of Drohobych. The Oriv and Ulychno reservoirs are developed individually, divided by a zone lacking industrially productive collectors. The Ulychno reservoir was penetrated by well No. 1-Ulychno. Within the 3,136–3,141 m interval of Menilite Formation deposits, an oil inflow of 8.6 t/d and a gas flow of 775 m^3/d were obtained. The Oriv reservoir was penetrated by well No. 21-Oriv. The productive interval is also the Menilite Formation, with oil production of 48.5 t/d and gas production of 12.35 thousand m^3/d within the 3,185–3,288 m interval (Ivaniuta, 1998).

The geological structure of the field includes flysch deposits of the Stryi, Yamna, Maniava, Vyhoda, Bystrytsia, and Menilite formations, as well as Neogene molasse deposits of the Polianytsia and Vorotyschcha formations.

Hydrogeochemical settings of the field were studied based on 21 water samples. Deep aquifer waters are predominantly Na-Cl, occasionally Ca-Na-Cl composition, while in shallower intervals, waters are mainly Ca-Na-SO_4-HCO_3 composition. Overall, groundwater TDS increases from 36.9 to 285.6 g/L with increasing depth. Quasi-stagnant hydrodynamic conditions, favorable for hydrocarbon preservation, begin at depths greater than 2,500 m within the structure (Fig. 6).

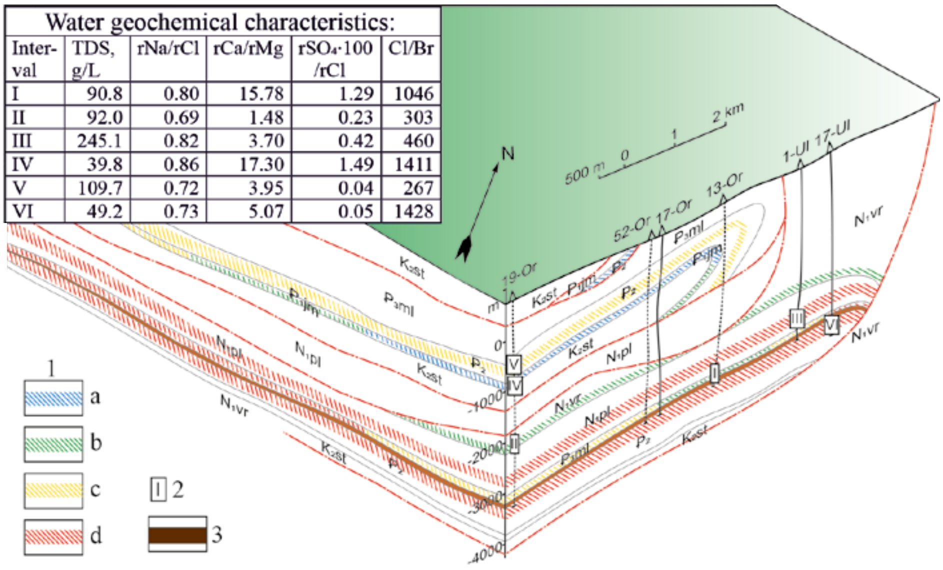


Fig. 6. Block diagram of hydrogeochemical settings at the Oriv-Ulychno oil field (geological basis according to (Ivaniuta, 1998)). *1* – groundwater distribution by TDS: *a* – <50 g/L, *b* – 50–100 g/L, *c* – 100–150 g/L, *d* – >150 g/L; *2* – well perforation interval (aquifer penetration); *3* – oil reservoir

Oriv reservoir waters are distributed across a wide stratigraphic range, from the Upper Cretaceous Stryi Formation to the Neogene Vorotyschcha Formation. No systematic variations in mineralisation or chemical composition of waters are observed either across different-aged strata or at varying aquifer depths.

A characteristic feature of formation waters from non-productive wells of the Ulychne reservoir is their low mineralisation and low degree of metamorphism. Formation waters from productive wells, despite being sampled from strata of different ages, are characterized by significantly higher mineralisation than those from non-productive wells. This contrast may indicate isolated hydrodynamic conditions favourable for hydrocarbon preservation.

Dolyna Oil Field. The Dolyna oil field is located in the Dolyna District of the Ivano-Frankivsk Region, 5 km from the city of Dolyna. Tectonically, it is in the first fold tier of the central part of the Boryslav-Pokuttia zone.

The geological structure includes flysch deposits of the Upper Cretaceous (Stryi Formation), Paleocene (Yamna Formation), Eocene (Maniava, Vyhoda, and Bystrytsia formations), Oligocene (Menilite Formation), and Neogene molasse deposits (Polianytia and Vorotyschcha formations).

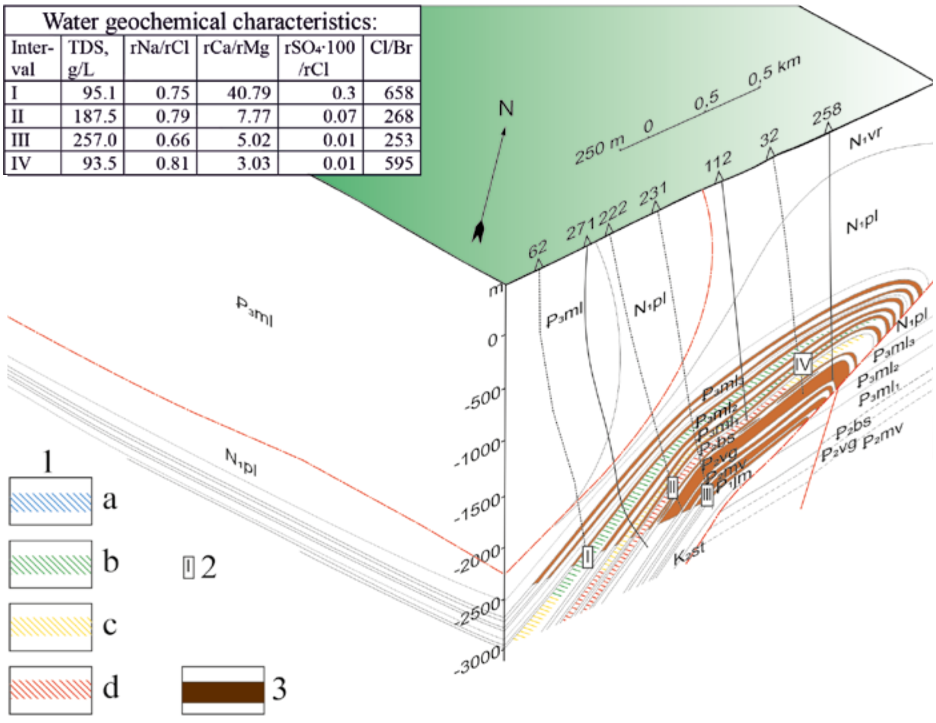
Hydrocarbons occur from the Vorotyschcha Formation of the Miocene to the Eocene, but commercial accumulations are found only in the Menilite, Bystrytsia, Vyhoda, and Maniava formations, where oil is hosted in sandstone and siltstone layers. Reservoirs share a common oil–water contact and are massive, layered dome-shaped tectonically sealed structures. The natural reservoir regime is elastic and gas-saturated. Initial recoverable reserves were 38,320 t of oil and 12,963 million m³ of dissolved gas (Ivaniuta, 1998).

Aquifers of the Dolyna field are associated with Eocene and Oligocene reservoir rocks. Sandstone interbeds of the Vorotyschcha series (lower Miocene) are also aquifers. Formation water sampling was conducted in the 2,760–3,083 m interval, corresponding to hydrocarbon-bearing horizons). Waters are predominantly of Na-Cl, Ca-Na-Cl with occasional Ca-Na-HCO_3-Cl composition. No clear correlation between TDS in water (61–257 g/L) and depth within this interval was identified.

As with most Boryslav-Pokuttia region fields, Dolyna oil accumulations occur under hydrodynamic conditions favorable for preservation, reflected in high mineralisation and metamorphism of formation waters and low sulphate contents (Fig. 7).

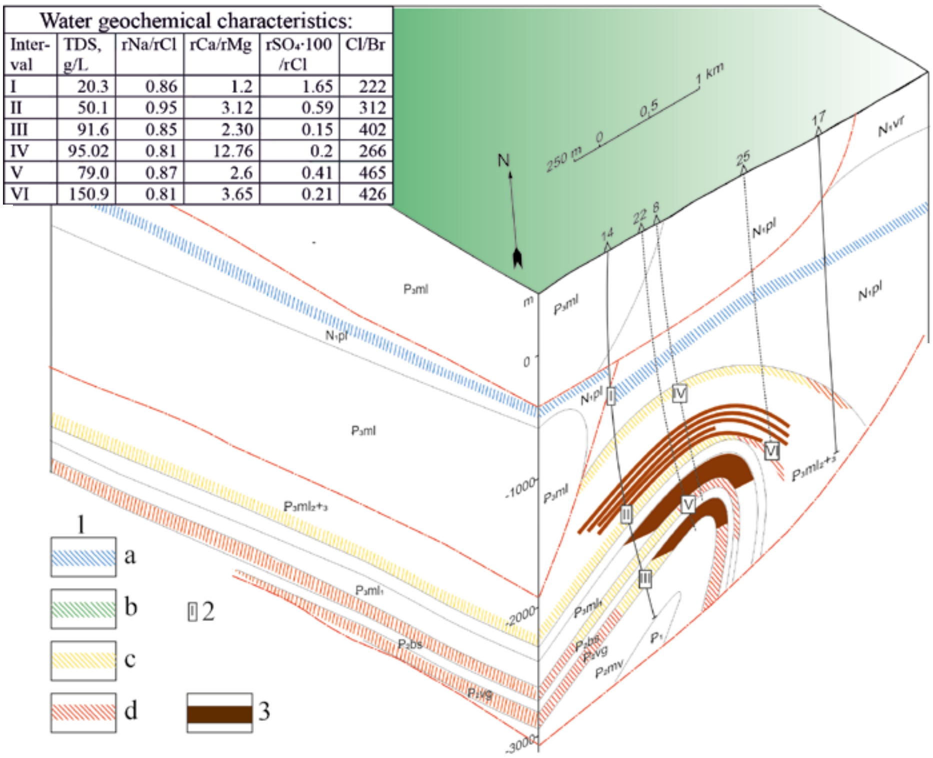
Strutyn Oil Field. The Strutyn oil field is located in Rozhniativ District, Ivano-Frankivsk Region, 7 km away from the town of Rozhniativ. Major oil accumulations are hosted in the Vyhoda Formation and the lower Menilite subformation of the North-Strutyn and Strutyn blocks, explored by 36 wells (33 in lower Menilite reservoirs, 2 in Vyhoda Formation, and one intersecting both).

Tectonically, the field is associated with the Upper-Strutyn fold – an asymmetrical north-west trending anticline measuring 15×3.5 km. The geological structure of the Upper-Strutyn fold includes flysch deposits of the Upper Cretaceous (Stryi Formation), Paleocene, Eocene (Maniava, Vyhoda, Bystrytsia formations), Oligocene (Menilite Formation), and Neogene molasse deposits (Polianytsia and Vorotyschcha formations) (Ivaniuta, 1998).



Inter-val	TDS, g/L	rNa/rCl	rCa/rMg	rSO₄·100 /rCl	Cl/Br
I	95.1	0.75	40.79	0.3	658
II	187.5	0.79	7.77	0.07	268
III	257.0	0.66	5.02	0.01	253
IV	93.5	0.81	3.03	0.01	595

Fig. 7. Block diagram of hydrogeochemical settings at the Dolyna oil field (geological basis according to (Ivaniuta, 1998)). *1* – groundwater distribution by TDS: *a* – <50 g/L, *b* – 50–100 g/L, *c* – 100–150 g/L, *d* – >150 g/L; *2* – well perforation interval (aquifer penetration); *3* – oil reservoir



Inter-val	TDS, g/L	rNa/rCl	rCa/rMg	rSO₄·100 /rCl	Cl/Br
I	20.3	0.86	1.2	1.65	222
II	50.1	0.95	3.12	0.59	312
III	91.6	0.85	2.30	0.15	402
IV	95.02	0.81	12.76	0.2	266
V	79.0	0.87	2.6	0.41	465
VI	150.9	0.81	3.65	0.21	426

Fig. 8. Block diagram of hydrogeochemical settings at the Strutyn oil field (geological basis according to (Ivaniuta, 1998)). *1* – groundwater distribution by TDS: a – <50 g/L, b – 50–100 g/L, c – 100–150 g/L, d – >150 g/L; 2 – well perforation interval (aquifer penetration); 3 – oil reservoir

Aquifers are developed within Eocene deposits (Vyhoda and Bystriv formations), Oligocene (Menilite Formation), and Miocene (Polianytsia and Vorotyschcha formations). Sampling was conducted at depths ranging from 810 m to 3,555 m. Waters from shallow horizons are predominantly of Ca-Na-HCO_3-Cl, whereas deeper waters shift to Na-Cl or Ca-Na-Cl composition (Fig. 8).

A clear trend of increasing water mineralisation with depth is observed throughout the section, irrespective of stratigraphic horizon. Waters with TDS ranging from 7 to 35 g/L occur within the 810–2,650 m interval and likely contain mixtures of paleo- and modern infiltrated waters.

Oil accumulations are delineated by aquifers in which TDS exceeds 50 g/L and waters exhibit a pronounced degree of metamorphism.

Bytkiv-Babche Oil and Gas Condensate Field. The Bytkiv-Babche oil and gas condensate field is located in the Nadvirna District, Ivano-Frankivsk Region, 7 km away from the town of Nadvirna, and forms a partof Bytkiv oil-industrial area.

Structurally and tectonically, the field is associated with the Bytkiv fold group in the central part of the Borislav-Pokuttia subzone of the Inner Carpathian Foredeep. It is overlain by thrust, strongly deformed Paleogne and Upper Cretaceous deposits of the Skyba Zone of the Carpathian Folded Belt. The field features overthrust-listric tectonic style. Hydrocarbon reservoirs are localized within the Berehova thrust, within the first and second fold tiers of the Borislav-Pokuttia zone.

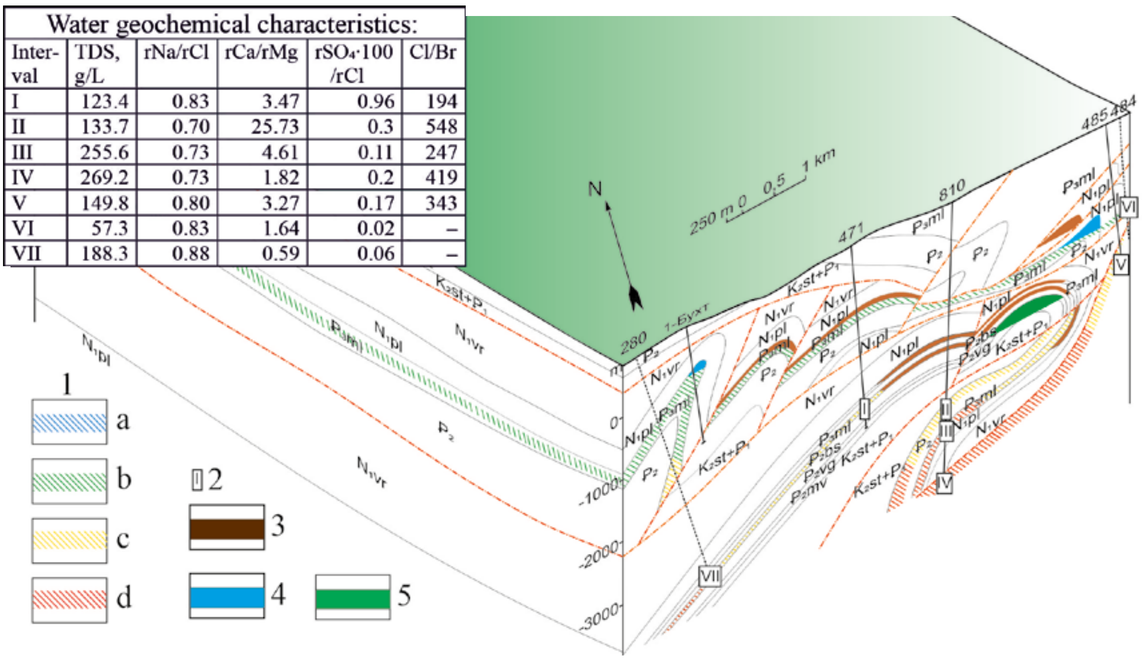
Hydrogeochemical analysis was carried out on 57 water samples. Aquifers are hosted in porous flysch reservoirs of the Upper Cretaceous (Stryi Formation, K_2st), Eocene (Maniava ₽$_2$mv, Vyhoda ₽$_2$vg formations), and Oligocene (Menilite Formation, ₽$_3$ml). Waters are predominantly of Na-Cl, less commonly Ca-Na-Cl composition. TDS ranges from 6 to 299 g/L and shows no systemic dependence with the stratigraphy or depth. Waters are generally metamorphosed, as indicated by rNa/rCl ratios lower than of seawater and slightly elevated rCa/rMg values; this pattern is also observed in weakly mineralised waters.

Unlike the previously analyzed fields, hydrocarbon accumulations (oil, gas condensate, gas) at the Bytkiv-Babche field are mostly associated with waters exhibiting TDS of 50–100 g/L (Fig. 9). According to Cl/Br genetic ratios, the majority of waters fall within the evaporitogenesis interval, extending from Black Sea water to the onset of halite deposition. Low rSO_4×100/rCl values in contour and basal waters indicate active sulphate reduction processes.

5. Conclusions

In the Boryslav-Pokuttia OGBA, principal factors controlling the hydrogeochemical characteristics of aquifers are paleohydrogeological evolution and the level of hydrogeological isolation. Prolonged and intensive dynamo-elisional processes, thrust-folded structure, numerous disjunctive faults, and the presence of salt-bearing deposits have resulted in the formation of a complex hydrogeochemical system that lacks distinct structural zonation.

Most aquifer waters are highly mineralised Na-Cl brines, Ca-Na-Cl or Mg-Ca-Na-Cl brines occur less commonly. Genetically, these are residual sedimentary brines derived from salt basins at various stages of concentration. Brines formed through leaching of salt-bearing molasses occur less frequently. The first type is distinguished by elevated concentrations of trace elements and distinctive genetic indicators.



Water geochemical characteristics:

Interval	TDS, g/L	rNa/rCl	rCa/rMg	rSO_4·100/rCl	Cl/Br
I	123.4	0.83	3.47	0.96	194
II	133.7	0.70	25.73	0.3	548
III	255.6	0.73	4.61	0.11	247
IV	269.2	0.73	1.82	0.2	419
V	149.8	0.80	3.27	0.17	343
VI	57.3	0.83	1.64	0.02	–
VII	188.3	0.88	0.59	0.06	–

Fig. 9. Block diagram of hydrogeochemical settings at the Bytkiv-Babchyn oil and gas condensate field (geological basis according to (Ivaniuta, 1998)). *1* – groundwater distribution by TDS: *a* – <50 g/L, *b* – 50–100 g/L, *c* – 100–150 g/L, *d* – >150 g/L; *2* – well perforation interval (aquifer penetration); *3* – oil reservoir; *4* – gas reservoir; *5* – gas condensate reservoir

The presence of highly mineralised waters in flysch reservoirs is attributed to their expulsion from clayey-salt Miocene molasses and the replacement of ancient sedimentary or infiltration waters during the dynamo-elisional stage of hydrogeological evolution. Mixtures of these three water types predominate.

Less frequently, aquifers contain mineralised and saline waters (TDS < 30 g/L) enriched in HCO_3 and SO_4 contents. Geochemically, these are identified as mixtures of ancient or modern infiltration waters with sedimentary thalassogenic ones. These waters are found within zones of active or restricted water exchange at depths up to 2,000–2,500 m.

The final stage influencing groundwater hydrogeochemistry was metamorphism, manifested by depletion of Na and Mg as a result of ion-exchange reations with water-bearing rocks. These processes developed only in hydrogeologically closed structures and depended on the duration and intensity of water-rock interaction.

The formation of hydrocarbon accumulations in the Boryslav-Pokuttia OGBA is associated with the final cycle of its paleohydrogeological development – the dynamo-elision stage. During this stage, highly mineralised brines from clayey salt-bearing molasse were expelled into reservoir rocks. These brines are characterized by specific geochemical parameters that minimize the biochemical oxidation of hydrocarbons. During the dynamo-elision stage, hydrodynamically closed traps were formed, which contributed to the mechanical preservation of the accumulations.

Indirect hydrogeochemical indicators of hydrocarbon potential in the Boryslav-Pokuttia region include high mineralisation and water metamorphism, Na-Cl or Ca-Na-Cl composition, enrichment in microcomponents, and low SO_4 concentrations. Collectively, these characteristics indicate a closed hydrogeodynamic system offering favourable conditions for the formation and preservation of hydrocarbon accumulations.

Метою цього дослідження було вивчення гідрогеохімічних характеристик водоносних горизонтів Бориславсько-Покутського нафтогазоносного району, дослідження ґенези підземних вод та їх впливу на умови формування та збереження вуглеводневих скупчень, а також ідентифікація гідрогеохімічних критеріїв нафтогазоносності. Методологія дослідження спиралася на статистичну та графічну обробку архівних даних і подальшу інтерпретацію отриманих результатів. Також було застосовано палеогідрогеологічний аналіз.

Було встановлено, що основними факторами, що контролюють гідрогеохімічні параметри водоносних горизонтів у цьому районі, є палеогідрогеологічна еволюція та ступінь гідрогеологічної ізоляції. Тривалий та інтенсивний динамо-елізійний розвиток, складчасто-насувна будова, численні диз'юнктивні розломи та наявність соленосних відкладів призвели до формування складної гідрогеохімічної системи, яка не має чіткої зональності.

Генетично більшість вод є седиментогенними залишковими розсолами евапоритових басейнів або розсолами, що утворилися внаслідок вилуговування соленосних моласових відкладів, а також їх сумішами. На невеликих глибинах зрідка трапляються мінералізовані та солоні води, збагачені гідрокарбонатами та сульфатами. На основі геохімічних показників ці води ідентифікуються як суміші давніх або сучасних інфільтраційних вод із седиментогенними таласогенними водами.

Непрямими гідрогеохімічними критеріями нафтогазоносності Бориславсько-Покутського нафтогазоносного району є такі: висока мінералізація та метаморфізація вод, їх Na-Cl або Ca-Na-Cl склад, збагачення мікроелементами та мікрокомпонентами, а також низька концентрація сульфатів. У сукупності ці ознаки вказують на замкнуту гідродинамічну систему, сприятливу для формування та збереження скупчень вуглеводнів.

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