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POLLUTION OF UNDERGROUND WATER IN THE ODRA VALLEY IN THE REGION OF WROCLAW

Chemical composition of quaternary underground waters in the Odra Valley has been studied. A modified method of hydrochemical background determination has been successfully applied. In almost all of the area investigated the underground waters are so polluted that they cannot be used for drinking purposes. In the whole area investigated agricultural sources pollute underground waters, whereas industrial centres of pollution are in the industrial area and infiltration intake.

NOTATION

- BH – hydrochemical background,
 \bar{c} – arithmetical mean,
 c_{ei} – concentration of i -th species in infiltrating water from soil,
 c_{hi} – concentration of i -th species in surface overland flow and throughflow,
 c_{ri} – concentration of i -th species in precipitation,
 E – evaporation and evapotranspiration, m^3/m^2 a year,
 H – overland flow and throughflow, m^3/m^2 a year,
 I_e – infiltration from soil, m^3/m^2 a year,
 M_i – quantity of i -th species, g/m^2 a year,
 M_{ai} – quantity of i -th species sorbed from atmosphere,
 M_{di} – quantity of i -th species in emitted gasses (for example denitrification),
 M_{ei} = $I_e c_{ei}$ – quantity of i -th species in water infiltrating from soil,
 M_{fi} – quantity of i -th species in fertilizers,
 M_{hi} = $H c_{hi}$ – quantity of i -th species in overland flow and throughflow,
 M_{mi} – quantity of i -th species due to mineralization of organic matter,
 M_{ri} = $P c_{ri}$ – quantity of i -th species in precipitation,
 M_{si} – quantity of i -th species in dust sediments,
 M_{uIi} – quantity of i -th species in inflow of underground water,
 M_{uIIi} – quantity of i -th species in outflow of underground water,
 M_{vi} – quantity of i -th species in crops,

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- P – annual precipitation, m^3/m^2 a year,
 Q_{uI} – inflow of underground water,
 Q_{uII} – outflow of underground water,
 σ – standard deviation,
 ΔZ – change of soil moisture, m^3/m^2 a year.

1. INTRODUCTION

Underground waters are the main source of drinking water. A large amount of underground waters comes from shallows aquifer and that is why they are very susceptible to pollutions. In the Odra Valley, where the present study of chemical composition of underground waters has been carried out, such a situation occurs. The underground waters of quaternary layer were studied in the Odra Valley from

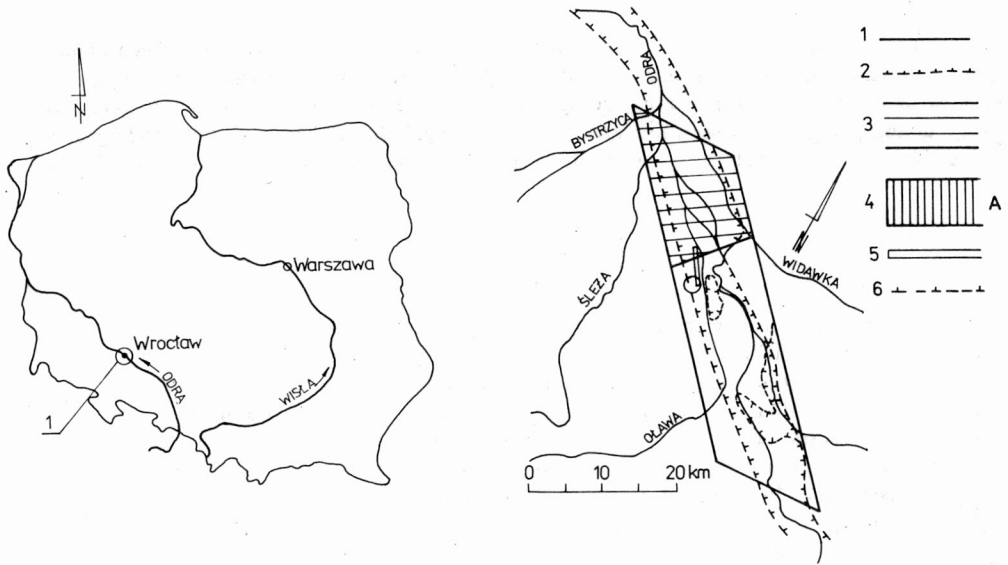


Fig. 1. Sketch of the area investigated

1 – boundary of the area, 2 – boundary of the paravalley, 3 – Wroclaw area, 4 – industrial region A, 5 – infiltration intake, 6 – forest area

Brzeg Opolski up to the northern perimeter of Wroclaw. The area investigated is shown in fig. 1. It comprises an agricultural area (it occupies the major part of the area investigated), industrially polluted area (4), Wroclaw city area (3), infiltration water intake (5), and forest area (6). A smelter and power plant in area A are situated in immediate vicinity of the south part of infiltration intake I.

The chemistry of underground water in the Odra Valley has not been fully studied yet. Some information can be found in a monograph by RÓŻYCKI [1]

devoted to the hydrogeology of this region, papers [2], [3] and unpublished reports about pollution of underground waters. Also JANIÁK [4] describes aggressive interaction of underground waters with the foundations of buildings.

Quaternary aquifer consists of sands of different grain sizes which form a layer of average thickness of 3 m and up to 20 m in the vicinity of the valley line. The water level in 63 of the studied wells varied from 0.5 m to 3 m below land surface (bls) and in 3 wells it ranged from 4 m to 8 bls. The depth of most of the wells varied from 4 m to 6 m. For 9 wells of infiltration intake it was from 8 m to 12 m, and for two others from 10 m to 20 m.

The aim of this paper is to apply the modified method of hydrochemical background determination in order to indicate the polluted areas of underground water and the sources of pollution.

2. METHODS

The quaternary underground water samples were taken five times in the period from December 1982 to November 1983, twice in winter when the soil was frozen, once in spring when the water level was high, once in summer and once in autumn during a long-lasting drought.

Chemical analyses were carried out according to Polish Standards (close to WHO methods). Heavy metals were determined by means of the Atomic Absorption Spectroscopy method [2]. The hydrochemical background was determined from differential distribution curves of concentration of each chemical element in underground waters. The analysis of integral and differential curves of concentration distribution of the elements occurring in the area investigated showed that the curves are typical of heterogeneous distribution. An example of the differential distribution curve of chromium concentration is shown in fig. 2. This curve, as well as those for other chemical elements, is the sum of concentration distributions. The first maximum is characteristic of unpolluted underground waters. It was found by means of the χ^2 test that the concentration distribution within the first maximum (for $c \leq c_I$ in fig. 2) is normal. The results of the χ^2 test are presented in tab. 1. The hydrochemical background (maximal concentration of unpolluted underground waters) was calculated from the formula

$$BH = \bar{c} + 3|\sigma|. \quad (1)$$

The polluted area of underground waters was determined as a circumference of the area in which the arithmetical mean of the concentrations during the whole period of investigations is greater than the hydrochemical background calculated by the above described method. In table 2 there are presented calculated values of hydrochemical background as well as Polish and WHO Standards for drinking water.

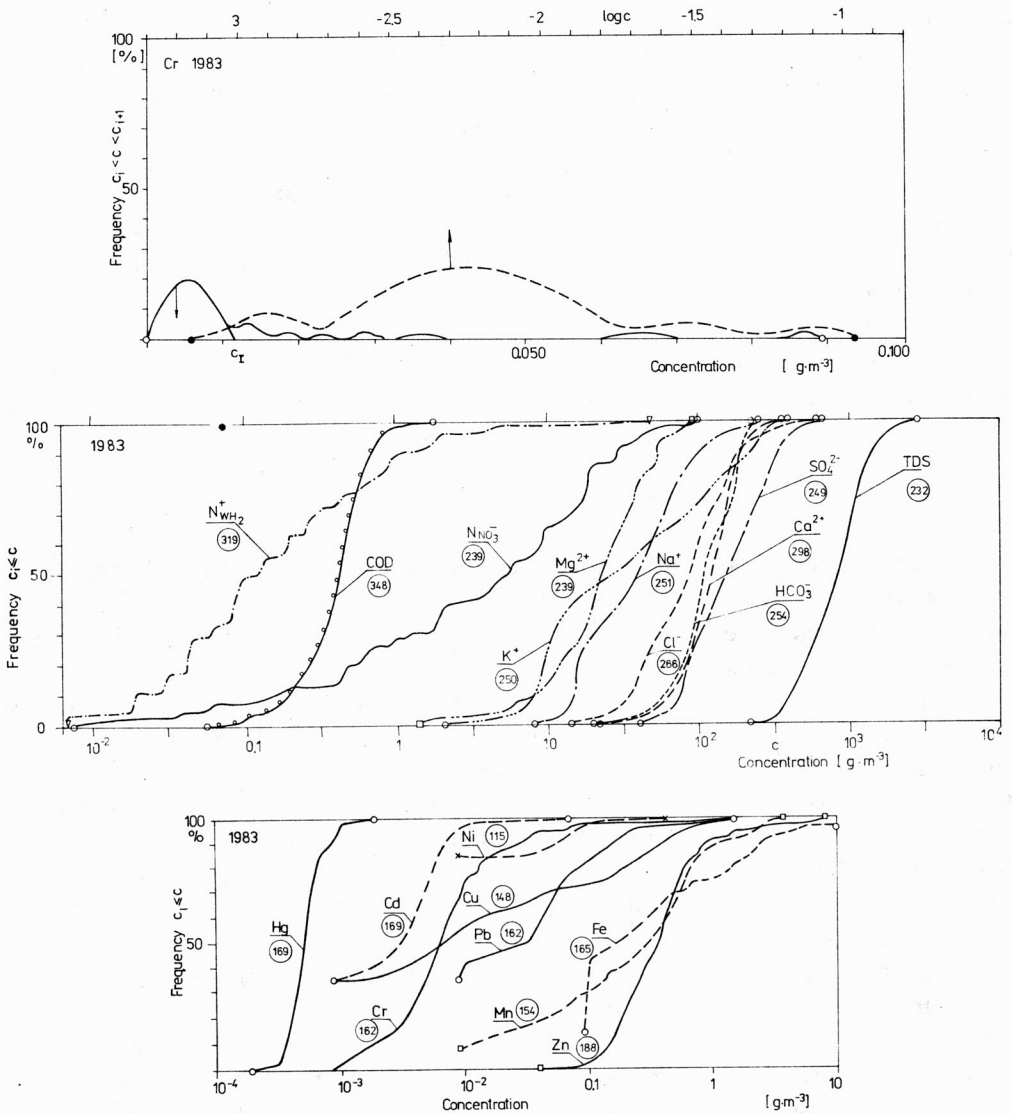


Fig. 2. Distribution of concentrations of the studied determinations
 (n) — number of samples

The concentration of infiltration substance from the rural soil was calculated on the basis of water and ion mass balances (fig. 3).

The water and mass of each constituent of the soil were balanced according to the following equations:

$$P = H + E + I_e + \Delta Z, \quad (2)$$

Table 1

Test χ^2 for first maximum. Normal distribution

Species	χ^2	χ^2_α $\alpha = 0.05$	P	Number of samples Σn	$n_i/\Sigma n$ %
TDS	4.49	5.49	0.12	232	41
Hg	0.47	5.49	0.80	162	86
Cr	4.18	7.82	0.25	160	78
Zn	1.14	7.82	0.77	188	54
SO ₄ ⁻	5.47	11.7	0.40	249	45
Cl ⁻	1.72	9.48	0.78	266	36
N ⁻ _{NO₃}	0.47	3.84	0.49	239	16
HCO ₃ ⁻	4.82	9.48	0.32	254	61
Na ⁺	0.29	7.82	0.42	254	36
K ⁺	1.80	7.82	0.42	250	36
Ca ⁺⁺	4.06	11.07	0.55	298	33
Mg ⁺⁺	3.14	5.49	0.21	239	84

n_i — number of samples in the interval of the first maximum; P — probability; α — level of coincidence.

Table 2

Hydrochemical background of quaternary underground water of the investigated area and standards for drinking water

Species	Hydrochemical background (ROSZAK [3])	Standards for drinking water	
		Polish, 1977	WHO, 1983
Cd	g Cd m ⁻³	0.0089	0.05
Cr	g Cr m ⁻³	0.013	0.05
Cu	g Cu m ⁻³	.	0.5
Hg	g Hg m ⁻³	0.00084	0.001
Ni	g Ni m ⁻³	.	0.1
Pb	g Pb m ⁻³	0.12	0.1
Zn	g Zn m ⁻³	0.39	5.0
Fe	g Fe m ⁻³	.	0.5
Mn	g Mn m ⁻³	.	0.1
Na ⁺	g Na ⁺ m ⁻³	35.5	.
K ⁺	g K ⁺ m ⁻³	26.3	.
Ca ⁺⁺	g Ca ⁺⁺ m ⁻³	134.0	.
Mg ⁺⁺	g Mg ⁺⁺ m ⁻³	521	.
NH ₄ ⁺	g N _{NH₄} ⁺ m ⁻³	.	0.5
NO ₃ ⁻	g N _{NO₃} ⁻ m ⁻³	1.0	10.0
Cl ⁻	g Cl ⁻ m ⁻³	81.0	300.0
SO ₄ ⁻	g SO ₄ ⁻ m ⁻³	160.0	200.0
HCO ₃ ⁻	g HCO ₃ ⁻ m ⁻³	419.0	.
TDS	kg · m ⁻³	0.8	0.6
pH	.	.	6.5–8.5

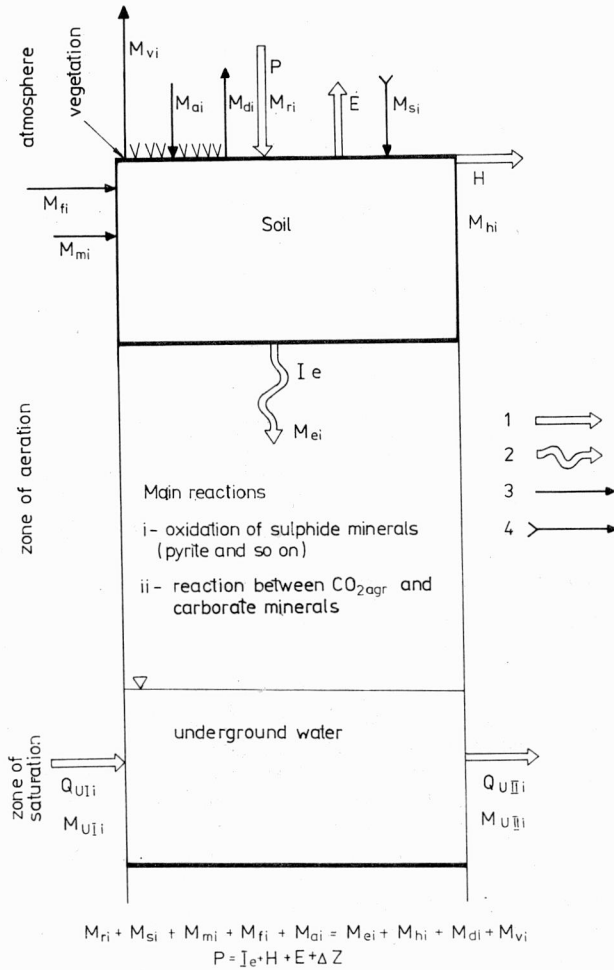


Fig. 3. Scheme of the processes in the first water layer

1 - precipitation, evaporation and evapotranspiration, surface runoff and interflow, ground water flow, 2 - infiltration, 3 - fertilization, absorption and evolution of gas to yield crops, 4 - sedimentation of dust.

$$M_{ri} + M_{fi} + M_{mi} + M_{ai} + M_{si} = M_{ei} + M_{vi} + M_{di} + M_{hi}. \quad (3)$$

In the mass balance the following values are neglected:

Quantity of dust in the rural area.

Quantity of M_{hi} in overland flow and throughflow. The overland flow in rural soil is not great and species concentration in it is small.

The mass balance of soil constituents is presented in tab. 3. The determination of the M_{mi} , M_{hi} , M_{ai} , and M_{di} quantities in large areas of various cultivations is not easy. Therefore, first the values of the ratios $M_{ei}/(M_{fi} + M_{mi} + M_{ri})$ for nitrate nitrogen, potassium and phosphorus were calculated according to PONDEL [5]. Next,

Table 3

Mass balance in soil

1	$M_{eN}/(M_{fN} + M_{mN} + M_{rN})$ kg N ha ⁻¹ y. ⁻¹	0.026–0.46 [5]; 0.32 [13]	
	$M_{eK}/(M_{fK} + M_{mK} + M_{rK})$ kg K ₂ O ha ⁻¹ y. ⁻¹	0.0023–0.61 [5]	
	$M_{eP}/(M_{fP} + M_{mP} + M_{rP})$ kg P ₂ O ₅ ha ⁻¹ y. ⁻¹	0.000004–0.0036 [5]	
2	M_{rN}	kg N ha ⁻¹ y. ⁻¹	10 [5], [13]; 15 [14]; 22–55 [15]
	M_{rK}	kg K ₂ O ha ⁻¹ y. ⁻¹	2.2–5.5
	M_{rMg}	kg Mg ha ⁻¹ y. ⁻¹	0.6–2.6
	M_{rNa}	kg Na ha ⁻¹ y. ⁻¹	1.5–4.5
	M_{rZn}	kg Zn ha ⁻¹ y. ⁻¹	0.50–5.68 [15]
	M_{rCd}	kg Cd ha ⁻¹ y. ⁻¹	0.006–0.017 [15]
	M_{rCu}	kg Cu ha ⁻¹ y. ⁻¹	0.48–2.52 [15]
	M_{rNi}	kg Ni ha ⁻¹ y. ⁻¹	0.018–0.052 [15]
	M_{rPb}	kg Pb ha ⁻¹ y. ⁻¹	0.19–2.09 [15]
	M_{rSO_4}	kg SO ₄ ⁼ ha ⁻¹ y. ⁻¹	66.2–148 [15]
3	M_{mN}	kg N ha ⁻¹ y. ⁻¹	30 [5], [13]; 30–60 [14]
4	M_{mK}	kg K ₂ O ha ⁻¹ y. ⁻¹	40 [5]
5	M_{mP}	kg P ₂ O ₅ ha ⁻¹ y. ⁻¹	15 [5]
Values assumed for calculation			
6	M_{rN}	kg N ha ⁻¹ y. ⁻¹	10
	M_{rK}	kg K ₂ O ha ⁻¹ y. ⁻¹	5
7	M_{mN}	kg N ha ⁻¹ y. ⁻¹	30
8	M_{mK}	kg K ₂ O ha ⁻¹ y. ⁻¹	40
9	M_{mP}	kg P ₂ O ₅ ha ⁻¹ y. ⁻¹	15
10	I_e	m ³ m ⁻² y. ⁻¹	0.53–1.35

the representative values of M_{rN} , M_{rK} , M_{mN} , M_{mK} , M_{mP} were chosen and from an inquiry the values of M_{fN} and M_{fK} and M_{fP} were calculated. The quantities of nitrogen, potassium and phosphorus given in tab. 4 are products of the ratio $M_{ei}/(M_{fi} + M_{mi} + M_{ri})$ (the first line in table 4) and the sum of suitable quantities (line 6+7–9). The quantities of TDS, Cl⁻, SO₄²⁻, Ca, Mg, B, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni and Zn, calculated on the basis of results of an inquiry as well as information about the composition of fertilizers [6], [7] and their quantities taken by plants [7], are given in tab. 4.

The effective infiltration I_e , calculated from Turc's formulae and based on meteorological data for yearly precipitation and mean temperatures in Wrocław and Oława, varied from 0.039 m³/m² a year to 0.136 m³/m² a year. The calculated range of concentrations of substances in infiltration water from the soil is presented in tab. 5.

Table 4

Substance loads infiltrating from the soil
to underground water

Species	Load ($\text{g m}^{-2} \text{y}^{-1}$)
$\text{N} = \text{N}_{\text{NO}_3^-} + \text{N}_{\text{NH}_4^+}$	0.313–5.64
K	0.035–8.24
Ca**	1.60*–75.2
Mg**	0.64*–28.1
Na**	0.53–0.93
Cl**	5.74
S** as SO_4^{2-}	15.3–23.5
TDS	21.0*–33.4* 212–225**
B	0.042
Cd**	0.0021–0.0037
Co**	0.00094
Cr**	0.025–0.10
Cu	0.215
Hg**	0.004–0.015
Mn	0.055
Mo	0.00007
Ni**	0.0035–0.0069
Pb**	0.019–0.209
Zn	0.06–0.745

* without soil lime; ** without the amount assimilated by plants.

Table 5

Chemical composition of ground water of the rural area

Species	Concentration (min-max)				
	Lysimeter water	Drainage water	Ground water in the forest area	Calculated	
	[16]				
1	2	3	4	5	
Na**	g Na m^{-3}	2.1–23.0	9.4–57.0	0.3–14.0	4.0–22.1
K	g K m^{-3}	0.1–53.0	0.0–165	0.2–13.8	0.25–196
Ca**	g Ca m^{-3}	18.3–219	66.0–502	.	11.9*–1418
Mg**	g Mg m^{-3}	6.7–36.0	5.0–53.4	.	4.9*–530
NO_3^-	g N m^{-3}	0.9–118.0	0.0–31.3	0.0–109	2.4–134***
NH_4^+	g N m^{-3}	0.1–10.4	0.0–1.6	0.2–143	.
Cl^- **	$\text{g Cl}^- \text{m}^{-3}$	20.7–36.4	18.4–165	tr.–34.5	43.5–141
SO_4^{2-} **	$\text{g SO}_4^{2-} \text{m}^{-3}$	11.3–45.3	14.0–370	tr.–800	11.6–559

		1	2	3	4	5
HCO ₃ ⁻	g HCO ₃ ⁻ m ⁻³		45.6-132.2	.	0.1-245	.
TDS	kg m ⁻³		.	.	.	0.26*-0.63* 1.61-5.36
pH			5.8-7.5	5.5-8.1	5.8-7.2	.
B	g B m ⁻³		.	.	.	≤ 0.08
Cd**	g Cd m ⁻³		.	.	.	0.03-0.36
Co**	g Co m ⁻³		.	.	.	≤ 0.022
Cr**	g Cr m ⁻³		.	.	.	0.07-0.60
Cu	g Cu m ⁻³		.	.	.	≤ 4.1
Hg**	g Hg m ⁻³		.	.	.	0.03-0.36
Mn	g Mn m ⁻³		.	.	.	≤ 1.0
Mo	g Mo m ⁻³		.	.	.	0.0
Ni**	g Ni m ⁻³		.	.	.	0.026-0.16
Pb**	g Pb m ⁻³		.	.	.	0.14-5.0
Zn	g Zn m ⁻³		.	.	.	0.44-14.1

* - without soil lime; ** - without the amount assimilated by plants; *** - $N = N_{NO_3^-} + N_{NH_4^+}$

3. RESULTS AND DISCUSSION

Chemical composition of underground water (tab. 6) is of great diversity. It is typical of underground waters of a valley and paravalley and is in agreement with the results obtained by BŁASZCZYK [8] and GÓRSKI [9]. The investigated underground waters are of multi-ions type, the dominant ions being calcium and sulphate or chloride and occasionally potassium, sodium and nitrate. Only from a small part of the investigated area water can be used for drinking purposes either directly or after simple treatment (iron and manganese removal). Waters occurring in the remaining area are not suitable for drinking because concentrations of TDS, nitrate, seldom sulphate and sometimes chromium, mercury, lead and chloride exceed the recommended limits. These areas are presented in fig. 4.

The areas in which the mean concentrations exceed the value of hydrochemical background are shown in fig. 5. The mean concentrations of the following heavy metals: Hg, Cr, Pb, Zn exceed the hydrochemical background in the industrial area A and infiltration intake and in the case of zinc also in the agricultural area. My previous papers [2], [3], hydrogeological sketch (fig. 6) and hydrochemical cross section (fig. 7) prove that the smelter and electrical power plant (area A) are the sources of underground water pollution with mercury, chromium, lead and zinc in the area A and infiltration intake. Thus the presence of mercury, lead and chromium in underground water is an indicator of industrial pollution. Zinc and other trace

Table 6

Chemical composition (Dec. 1982–Nov. 1983) of quaternary underground waters in the investigated area (ROSZAK [3])

Species	Concentration (min–max), g · m ⁻³		
	All results excluding those for region A and infiltration intake	Region A	Infiltration waters' intake
Cr	0.0006–0.010	0.0010–1.08	0.0020–0.0870
Zn	0.10–2.95	0.05–1.09	0.12–8.46
Cd	≤ 0.0009–0.015	≤ 0.0009–0.01	≤ 0.0009–0.015
Cu	≤ 0.0009–0.04	≤ 0.0009–0.31	0.15–1.46
Ni	≤ 0.0009–0.39	≤ 0.0009–0.11	≤ 0.0009–0.22
Pb	≤ 0.0009–0.13	≤ 0.0009–0.20	≤ 0.009–1.43
Hg	0.00028–0.00080	0.00032–0.00140	0.00028–0.00184
Fe	≤ 0.09–5.76	≤ 0.09–1.5	0.1–25.0
Mn	≤ 0.009–2.22	≤ 0.009–3.21	0.04–3.61
Na ⁺	8.9–139.1	1.26–244.9	11.9–51.2
K ⁺	4.1–348.6	7.5–153.6	6.6–112.2
Ca ⁺⁺	41.1–238.5	100.2–285.6	64.1–112.2
Mg ⁺⁺	3.6–81.4	12.2–38.7	3.6–22.6
N _{NO₃} ⁻	≤ 0.009–100.0	0.6–60.0	≤ 0.009–2.0
Cl ⁻	15.3–620.8	38.0–470.4	33.7–110.3
SO ₄ ⁼	60.5–482.4	30.7–358.6	7.7–394.1
HCO ₃ ⁻	61.5–629	134–624	97.5–232
TDS	226–2026	462–2581	308–771
pH	5.9–7.55	5.7–7.5	5.9–7.3
phenol	0.001–0.015	0.004–0.010	≤ 0.0009–0.010
γHCH + DDT	0.00003–0.00006	≤ 0.000009–0.0098	0.00001–0.00008

elements (B, Cd, Co, Cr, Mn, Mo and Ni) are introduced to cultivated soil with phosphatic fertilizers and soil lime or substances added to them [6], [7]. Trace elements, except boron and magnesium, are very hazardous to environment after being released to soil [10], [11]. Their ability to migrate varies [12]. Boron and zinc migrate very easily; chromium, cadmium, cobalt, copper, manganese and nickel, less easily, whereas molybdenum does not migrate in soil water (pH 6.0–7.5 and redox potential $E_h = 200$ –300 mV).

The maximum zinc concentration (tab. 5), calculated as the sum of its input from the fertilizer and precipitation, exceeds the hydrochemical background. It indicates that agriculture is responsible for pollution of underground waters with zinc in some parts of the area investigated.

Mean concentrations of nitrate, chloride and TDS exceed the hydrochemical background in the prevailing part of the area, whereas potassium and sodium in the

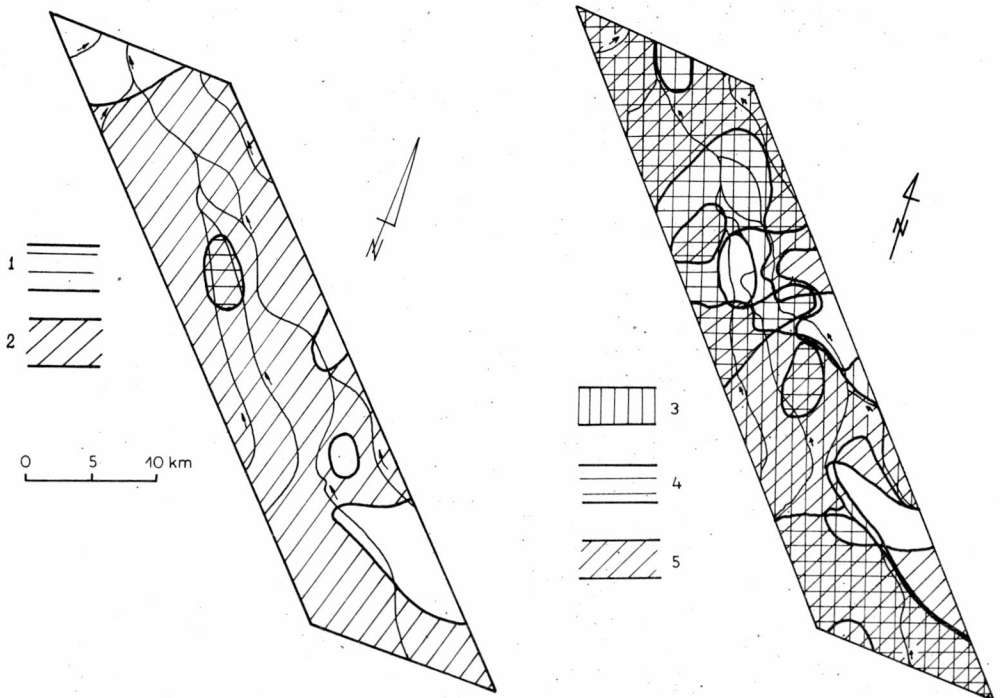


Fig. 4. Hydrochemical map of the area investigated. The marked regions are characterized by the following concentrations:

- 1 - $\text{Hg} > 0.001 \text{ gm}^{-3}$ or $\text{Cd} > 0.05 \text{ gm}^{-3}$ or $\text{Cr} > 0.05 \text{ gm}^{-3}$ or $\text{Pb} > 0.1 \text{ gm}^{-3}$ or $\text{Cu} > 0.5 \text{ gm}^{-3}$ or $\text{Zn} > 5.0 \text{ gm}^{-3}$,
- 2 - $\text{Fe} > 0.5 \text{ gm}^{-3}$ or $\text{Mn} > 0.1 \text{ gm}^{-3}$,
- 3 - $\text{TDS} > 0.6 \text{ kg m}^{-3}$,
- 4 - $\text{SO}_4^{2-} > 200 \text{ gm}^{-3}$ or $\text{Cl}^- > 300 \text{ gm}^{-3}$,
- 5 - $\text{N}_{\text{NO}_3} > 10 \text{ gm}^{-3}$

prevailing part of the agricultural area and sulphate in nearly a half of the area. High nitrate concentrations in the Wrocław area are due to their inflow from the rural area to the zone of drainage. Maximum concentrations of nitrate, potassium, chloride, sulphate and sodium, calculated on the basis of fertilizer doses, as well as concentrations of nitrate and potassium in lysimeter and drainage waters are greater than those in hydrochemical background (tab. 5).

Taking the above into account, it may be stated that nitrate and potassium are indicators of underground waters' pollution by agriculture. The values of maximum concentrations of chloride, sulphate and sodium in drainage waters in the rural area indicate that agriculture is their source. However, these maximum concentrations cannot be treated as the only indicator of agricultural pollution since industry and sewage can also contribute to it.

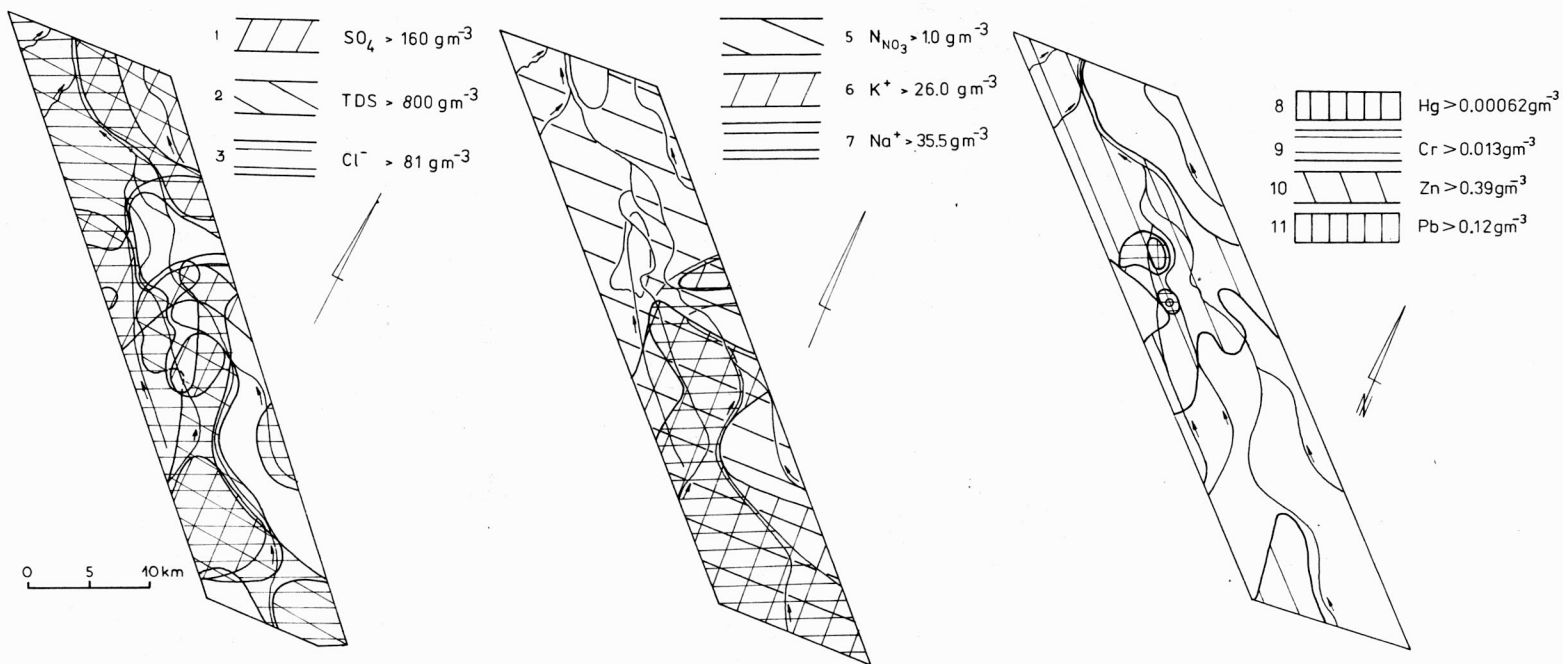


Fig. 5. Map of pollutions

Concentrations of species in the marked region exceed these of hydrochemical background

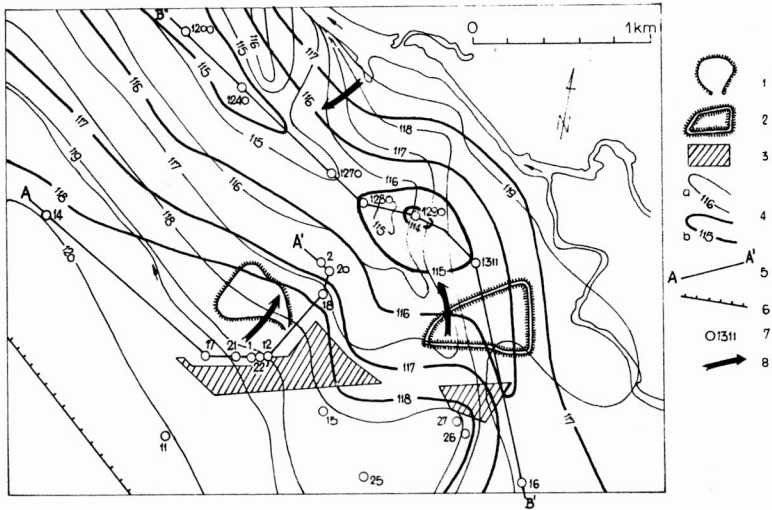


Fig. 6. Hydrogeological sketch of the area A

1 - dump, 2 - settling pond, 3 - industrial plant, 4 - hydroischipses: a) March 1977, b) Sept. 1983, 5 - hydrochemical cross section, 6 - boundary of paravalley, 7 - supply wells, 8 - ground water stream

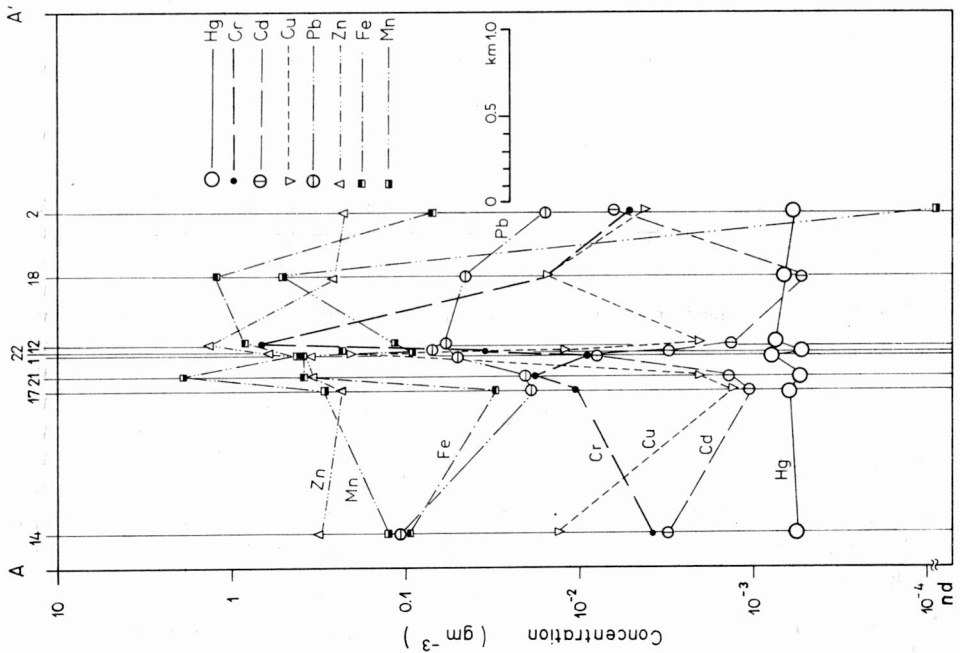


Fig. 7. Hydrochemical cross-section A-A', mean Dec. 1982 - Nov. 1983 (see fig. 6)

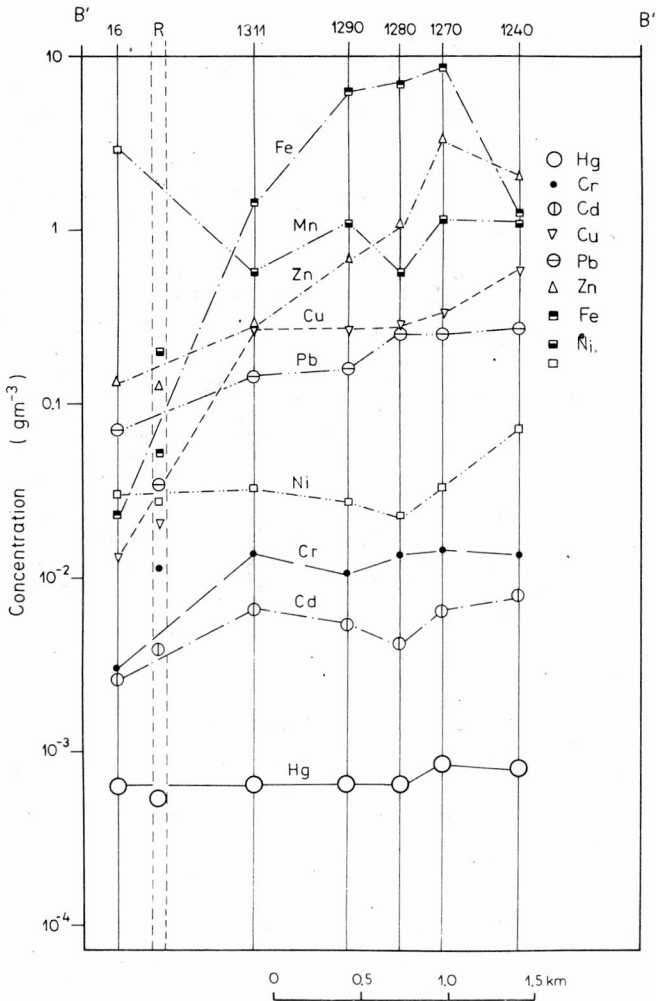


Fig. 7. Hydrochemical cross section B'-B'', mean Dec. 1982 - Nov. 1983 (see fig. 6)

R - Olawa river

4. CONCLUSIONS

The obtained results allow me to draw the following conclusions:

1. The modified method of hydrochemical background determination makes it possible to determine the area of underground water pollution and its sources (agricultural or industrial).

2. Quaternary underground waters in almost all of the investigated area are highly polluted with nitrate and soluble substance (TDS) from agricultural and industrial sources. Besides, in the industry area A and infiltration intake the

concentrations of lead, chromium and mercury in underground waters exceed admissible standards for drinking water.

The smelter and power plant in area A pollute the underground water with lead, chromium and mercury both in the infiltration intake and the area A.

3. Agriculture causes pollution of underground water in almost all of investigated area except the infiltration intake. Therefore the areas of underground water supply should be excluded from intensive agricultural activity. Pollution of underground waters with lead, chromium and mercury in industrial area A and the infiltration intake area makes the water unsuitable for drinking purposes.

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ZANIECZYSZCZENIE WÓD PODZIEMNYCH W DOLINIE ODRY W OKOLICY WROCŁAWIA

Zbadano skład chemiczny wód podziemnych w czwartorzędowych utworach w dolinie Odry w okolicy Wrocławia. W badaniach zastosowano zmodyfikowaną metodę tła hydrochemicznego do wyznaczenia obszarów zanieczyszczonych. Wody podziemne są zanieczyszczone na prawie całym obszarze w stopniu uniemożliwiającym ich wykorzystanie do picia. Ogniska rolnicze zanieczyszczają wody podziemne na całym obszarze intensywnej gospodarki rolnej, a ogniska przemysłowe na obszarze przemysłowym A i w ujęciu infiltracyjnym.

ЗАГРЯЗНЕНИЕ ПОДЗЕМНЫХ ВОД В ДОЛИНЕ ОДЕРА В ОКРЕСНОСТИ ВРОЦЛАВА

Исследован химический состав подземных вод в четвертичных отложениях в долине Одера в окрестности Вроцлава. В исследованиях применён модифицированный метод гидрохимического фона для обозначения загрязнённых территорий. Подземные воды загрязнены почти на всей территории в такой степени, которая делает невозможным использование их для питья. Сельское хозяйство загрязняет подземные воды на всей территории его интенсивного развития, а промышленность — на промышленной территории А и в инфильтрационном водозаборе.