

## Content of dissolved oxygen and carbon dioxide in rainwaters and groundwaters within the forest reserve of the Kampinos National Park and the urban area of Warsaw, Poland

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Research were conducted within two experimental fields differing from each other in land use. The source of percolating water and shallow groundwater within both fields is primarily the rainwater which controls their ionic and gaseous content. Considerable air pollution affects the rainwater falling on Warsaw. The chemical composition of the rainwaters should be considered as the first factor responsible for the observed differences in ionic and gaseous composition of percolating water within the two experimental fields. Subsequent chemical changes of these waters during infiltration depend on the character of the geologic profile and the rate of infiltration.

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### INTRODUCTION

Contents of dissolved oxygen and carbon dioxide in rainwater and shallow groundwater have been studied within two experimental fields that differ from each other in land use.

The experimental field in Granica, located within the forest area of Kampinos National Park is considered to be the example of natural hydrogeologic conditions (Fig. 1). It lies in an area of the lowest possible anthropogenic interaction, beyond the effects of agricultural activities. Possible effects of industrial activity might occur only by transport of atmospheric impurities brought into soil by percolating water.

The experimental field within the Research Station of the Faculty of Geology, University of Warsaw, in Warsaw, shows considerable anthropogenic effects, with hydrogeological conditions strongly and constantly affected by human activities (Fig. 1). The rainwater here has a different chemical composition to that in Granica; increased values of pH and electrical conductivity undoubtedly are the result of contamination.

Considerable scientific research has been conducted in these areas. Initially this involved groundwater dynamics and chemistry, but with little attention paid to dissolved gas phases (Macioszczyk, 1987; Macioszczyk and Witczak, 1999). The

content of gases, first of all the most reactive ones such as CO<sub>2</sub>, together with the ionic composition of water sample is needed to solve many problems concerning chemical equilibria in groundwater (Dowgiałło, 1988). This significant role of gases in affecting hydrogeochemical processes stimulated the research described below.

The contents of oxygen and carbon dioxide have been taken into consideration because the shallow groundwater is “saturated” with respect to these gases and seems to form a kind of equilibrium system which determines the hydrogeological and hydrogeochemical parameters of the particular environment.

Generally, oxygen is responsible for redox conditions and seems to determine the directions of different processes due to its high activity in reactions of oxidizing such elements as N, Mn, S, Fe and organic matter. Thus, oxygen seems to control the content of different elements in groundwater. However, the dissolved oxygen in groundwater occurs usually to a specific depth which is controlled by local geologic, hydrogeological and climatic settings. The content of dissolved oxygen is highest in shallow groundwaters and tends to decrease with depth.

The importance of the carbon dioxide in groundwater is connected first of all with its high reactivity. On the one hand the dissolved CO<sub>2</sub> in water intensifies the dissolution of different minerals. On the other hand the dilution in water of CO<sub>2</sub>

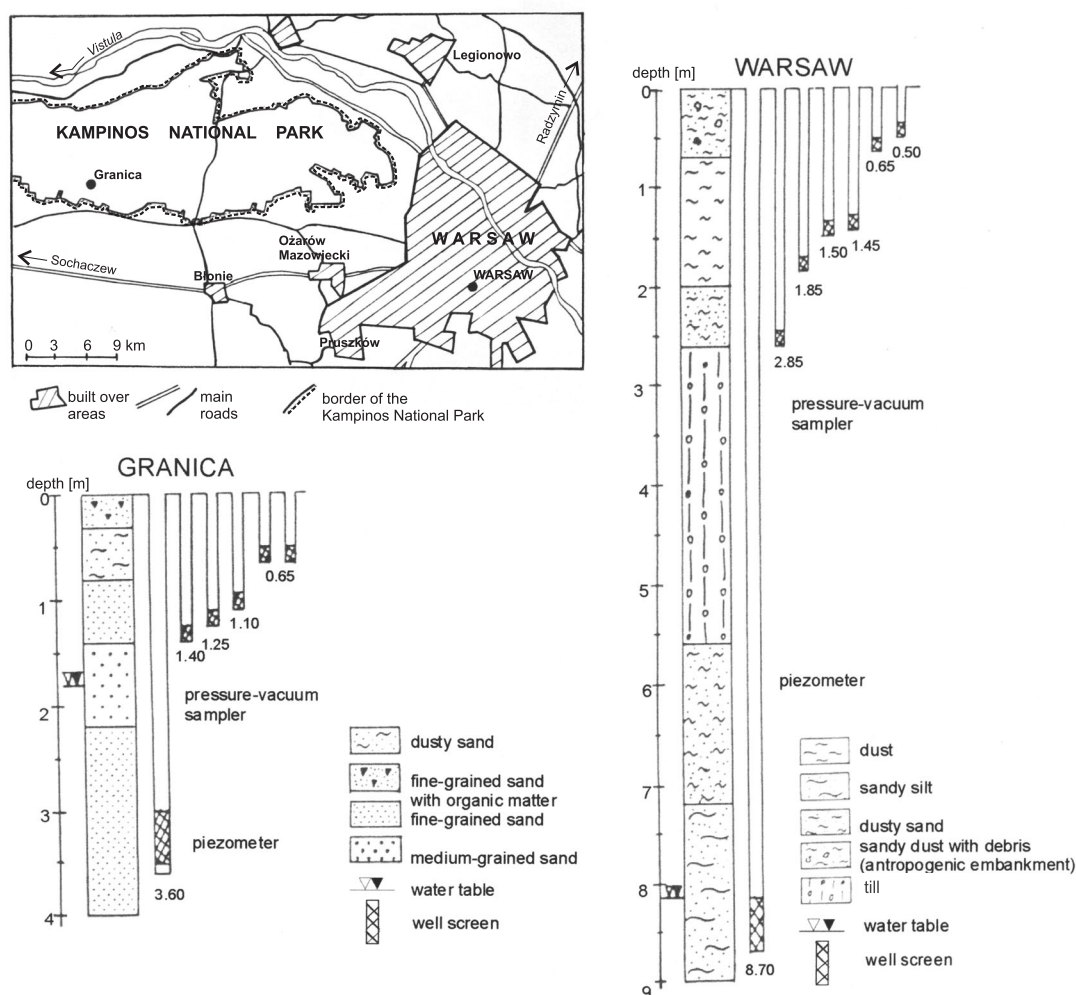


Fig. 1. Locations of the experimental fields, geological profile and arrangement of piezometers for hydrochemical sampling

itself is the source of  $\text{HCO}_3^-$  ions. Generally, carbon dioxide may occur in water in different forms which depends on the pH of the water. A considerable proportion of carbon dioxide is produced in the A-horizon of soil by plant-root respiration and aerobic decay of organic matter, including humic and other plant materials (Langmuir, 1997). The experimental fields are both covered by grass, though that at Granica is located within a forest reserve.

It must be also stressed that the carbon dioxide dissolved in water determines one of the most important kind of equilibria — the carbonate equilibrium, which is responsible for the chemistry of fresh and weakly mineralized waters (Macioszczyk, 1987; Dowgiałło, 1988), as are under consideration in this paper.

#### CHARACTERISTIC OF THE EXPERIMENTAL FIELDS

Rainwaters, percolation waters and shallow groundwaters were studied within the two experimental fields. Facilities for rainwater sampling were thus installed: the pressure vacuum samplers for percolation water sampling; and piezometers for shallow groundwater sampling (Fig. 1).

Placing pressure vacuum samplers at comparable depths within research fields of different land use allowed comparison

of the chemical and physical characteristics of waters formed in natural (forest reserve at Granica) and urban (experimental field in Warsaw) settings.

In such investigations it is important to note the geologic settings and the depths of unsaturated zones within the experimental fields. At Granica this zone is composed primarily from fine- and medium-grained sands with some additional dust and organic matter in the upper part; the entire profile up to 1.6 m depth is devoid of calcium carbonate and clay. The main component of the sands is quartz. Its content tend to increase with depth up to 80% in the lower part of the profile. Therefore, the scarcity of alkaline components in the sands causes their acidic reaction (Małecki, 1998).

Within the experimental field in Warsaw the geological profile begins with an anthropogenic layer comprising sand-laden dust and varied debris. Then, down to 2 m depth, dust occurs which, gradually with depth, becomes dusty sand, which is then underlain by till 3 m thick. The till seems to separate percolation waters from the first groundwater table found at 8 m depth in a silty and sandy aquifer (Fig. 1).

Hydrogeological investigations in these experimental fields showed that the mean groundwater levels are found at depth of 1.8 and 8.2 m at Granica and Warsaw respectively. Thus, the thicknesses of unsaturated zones as well as differences in geo-

logical settings appear to be important causes of varying infiltration conditions.

Within the experimental field at the rainwater infiltration conditions are good. This is shown both by observations of how groundwater reacts to precipitation and by the calculation. The time of rainwater inflow to particular pressure vacuum samplers (located at different depths) at Granica was calculated using the Bindeman equation modified by Macioszczyk (1999) and adopting, after Małecki (1998), parameters regarding the unsaturated zone and the value of recharging infiltration.

Knowing when rainwater infiltrates into a particular depth of a geological profile is important. This allows prediction of the influence of different hydrogeochemical processes which take place in the unsaturated zone upon changes in the chemical composition of the infiltrating rainwater. It has been shown by Małecki (1998) that the grade of surface evaporation directly affects levels of shallow groundwater mineralization and seems to be proportional to TDS (total dissolved solids). Both experimental fields are located in the same climatic zone, and thus levels of surface evaporation are assumed to be comparable. Recently, stable isotopes of deuterium (D) and oxygen-18 ( $^{18}\text{O}$ ) have been used in attempts to quantify transpiration, evaporation or the movement of soil-water in the soil-plant-atmosphere system (Hsieh *et al.*, 1998; Tindall *et al.*, 1999).

Rainwater infiltration times at Granica are within the range of a few days (Pawlicka, 2000). To be more specific, to the deepest sampled (1.4 m) rainwater inflow took place within 5 days. The rapid infiltration causes waters to have brief contact with minerals in of the aeration zone, and this seems to be corroborated by their chemical composition. Within the research field in Warsaw, though, the infiltration of percolation water to the same depth (1.4 m) takes about 7 times longer than at Granica. The infiltration time to the first groundwater table is much longer in Warsaw due to differences in the geological profile and in aeration zone thickness.

#### FIELD AND LABORATORY TECHNIQUES

The field research was conducted every month during a one-year period from June 2000 to June 2001. The field study included measurement of water temperature, pH, oxidation/reduction values, electrical conductivity and content of dissolved oxygen and carbon dioxide. Methods used to determine these parameters are shown in Table 1.

Water samples were collected for laboratory tests according to updated sampling procedures described in: Witczak and Adamczyk (1994, 1995), Hermanowicz *et al.* (1999), Weight and Sonderegger (2000), and Polish Standards (PN-88/C-04632/04). Laboratory tests included determination of major constituents of water as well as aggressive  $\text{CO}_2$ . Twice a year (in December 2000 and June 2001) minor and trace elements in the water samples and also the contents of dissolved organic carbon (DOC) and silica were determined at the Central Chemical Laboratory of Polish Geological Institute.

Table 1

#### Applied field techniques

Parameter	Applied equipment or measurement techniques
Content of oxygen [mg/dm <sup>3</sup> or %]	multifunctional metre type 18.26 by Eijkelkamp Corp.
pH	microcomputer pH-metre CP-315 <sub>M</sub> with glass-chlorinesilver electrode
Redox potential [mV]	microcomputer pH-metre CP-315 <sub>M</sub> with redox platinum electrode
Conductivity [mS/cm]	microcomputer conductivity-metre CP-317
Free carbon dioxide [mg/dm <sup>3</sup> ]	water sample titration by NaOH solution

#### RESULTS

The rain and percolation waters studied belong to two hydrogeochemical classes:  $\text{SO}_4\text{-HCO}_3\text{-Ca}$ , and  $\text{HCO}_3\text{-SO}_4\text{-Ca-Na}$ , within the experimental fields at Granica and Warsaw respectively. Among 18 determined minor and trace elements the following were above the detection limit: Ba, Sr, Mn, Zn, Al, Fe at Granica, and Ba, Sr, Mn, Zn, B, Cu, Al, Fe in Warsaw.

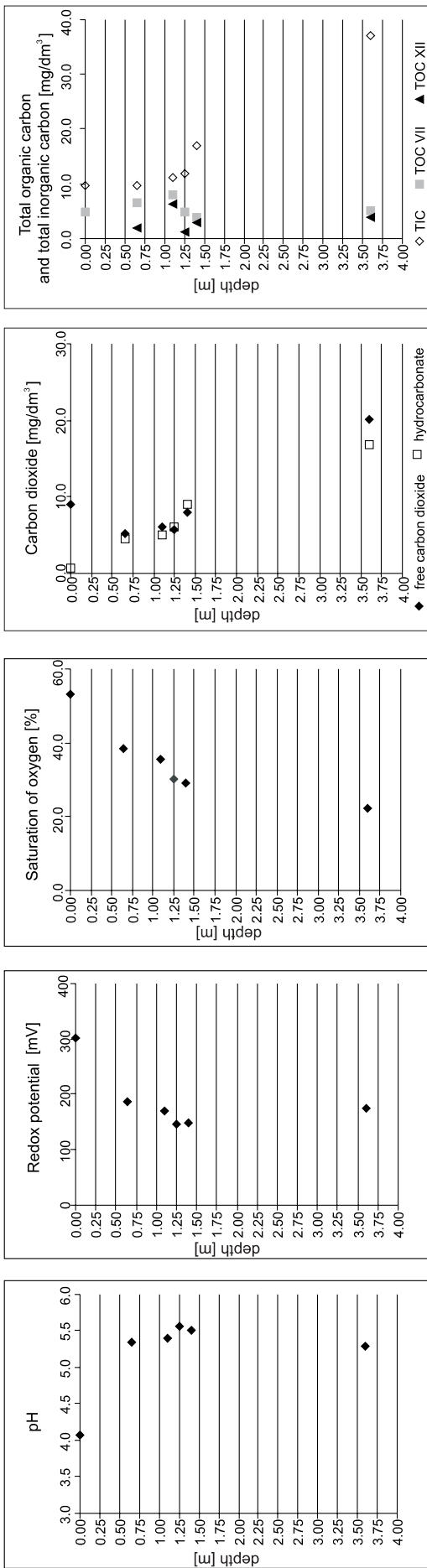
Total dissolved solids (TDS) of the waters studied in the aeration and saturation zones at Granica were about 50 mg/dm<sup>3</sup>. Much higher values of TDS, about 850 mg/dm<sup>3</sup>, were present in the equivalent waters within the experimental field at Warsaw. The factors responsible for such large difference in the TDS values of the waters in the two fields include:

- considerable contamination of rainwater within the Warsaw conurbation;
- a much thicker aeration zone in Warsaw than at Granica (8.2 m to 1.8 m respectively);
- much longer times of rainwater infiltration at Warsaw than at Granica;
- differences in the geological profiles of the two fields.

Within both experimental fields there is good correlation between groundwater temperature and climatic conditions, primarily because the first groundwater table occurs at considerable depth. The measured groundwater temperature by the piezometer at Granica during the winter period averaged 6°C whereas it exceeded 15°C over the summer period. In Warsaw, the groundwater temperature during the summer period was comparable to that of Granica but during winter period it was higher by about 2°C.

Measured values of electrical conductivity in waters of the aeration and saturation zones at Granica were approximately the same at different depths and amounted to about 0.06 mS/cm. Similar values were measured also in the rainwater, and this close correspondence is an effect of rapid infiltration through a monotonous geologic profile. Within the experimental field in Warsaw the rainwater showed slightly higher

### GRANICA



### WARSAW

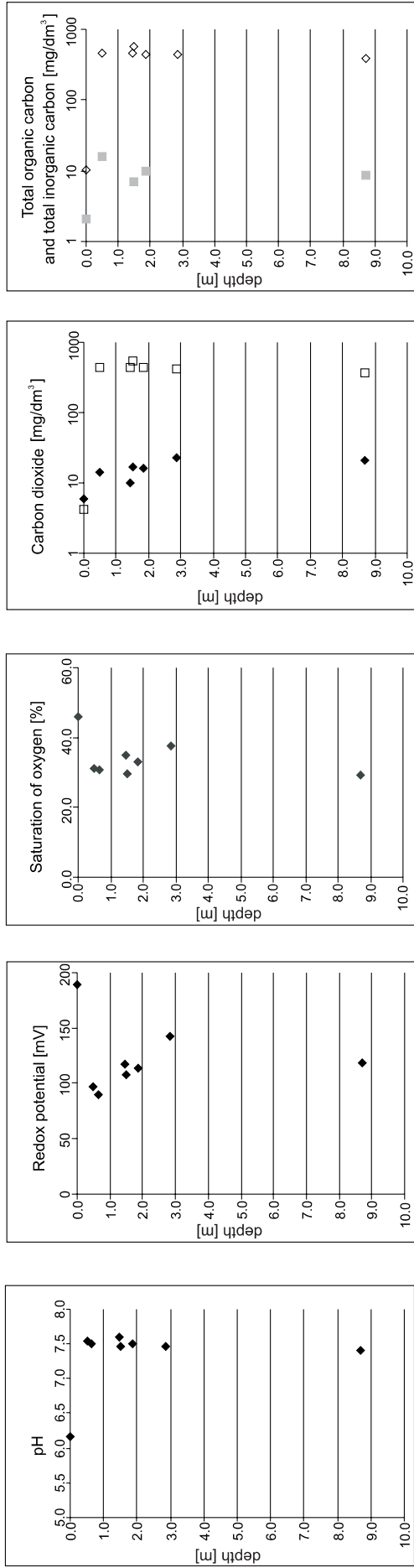


Fig. 2. Relationship between selected chemical parameters and depth of sampling of aeration and saturation zone at Granica and in Warsaw



Table 2

**Concentrations of selected components and gases in the area of Żwirki i Wigury and Banacha streets (after Małecka *et al.*, 1993)**

Ingredients	Concentrations [mg/dm <sup>3</sup> ]	
	measured	allowed
Dust	0.50	0.12
Nitrite oxides NO, NO <sub>2</sub> , NO <sub>3</sub>	0.43	0.15
Carbon oxide CO	4.21	1.0
Sulfur dioxide SO <sub>2</sub>	0.17	0.2
Carbon dioxide CO <sub>2</sub>	937	–

values of electrical conductivity; during the period of study these values ranged from 0.03 to 0.11 mS/cm, with a mean value of about 0.09 mS/cm. The electrical conductivity of percolation and groundwaters reached about 0.8 mS/cm. These trends were supported by values of TDS and laboratory-determined values of dry residue.

The waters of the aeration and saturation zones at Granica yielded similar values of pH of 5.4–5.6, indicating a moderately acidic environment. These rather low values of pH are likely an effects of the low pH value of the rainwater (about 4.0), which thus seems to strongly influence the chemical composition of the groundwaters. The pH of present-day rainwater is usually below 5.7, mostly because of the presence of SO<sub>2</sub>, which forms sulfuric acid, and of smaller amounts of HNO<sub>3</sub> and HCl, all chiefly from the burning of fossil fuels (Stumm and Morgan, 1996; Andrews *et al.*, 2000). Acid precipitation occur when occurs the such kinds of atmospheric pollutants are washed out by rain. Even in pristine locations, natural organic acid from plants are volatilized and dissolved in water droplets, contributing to rain acidity (Langmuir, 1997).

Relatively rapid infiltration as well as a moderately acidic soil environment appear to be responsible for the similarity of the pH of percolation and groundwaters at Granica (Fig. 2), where the lack of calcium carbonate in the geological profile means there is no natural buffer to neutralise acidic rainwaters during infiltration. At Granica, also, there is a scarcity of clay fraction and humic substances, which are important in determining the sorption capacity of the rock environment (Grabowska-Olszewska, 1990). The sorption capacity of this profile is thus very low (Małecki, 1998). Within the experimental field in Warsaw the pH values of waters in the aeration and saturation zones were also similar, trending within a range of 7.35–7.55. The pH values of rainwater were also higher in Warsaw, from 5.00 to 6.20 (Fig. 2); this seems to reflect specific conditions of the urban environment. Similar conclusions were obtained after study of the most polluted areas of Gdańsk (Polkowska, 2001). Studies of air quality conducted in the nineties at the scientific station in Warsaw clearly revealed that permitted levels were exceeded (Table 2) (Małecka *et al.*, 1993). Excess values of dust, nitrite oxides, carbon oxides and sulfur dioxide tended to decrease with distance from roads.

The redox values of unsaturated zone waters within the both experimental fields show reverse trends. At Granica Eh

values tend to decrease with depth from about 200 mV measured at the surface to about 160 mV at a depth of 1.4 m. In Warsaw, within the zone of aeration, measured Eh values tend to increase with depth from about 100 mV to about 140 mV. Groundwaters of the both experimental fields have Eh values similar to the mean value of its aeration zone. The highest Eh values were determined in rainwaters.

## CONTENT OF OXYGEN AND CARBON DIOXIDE

Measured values of oxygen content are expressed in percent as a degree of the saturation of water by oxygen. Monthly measurements corroborated the temperature dependency of the oxygen content in water. A decrease in water temperature causes an increase in the dissolution of oxygen because lower temperatures usually favour the dissolution of gases. Thus within both research fields the highest content of dissolved oxygen in groundwaters were measured during the winter (e.g. results from Warsaw shown in Figure 3).

Despite seasonal variations in the content of dissolved oxygen, its mean values for the entire research period show similar trends to the redox values obtained from the research fields. The content of the dissolved oxygen decreases with depth at Granica whereas it increases with depth in Warsaw (Fig. 2). At Granica these values trended from 23% in groundwater (piezometer reading) to 40% in percolation water of the shallowest sample. The highest oxygen content, about 60%, was measured in rainwater which seems to be the main source of the dissolved oxygen in percolation waters and groundwaters. Rather small differences in oxygen content at particular depths of the aeration zone at Granica are due to rapid infiltration, the rather monotonous lithology of the profile and, most importantly, a lack of organic matter.

In Warsaw, the content of the dissolved oxygen in waters increases with depth within the monitored aeration zone from 30 to 40%. The highest oxygen content, about 45%, was measured in rainwater. As can be noticed, the rainwaters in Warsaw are much poorer in dissolved oxygen than those of Granica (Fig. 2).

Total inorganic carbon dioxide can be divided into “free” CO<sub>2</sub> and bounded CO<sub>2</sub> (Macioszczyk, 1987). Free carbon dioxide occurs in water as dissolved (99%) “aqueous” carbon dioxide (CO<sub>2</sub> aq) and carbonic acid (H<sub>2</sub>CO<sub>3</sub>) (1%). The bounded carbon dioxide occurs in form of carbonate (CO<sub>3</sub><sup>2-</sup>) and hydrocarbonate (HCO<sub>3</sub><sup>-</sup>) ions (Drever, 1982; Fetter, 1994; Appelo and Postma, 1996; Stumm and Morgan, 1996). “Aggressive” CO<sub>2</sub> is that which occurs in water in higher amounts than is needed to balance the carbonate equilibrium. Water containing aggressive CO<sub>2</sub> usually has negative values of saturation index (SI) and is corrosive to the rock environment, concrete and some metals. In the case of weakly mineralized waters, where there are no other acids, the pH is the main factor which controls the concentration relationship between free CO<sub>2</sub>, hydrocarbonate CO<sub>2</sub> and carbonate CO<sub>2</sub>. In acidic environments free CO<sub>2</sub> is dominant whereas in neutral environments it is hydrocarbonate CO<sub>2</sub> and in alkalis it is carbonate CO<sub>2</sub> (Drever, 1982; Fetter, 1994; Appelo and Postma, 1996; Stumm and Morgan, 1996).

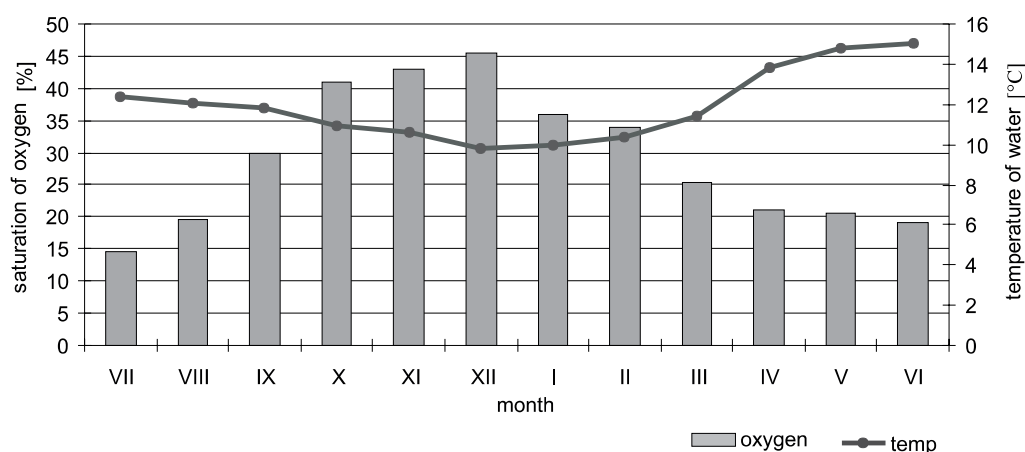


Fig. 3. The temperature dependence of the content of the dissolved oxygen in groundwater; (piezometer in Warsaw)

Laboratory analyses carried out by the author corroborated the pH dependency of different forms of  $\text{CO}_2$  in water. In groundwater from Granica, in which pH ranged from 5.4 to 5.6, the content of free  $\text{CO}_2$  was considerable whereas in groundwater from Warsaw, in which the pH was neutral,  $\text{HCO}_3^-$  ions were dominant. In both ranges of pH, carbonate  $\text{CO}_2$  was absent; that is why it was not detected during analytical tests. Chemical speciation in the carbonate system for groundwaters of both experimental fields are shown in Table 3. At Granica, ions of free  $\text{CO}_2$  and bicarbonate ( $\text{HCO}_3^-$ ) react mainly with  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions. However, the ionic forms of the dissolved chemical compounds are dominant. In Warsaw, bicarbonates prevail over free  $\text{CO}_2$ . They react mainly with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  ions.

There is about twice as much free  $\text{CO}_2$  in groundwater than in percolation water at Granica, and there is a gradual rise of free  $\text{CO}_2$  with depth (Fig. 2). The lowest values, about  $5 \text{ mg/dm}^3$ , and the highest, about  $21 \text{ mg/dm}^3$ , were measured in percolation water in the shallowest sampler and groundwater in the piezometer respectively. Similar trends can be seen in relation to hydrocarbonate  $\text{CO}_2$  (Fig. 2). Generally, the quantity of free  $\text{CO}_2$  and hydrocarbonate  $\text{CO}_2$  are similar at given depths of the monitored aeration zone. An exception may be seen only in rainwater, primarily due to the much lower pH, in which the content of hydrocarbonate  $\text{CO}_2$  is very low.

Within the experimental field in Warsaw there are higher concentrations of  $\text{HCO}_3^-$  ions in rainwater than at Granica, due to its higher pH. The relationship between concentrations of free  $\text{CO}_2$  and hydrocarbonate  $\text{CO}_2$  in percolation and groundwater are very variable (Fig. 2). At the particular depths of the aeration zone the content of free  $\text{CO}_2$  shows a modest increase from about 10 to about  $20 \text{ mg/dm}^3$  and finally in the saturation zone it reaches a value about  $20.2 \text{ mg/dm}^3$ . In the waters analysed hydrocarbonate  $\text{CO}_2$  is dominant; its concentration tends to decrease with depth from about 445 to about  $365 \text{ mg/dm}^3$  (Fig. 2).

The total dissolved  $\text{CO}_2$  is the sum of all dissolved oxidized forms of carbon and its value remains constant until exchange with some other gas phase starts (Langmuir, 1997). In the case of the waters analysed from both experimental fields the total dissolved  $\text{CO}_2$  equals the sum of the free  $\text{CO}_2$  and hydrocarbonate  $\text{CO}_2$  because carbonate  $\text{CO}_2$  is absent. Usually the term “total inorganic carbon” (TIC) is used instead of the

term “total dissolved  $\text{CO}_2$ ”. As can be seen on Figure 2, the contents of TIC increase clearly with depth only within the experimental field at Granica.

The contents of total organic carbon (TOC) in waters of the both research fields have also been measured. The concentration of TOC was examined only twice (in December 2000 and June 2001) at Granica and only once (in June 2001) in Warsaw. On the basis of these tests it can be seen that in general the content of the organic carbon is lower than the inorganic one in waters from both fields. Also, there are seasonal fluctuations in content of the dissolved organic carbon: its concentration in waters of Granica was higher in summer than in winter. Such seasonal variations are also reported by, for instance, Chapelle

Table 3

Forms of occurrence of  $\text{CO}_2$  species in groundwater of both experimental fields

Species	Granica		Warsaw	
	M	Y	M	Y
$\text{H}_2\text{CO}_3^0_{\text{aq}}$	3927	3929	570.9	573.1
$\text{HCO}_3^-$	319.1	304.9	5785	5162
$\text{CO}_3^{2-}$	0.00267	0.00222	7.021	4.451
$\text{Ca}^{2+}$	373.8	299.6	3069	1945
$\text{CaHCO}_3^-$	0.871	0.832	110.5	98.19
$\text{CaCO}_3^0_{\text{aq}}$	0.00090	0.00090	11.93	11.96
$\text{Mg}^{2+}$	1.987	1.657	432.6	276.5
$\text{MgHCO}_3^+$	0.00566	0.00541	17.41	15.47
$\text{Na}^+$	464.9	443.9	2494	2219
$\text{NaHCO}_3^0_{\text{aq}}$	0.0139	0.139	6.421	6.442
$\text{K}^+$	15.33	14.63	27.29	24.18

M — molality ( $\mu\text{mol/dm}^3$ ); Y — activity ( $\mu\text{mol/dm}^3$ )

(1993). Generally contents of TOC are similar at particular depths of the aeration and saturation zones at Granica and Warsaw, respectively. But, there is about twice as much TOC in water from Warsaw.

It should be stressed that while the composition of soil gases is largely determined by soil mineral composition, vegetation, hydrology and climate, it is also affected by resident flora and fauna, and exchange with the atmosphere (Tindall *et al.*, 1999). Carbon dioxide is generated by plant roots, fauna and soil microbes (bacteria and fungi) as a result of respiration, involving the consumption of carbohydrates and oxygen. Larger CO<sub>2</sub> concentrations are often found in agricultural soils or in other soils rich in organic carbon and fixed nitrogen, which support enhanced rates of biological activity. Most organic compounds have very low solubility in water, however, though constraints offered by low solubility are often insufficient to prevent migration to groundwater (Tindall *et al.*, 1999). Dissolved organic carbon may percolate downwards in the unsaturated zone, perhaps in association with colloidal clay particles. Its aerobic bacterial oxidation can produce increased amounts of CO<sub>2</sub> with depth (Wood and Petraitis, 1984).

Groundwaters from both experimental fields contain CO<sub>2</sub> from different sources. First of all CO<sub>2</sub> in these waters comes from the atmosphere, infiltration of rainwater and organic activity within the soil (microbial respiration and root respiration). At Warsaw, the position of the experimental field near busy crossroads may also influence the content of CO<sub>2</sub> in the groundwater. Burning fuels in oxygenated environment produces CO<sub>2</sub>; limited access of oxygen produces carbon monoxides, and lack of oxygen produces the soot (Andrews *et al.*, 2000).

Three different techniques were used in order to determine the concentration of aggressive CO<sub>2</sub>:

- analytical (based on the reaction of water with marble),
- the Lehmann and Reuss computational method (Hermanowicz *et al.*, 1999),
- the graphic method.

The last two methods are indirect. According to the Polish Standard PN-74/C-04547/03 the analytical method should be used only for waters with alkalinity greater than 1 meq/dm<sup>2</sup>. Only the percolation and groundwaters from Warsaw's experimental field fulfil this criterion. Nevertheless, the other water samples (rain, percolation and groundwaters from Granica and rainwaters from Warsaw, the alkalinity of which ranged within 0.2–0.3 mv/dm<sup>3</sup>) have been also examined using this method. The results are comparable with those obtained using other methods as seen in Table 4.

Laboratory tests revealed the presence of aggressive CO<sub>2</sub> in the rainwater of both experimental fields. It was present also in percolation and groundwaters at Granica where its concentration tended to increase with depth (Table 4) (Pawlicka, 2000).

The analytical and indirect methods used to determine concentrations of aggressive CO<sub>2</sub> were verified by hydrogeochemical modelling using the computer code *PCWAT-4*. Features of the waters in relation to particular mineral phases were examined on the basis of the saturation index (SI). The waters analysed at Granica revealed negative values of SI in relation to calcite, dolomite and aragonite. This means that they have the potential to dissolve these minerals. The absence of calcium carbonate within the geological profile at Granica seems to cor-

Table 4

Concentrations of aggressive carbon dioxide in rainwater, percolation water and groundwater determined using different techniques (experimental field at Granica)

Depth of water sampling [m]	Concentrations of the aggressive CO <sub>2</sub> [mg/dm <sup>3</sup> ]		
	Laboratory method	Computational method by Lenmann and Reuss	Graphic method
rainwater	8.9	9.0	9
0.65	no	5.2	5
1.10	no	6.0	6
1.25	5.7	5.9	6
1.40	9.1	8.0	8
3.60	16.2	20.2	20

no — not measured due to of lack of water sample

roborate this. According to Małeck (1998), percolation waters containing aggressive CO<sub>2</sub>, during their infiltration through the aeration zone, might cause its decalcification; some part of the calcium carbonate may be far-transported, and some — may be secondary deposited in deeper parts of the profile.

Within the experimental field in Warsaw the small volume of percolation and groundwater samples did not allow the determination of aggressive CO<sub>2</sub> by analytical methods. Nevertheless, other methods as well as modelling by *PCWAT-4* corroborated the absence of aggressive CO<sub>2</sub> in these waters. All of revealed positive values of SI in relation to calcite, dolomite and aragonite.

## CONCLUSIONS

The research focussed on the content and the role of CO<sub>2</sub> and O<sub>2</sub> in the initial part of the hydrogeochemical cycle from rainwater through percolation water to shallow groundwater within experimental fields differing from each other in land use.

The source of percolation water and shallow groundwater within both fields are primarily the rainwaters which undoubtedly control their ionic and gaseous composition.

Considerable emission of pollutants to the atmosphere affects primarily the rainwaters which, during their infiltration, become the main cause of degradation of the quality of percolation waters as well as shallow groundwaters.

The pollution of rainwater in Warsaw is evident. In comparison to the rainwater at Granica (an example of natural conditions), they have a higher electric conductivity due to a higher content of total dissolved solids. Heightened concentrations of particular ions appear to be an effect of atmospheric pollution where permitted concentrations of dusts, nitric oxides and carbon oxides are exceeded several times. Moreover, rainwater over Warsaw has a redox value about 100 mV lower than that of rainwater at Granica. It is also a direct effect of the diminution of oxygen concentration in this water.



Therefore, rainwater should be considered as the primary factor responsible for the observed differences in ionic and gaseous compositions of percolation waters within the two experimental fields. Farther chemical evolution of these waters during infiltration depends on the character of geologic profile and the rate of infiltration.

Important trends were observed in Eh values and oxygen concentration within the aeration zones of both experimental fields. In Warsaw, in the shallowest samples, water revealed Eh values of about 100 mV. At a comparable depth at Granica they revealed Eh values about two times greater. Similar relations were observed for the concentration of oxygen. Its concentration decreased with depth in percolation waters at Granica but tended to increase with depth in Warsaw. Its lower concentration in waters near the surface in Warsaw might be caused by different processes of oxidation of the organic matter, which is present in this profile in greater amounts than at Granica.

The results of the field and laboratory tests as well as of hydrogeochemical modelling indicate unequivocal domination of the free CO<sub>2</sub> over the hydrocarbonate CO<sub>2</sub> in waters analysed at Granica. The reverse trend was observed in waters of Warsaw experimental field.

At Granica the main species of CO<sub>2</sub> in groundwater react with Ca<sup>2+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>, but in Warsaw — with Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>. However, the ionic forms of the dissolved chemical compounds are dominant within the both experimental fields.

Concentrations of total organic carbon (TOC) in percolation and groundwater from Granica reveal seasonal variations. Concentrations are higher in summer than in winter.

Water from Warsaw contains about twice as much CO<sub>2</sub> in as does water from Granica.

Analytical methods and computer modelling used by the author indicate the presence of aggressive CO<sub>2</sub> in rainwaters of both experimental fields. In percolation and groundwaters aggressive CO<sub>2</sub> was observed only within the experimental field at Granica. The aggressiveness of these waters tended to increase with depth. They reveal the potential of dissolution of calcite, dolomite and aragonite because of negative values of SI.

*PCWAT-4* and *DATAGEN-4* have been used for hydrogeochemical modelling (see references).

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