Role of meteoric factors in chemical composition of vadose zone waters with special reference to research stations in Warsaw area

M. KADZIKIEWICZ-SCHOENEICH, J. J. MALECKI and M. FIC

Abstract

The chemistry of shallow circulation groundwaters is significantly influenced by precipitation, especially by load sizes of individual components, which are introduced to substratum together with meteoric waters (WAYNE 1985, MALECKA 1991, MALECKI 1995, 1998, MALECKI and MATYJASIK 2000). Chemical composition of percolating meteoric waters undergoes changes, which result from processes and reactions occurring in a liquid phase and also from interactions with solid particles (DYNOWSKA 1993).

In this research, detailed investigations were carried out to recognize structure and properties of soils and sediments present in the profiles studied and to determine hydrochemical characteristics of meteoric waters, percolating waters and groundwaters.

The investigations were carried out in the period 1999-2000 in three selected research sites, which showed different natural conditions and different land use. The first site was located in the centre of Warsaw agglomeration, the second was located in the agricultural area in Kampinos and the third in the forests of the protected area of Kampinos National Park at Granica research station.

The results of investigations revealed that chemical composition of shallow groundwaters in the areas built of Quaternary sandy sediments poor in carbonates and organic substance quickly responds to atmospheric precipitation. The influence of meteoric water is much less significant in the areas of differentiated lithology represented by Quaternary sediments containing silty and clayey fractions, organic substance, carbonates and amorphous forms of iron, aluminium and manganese.

1. Description of research stations and characteristic of solid particles of the studied profiles

The investigations of chemistry of meteoric water, percolating water and groundwater as well as studies on solid phase properties were carried out at three research stations located in central Poland. The first was located within Warsaw agglomeration at the research station of the Faculty of Geology, University of Warsaw. The second station was located in Kampinos in agricultural area adjacent to the protected area. The third station was located at research station in Granica in the forests of the protected area of Kampinos National Park.

The towns Granica and Kampinos are adjacent to each other and they are situated about 40 km west of Warsaw centre. The area of Kampinos National Park is adjacent to Warsaw of its western side and it represents a touristic-recreational

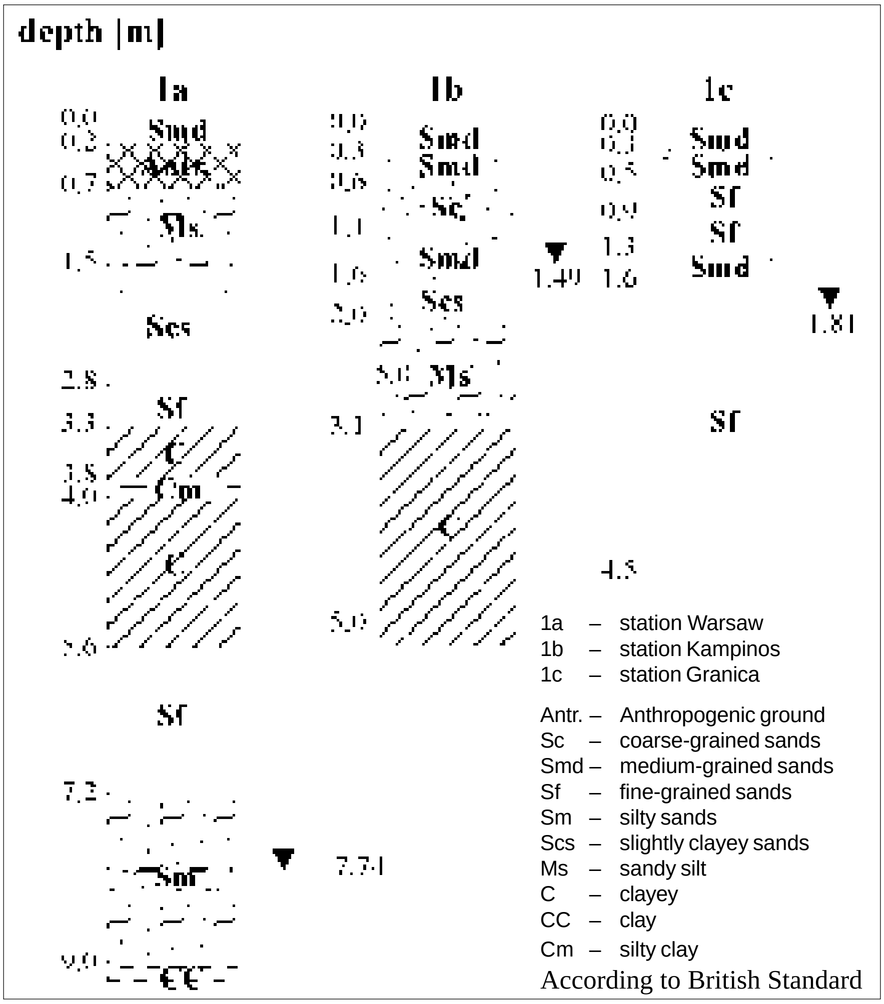

Figure 1: **Geological profiles**

Autoren: Monika KADZIKIEWICZ-SCHOENEICH, Univ. Prof. Dr. Jerzy J. MALECKI, Department of Geology, Warsaw University, PL-02089 WARSAW, wirki i Wigury 93, Dr. Michal FIC, Institut für Meliorationswesen und Grünlandforschung in Falenty, PL- 05090 RASZYN

Table 1: **Properties of solid particles in the studied profiles**

Sampling point	Depth [m.]	Reaction pH	Content of carbonates % $CaCO_3$	Content of organic substance I%	Clayey fraction %	Amorphous forms Al. - ox mmol+/kg	Fe - ox mmol+/kg	Mn - ox mmol+/kg
Warsaw Station	0-0.2	7.36	0.01	1.75	0	1.405	15.074	4.285
	0.2-0.7	7.58	5.25	0.32	0	0.964	15.449	1.906
	0.7-1.5	7.41	0.17	2.11	5	1.101	12.089	3.281
	1.5-2.8	7.15	0.06	1.41	5	0.582	14.414	0.518
	2.8-3.3	6.88	0	0.54	0	0.486	4.217	0.085
	3.3-3.8	6.11	0.03	2.24	20	1.097	17.491	1.279
	3.8-4.0	5.68	0.02	2.78	32	1.449	16.423	0.935
Kampinos Station	0-0.3	5.12	0.14	1.77	0	0.537	7.375	1.107
	0.3-0.6	6.25	0.26	0.51	0	0.448	5.405	0.821
	0.6-1.1	6.92	0	0.59	0	0.393	5.542	0.261
	1.1-1.6	6.91	0	1.09	0	0.504	8.277	0.429
	1.6-2.0	6.85	0.02	1.16	4.6	0.582	8.934	0.427
	2.0-2.7	7.51	0.82	1.43	7	0.623	11.705	0.835
	2.7-5.0	7.65	18.3	4.1	29	0.752	11.424	2.033
Granica Station	0-0.3	4.31	0	1.75	0	1.483	7.588	1.009
	0.3-0.5	4.52	0	1.11	0	1.497	6.329	0.235
	0.5-0.9	4.9	0	0.64	0	0.856	2.476	0.048
	0.9-1.3	5.24	0	0.39	0	0.471	1.825	0.048
	1.3-1.6	5.48	0	0.37	0	0.341	1.825	0.025

centre of the city (the so-called „green lungs of the capitol“).

At the three stations studied, geological profiles in vadose zone are represented by Quaternary deposits. The profile of **Warsaw site** was investigated down to the depth of 9 m b.g.l. Down to the depth of about 1m, anthropogenic filling deposits occur. They are underlain by silty and sandy deposits and clay (*Figure 1a*). Mean groundwater table in the period 1999-2000 for Warsaw station was 7,74 m b.g.l. In the upper part of the profile sandy fraction predominates (80-90%) and its percentage decreases with depth while the percentage of silty fraction (30-50%) and clayey fraction (10-30%) increases. The subsurface zone is rich in organic substance (1,75%) associated with a soil layer and in carbonates (5,25%), which are secondarily introduced to the environment from filling deposits (building ground, etc.). In the lower part of the profile within the clays and silts, the increase of organic substance is observed (2,24-2,78%). The reaction of the deposits studied changes with depth. In the upper part of the profile it is slightly alkaline (7,36-7,41 pH), lower - slightly acid (6,88-6,11 pH) and in the lowermost part the reaction value reaches 5,68 pH (*Table 1*). To describe a sorption complex in a solid phase, apart from determination of silty fraction and organic substance, the content of amorphous iron, aluminium and manganese was determined (*Table1*).

The Kampinos site is located in the marginal zone of Warszawa-Blonie terrace, which is significantly uplifted as related to the adjacent areas. This profile was investigated down to the depth of 5 m. In the upper part it is represented by sandy deposits, which are lower replaced by silty and clayey deposits (*Figure1b*). Mean groundwater table in this area was at the depth of 1,49 m b.g.l. in the period 1999-2000. As compared to Warsaw profile, the thickness of vadose zone at Kampinos site is much smaller.

The content of organic substance (1,77 %) and carbonates (0,14-0,26 %) in the subsurface zone decreases with depth. In the zone of coarse-grained and medium-grained sands, these substances are washed out and they are cumulated in sandy sediments and clays in the lower part of the profile (Iom=1,43-4,1% and $CaCO_3$ =18,3%).

The environment reaction changes from slightly acid (5,12 pH) in the subsurface zone to slightly alkaline and reaches values of 6,26-6,85 pH in the deepest part of the profile. The contents of amorphous iron, aluminium and manganese increase with depth (*Table1*).

The Granica profile is located within the Kampinos flood plain of the Vistula River. The plain is built of sandy sediments of different grain-size recognized down to the depth of 5 m (*Figure1c*). Mean groundwater table in the studied period was at the depth of 1,81 m. The content of organic matter in the subsurface zone (1,75 %) decreases with depth. The lack of carbonates in the whole profile and, in association with that, unfitness for environment buffering result in lower reaction, which is in the range from 4,31 pH in the subsurface zone to 5,48 pH in the lower part of the profile. Also the content of amorphous iron, aluminium and manganese decreases with depth (*Table 1*).

2. Chemistry of meteoric waters in the areas studied

The size of precipitation and its chemical composition were investigated in the period 1999-2000 in Warsaw and Kampinos areas. The former included Warsaw and was associated with the research station located in this town; the later included the research stations in Granica and Kampinos.

The location of the research stations made it possible to determine and register the influence of anthropogenic conditions on soil-water environment visible in changes of precipitation characteristics. The pollution of atmospheric air

Table 2: **Mean values of measured parameters in meteoric waters in the areas studied (n=240)**

Investigated parameters		Warsaw	Granica
Temperature	$[^0C]$	9.6	8.2
Reaction	[pH]	5.54	4.47
PEW	[mS/cm]	0.083	0.061
Oxygen content	$[O_2\,\%]$	43.5	36.9
TDS	$[mg/dm^3]$	70	31
Mean precipitation in 1999-2000	[mm]	600	

and associated processes of environment acidification are natural consequence of industrialization and urbanization. Increasing emission of acid gases (carbon, nitrogen and sulphur monoxides) with the presence of water results in acid rain origin.

The additional effect associated with this process is initiation of heavy metals present both in soil and those, which represent products of atmospheric dust transport (GALLOWAY et al. 1983, ALLOWEY 1995).

The station located in Warsaw makes it possible to monitor direct influence of human impact on the environment. The station in Granica, which is far removed from industrial plants and urban agglomeration and located in the protected zone, makes it possible to evaluate natural factors and to register anthropogenic influences of long-distance range.

In case of precipitation, investigations of following physico-chemical parameters were carried out: temperature, reaction (pH), electrolytic conductivity (EE), oxygen content (*Table 2*) and also measurements of precipitation amount and chemical composition.

The amount of precipitation in the period 1999-2000 was 600mm. The reaction of meteoric water was slightly acid and it was 5,54 pH for Warsaw area and 4,74 pH for Kampinos area. The investigated meteoric waters represent water of poor mineralization (TDS) - the mean amount of dry residue for Warsaw was 70 mg/dm^3 and for Granica it was 31 mg/dm^3.

The analyses of macro- and micro-composition of meteoric water made it possible to determine percentage of individual ions. Their mean values are shown in *Table 3* and *Figure 2*.

In case of the station in Warsaw, sulphate anions (19,86 mg/dm^3), nitrate anions (10,66 mg/dm^3), chloride anions (8,99 mg/dm^3), calcium cations (12,58 mg/dm^3) and sodium cations (7,47 mg/dm^3) predominate in the precipitation studied. In case of the station in Granica, chloride anions (6,75 mg/dm^3), nitric anions (8,57 mg/dm^3), sodium cations (5,40 mg/dm^3) and calcium cations (3,43 mg/dm^3) predominate. There is also a large percentage of copper and zinc noticeable in Granica (zinc - 1,22 mg/dm^3). The calculated loads of pollution, which were introduced to the substratum with wet precipitation in the period studied are shown in *Figure 3* and *4*.

Together with precipitation, a considerable amount of chlorides, sulphur, nitrate, sodium and calcium is introduced to the substratum. In Warsaw, there is clear influence of pollution centres of short-distance range; considerably larger values of loads entering the substratum

Table 3: **Characteristic of ion composition of the investigated meteoric water (n = 240)**

Station	HCO_3^- mg/dm^3	SO_4^{2-} mg/dm^3	Cl^- mg/dm^3	NO_3 mg/dm^3	Na^+ mg/dm^3	K^+ mg/dm^3	Ca^{2+} mg/dm^3	Mg^{2+} mg/dm^3	Cu^{2+} mg/dm^3	Zn^{2+} mg/dm^3
Warsaw	8.74	19.86	8.99	10.66	7.47	1.14	12.58	0.16	0.045	0.354
Granica	2.00	4.16	6.75	8.57	5.40	0.83	3.43	0.09	0.045	1.216

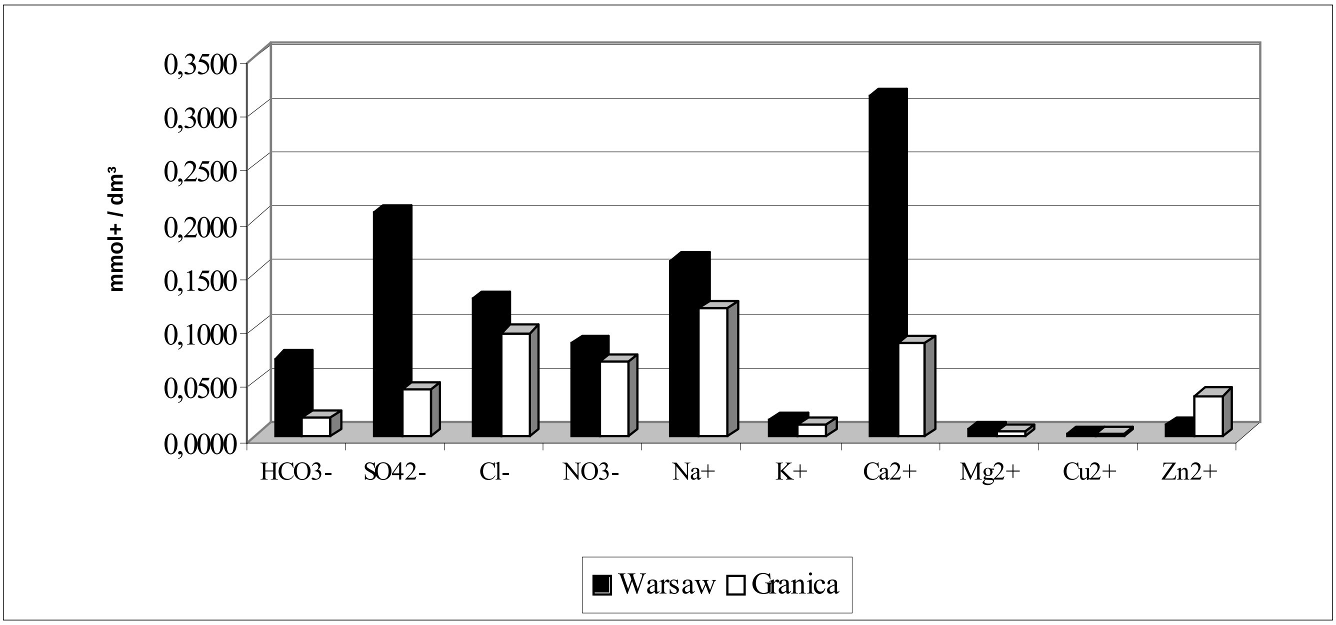

Figure 2: **Chemical composition of precipitation in the areas studied**

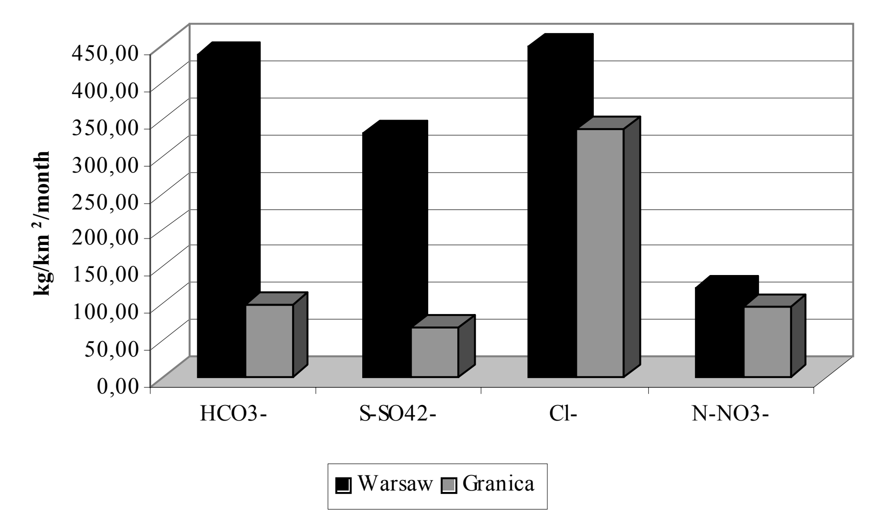

Figure 3: **Mean monthly loads of HCO_3^-, Cl^- and $N\text{-}NO_3^-$, which enter the substratum with wet precipitation**

with wet precipitation were registered there. Meteoric waters infiltrating the substratum introduce them to groundwater, but their final composition depends on processes and reactions, which occur in the border of solid and liquid phases.

3. Hydrodynamic characteristic of waters in vadose and saturation zones

The investigated percolating waters of vadose zone and groundwater of saturation zone show differentiated composition. This results from differences in geology of the areas studied, different land use, variability of the elements introduced to groundwater both with precipitation and laterally with groundwater and also from the variety of processes and reaction, which occur in the environment.

The groundwaters in Warsaw profile belong to waters of medium mineralization. Their mean value of dry residue is 851 mg/dm^3 in vadose zone and 680 mg/dm^3 in saturation zone. These are 5-ion bicarbonate-sulphate-chloride-calcium-sodium waters of slightly alkaline reaction from 7,17 to 7,52 pH (*Table 4* and *5*).

The groundwaters in Kampinos profile show high values of mineralization. Mean value of dry residue in vadose zone was 1520 mg/dm^3 and in saturation zone it was 1252 mg/dm^3. These are 5-ion sulphate-chloride-bicarbonate-sodium-calcium waters. In a deeper zone, proportions of ions change and bicarbonate-chloride-sulphate-calcium-sodium waters predominate. The reaction fluctuated between slightly acid to slightly alkaline (6.94-7.17 pH) in vadose zone and slightly alkaline (7,25 pH) in saturation zone.

The groundwaters in Granica profile show very low mineralization from 50 mg/dm^3 in vadose zone to 58 mg/cm^3 in saturation zone. These are two-ion sulphate-calcium waters of slightly acid reaction (5,09-5,80 pH) in the whole profile.

4. Influence of meteoric factors on chemical composition of waters studied - conclusions

The discussed results of chemical composition of the waters studied and their physico-chemical parameters reveal basic differences in composition, mineralization and reaction of meteoric water and groundwater. The comparison of chemistry of meteoric waters with percolating waters and groundwaters at the research stations in Warsaw and Kampinos shows that there is not any distinctive influence of meteoric factors on chemical composition of groundwaters. However, at the research station in Granica, such an influence is visible.

Table 4: **Physico-chemical parameters of percolating water and groundwater in the stations studied (mean values n=1200)**

Sampling point		Depth m	Temp. ^{0}C	Reaction pH	Potential oxidant-reduction mV	PEW mS/cm	Oxygen %
WARSAW Station	Vadose zone	0.47	14.4	7.36	68	1.037	28.6
		0.58	11.9	7.52	96	0.727	34.2
		1.13	17.0	7.17	57	0.790	24.0
		1.43	11.4	7.42	114	0.902	41.6
		1.52	13.0	7.35	111	0.923	27.7
		1.83	13.4	7.43	123	0.849	31.5
		2.84	13.2	7.41	145	0.920	41.0
	Saturation zone	7.74	12.9	7.40	91	0.825	22.8
KAMPINOS Station	Vadose zone	0.55	12.7	7.10	57	1.706	40.6
		0.95	12.5	7.17	46	2.135	36.3
		1.3	12.5	6.94	53	2.348	32.0
		1.75	12.7	7.00	47	2.525	25.7
	Saturation zone	1.49	12.4	7.25	-10	1.622	29.1
GRANICA Station	Vadose zone	0.65	10.8	5.57	197	0.054	48.0
		0.66	11.3	5.09	207	0.073	39.1
		1.11	13.3	5.56	176	0.074	34.2
		1.24	12.0	5.80	163	0.065	31.9
		1.36	11.4	5.65	166	0.063	31.7
	Saturation zone	1.81	11.3	5.48	192	0.063	22.8

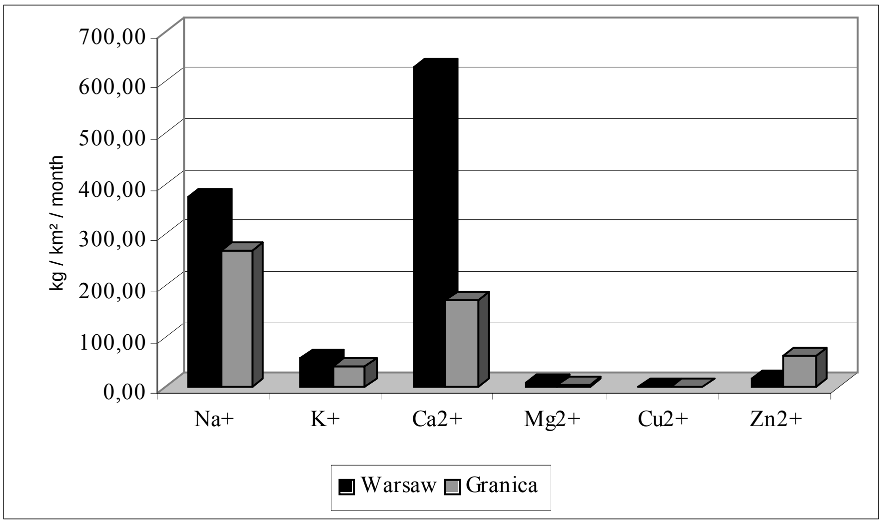

Figure 4: **Mean monthly loads of Na^+, K^+,Ca^{2+},Mg^{2+}, Cu^{2+}, Zn^{2+}, which enter the substratum with wet precipitation**

At the research stations in Warsaw and Kampinos, the intensity of processes occurring in a geological profile totally mask the initial chemical composition of precipitation, which leads to the origin of groundwaters of a quite different hydrochemical type. The factors influencing composition of shallow groundwaters in the research profiles in Warsaw and Kampinos include:

- **Lithology of sediments** - in Warsaw and Kampinos profiles the role of sandy fraction decreases with depth while the role of silty and clayey fraction increases. The clayey fraction, regardless its mineralogical composition, represented important adsorption centres. In Granica profile, predominating sandy fraction limited possibilities of ion bonding into mineral complexes.
- **Content of organic substance and amorphous Al, Fe and Mn,** which take part in sorption processes - positively higher content of these components in the whole profile in Warsaw and Kampinos and hardly any content in Granica profile.
- **Content of carbonates** - which condition pH of the environment, buffer the influence of precipitation and condition the directions of processes and reactions occurring between solid and liquid phases. In Granica profile no carbonates were registered, therefore both the soil and sediments in this area were devoid of protection mantel, which represents this compound.
- **Content of exchange cations** of alkaline character in a sorption complex. The determined participation of individual exchange cations Na, K, Ca and Mg revealed that the soil-sediment environment in Granica profile is very poor in these elements (Ca-ex: 0,74-0.89 $cmol_+$/kg, Mg-ex: 0,09-0,12 $cmol_+$/kg, K-ex: 0,04-0,06 $cmol_+$/kg, Na-ex: 0,05-0,12 $cmol_+$/kg). The largest percentage of exchange cations was determined in Warsaw profile (Ca-ex: 3,52-15,09 $cmol_+$/kg, Mg-ex: 0,47-2,84 $cmol_+$/kg, K-ex: 0,29-0,83 $cmol_+$/kg, Na-ex: 0,08-0,54 $cmol_+$/kg) and in Kampinos profile (Ca-ex: 1,75-11,08 $cmol_+$/kg, Mg-ex: 0,28-1,52 $cmol_+$/kg, K-ex: 0,19-0,41 $cmol_+$/kg, Na-ex: 0,12-0,35 $cmol_+$/kg).

The geology of Granica profile causes that a meteoric factor significantly influences composition of groundwaters. The groundwaters of this station distinctively inherited a hydrochemical type from meteoric water.

The results of the investigations show that the quality of meteoric waters plays an important role in chemical composition of shallow groundwaters, and intensity of their influence depends on the

Table 5: **Chemical composition of percolating waters and groundwaters in the stations studied (mean values n=2400)**

Sampling point	Depth [m.]	HCO_3^- mval/dm³	SO_4^{2-} mval/dm³	Cl^- mval/dm³	NO_3^- mval/dm³	Na^+ mval/dm³	K^+ mval/dm³	Ca^{2+} mval/dm³	Mg^{2+} mval/dm³	Cu^{2+} mval/dm³	Zn^{2+} Mval/dm³
WARSAW Station	0.47	0.4250	0.3816	0.0528	0.0099	0.4671	0.0122	0.3939	0.0114	0.0023	0.0030
Vadose zone	0.58	0.6556	0.1677	0.0539	0.0130	0.7561	0.0374	1.7684	0.0315	0.0016	0.0050
	1.13	6.0749	2.2898	1.0598	0.2554	1.5007	0.0128	7.5886	0.1974	0.0024	0.0103
	1.43	3.1127	0.2731	0.0528	0.0090	0.7103	0.0123	3.5633	0.2840	0.0008	0.0009
	1.52	5.2938	0.3673	0.1701	0.0237	0.4337	0.0067	5.2854	0.4667	0.0012	0.0020
	1.83	4.7715	1.3620	0.1616	0.1784	1.2684	0.0142	5.5216	0.3068	0.0011	0.0016
	2.84	0.7722	0.1796	0.0236	0.0000	0.5195	0.0118	0.9689	0.1110	0.0010	0.0024
Saturation zone	7.74	3.8874	1.3406	1.1614	0.1961	1.8428	0.0295	4.4193	0.1493	0.0011	0.0014
KAMPINOS Station	0.55	1.2911	5.1852	4.2360	0.1094	7.6978	0.4804	2.5236	0.1744	0.0016	0.0016
Vadose zone	0.95	1.8017	5.9652	7.2485	0.1566	11.8860	0.4158	2.9658	0.4102	0.0023	0.0013
	1.30	2.5802	7.6525	7.7342	0.1943	11.1468	0.3752	5.3755	0.7479	0.0014	0.0013
	1.75	4.2305	7.3696	8.3399	0.1438	11.2414	0.0738	7.8432	0.6153	0.0013	0.0013
Saturation zone	1.49	4.1708	2.9977	5.9526	0.1966	3.0748	0.0271	9.2157	0.4789	0.0013	0.0030
GRANICA Station	0.65	0.0569	0.1357	0.0358	0.0302	0.0765	0.0129	0.1731	0.0081	0.0010	0.0010
Vadose zone	0.66	0.0613	0.2565	0.0736	0.0658	0.1340	0.0085	0.2890	0.0247	0.0012	0.0018
	1.11	0.0552	0.1448	0.0526	0.0704	0.0926	0.0134	0.2191	0.0117	0.0011	0.0025
	1.24	0.0994	0.2280	0.0717	0.0790	0.1288	0.0180	0.3226	0.0127	0.0013	0.0012
	1.36	0.0823	0.2427	0.0931	0.0755	0.1315	0.0152	0.3321	0.0139	0.0012	0.0019
Saturation zone	1.81	0.1734	0.2275	0.0791	0.0721	0.1797	0.0479	0.2973	0.0330	0.0012	0.0013

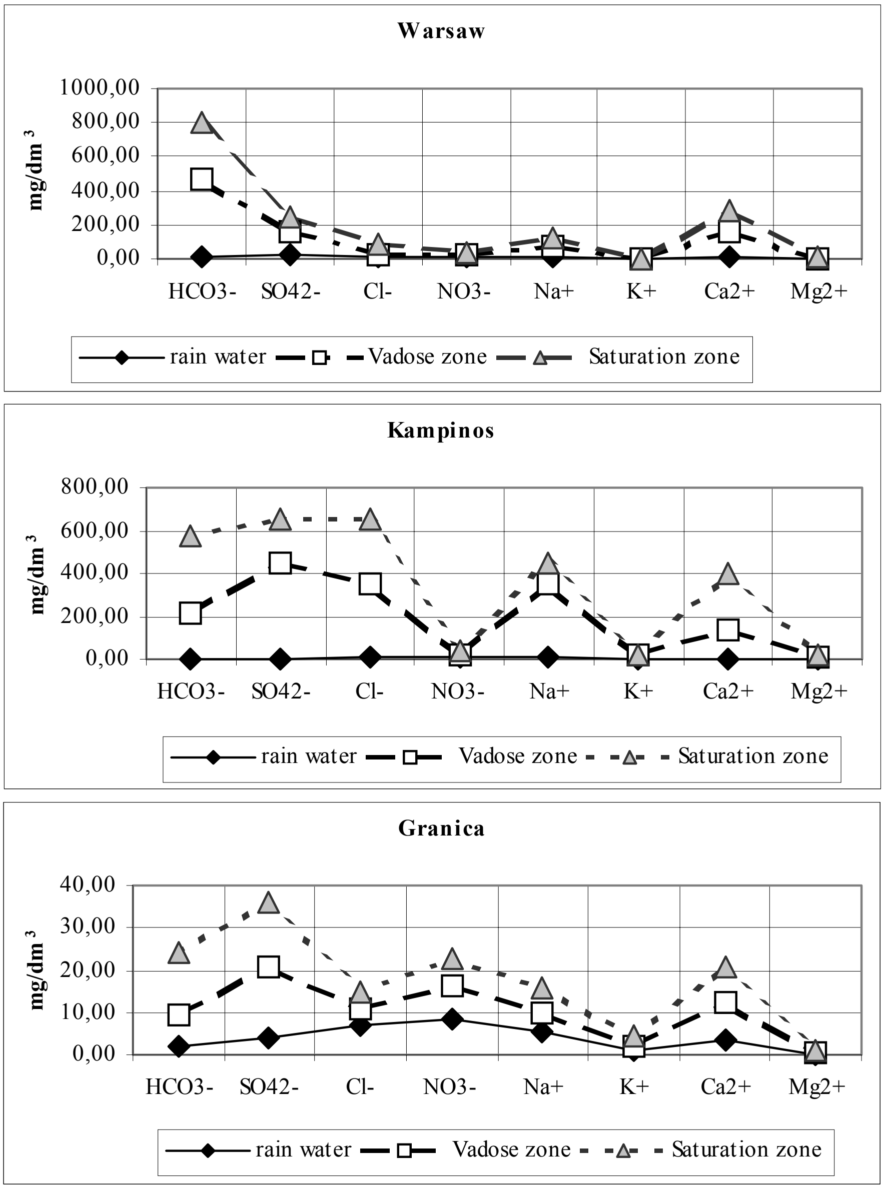

Figure 5: **Comparison of individual ions in meteoric waters, percolating waters and groundwaters at the stations studied (mean values)**

character of hydrochemical environment of vadose zone.

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