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CALCIUM AND MAGNESIUM IN UNDERGROUND WATERS AROUND A COMMUNAL WASTE DUMP

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Abstract

Contaminations carried by effluents from communal waste dumps are a serious threat to underground waters. The effluents may contain solutes washed away by precipitation and also organic and mineral substances that arise during anaerobic and aerobic waste decomposition. Aside of substances that are known to be harmful to the human health (heavy metals), the effluents may contain a large number of common elements which are not regarded harmful at natural concentrations. In effluents from "young" dumps, where the waste undergoes acidic fermentation mainly, calcium concentration may exceed 3,000 $mg \cdot dm^{-3}$ and that of magnesium reach 1,500 $mg \cdot dm^{-3}$. Effluents from "old" dumps, where methane fermentation dominates, most often contain up to 400 $mg \cdot dm^{-3}$ of calcium and 200 $mg \cdot dm^{-3}$ magnesium.

The aim of the work was to elucidtyate the character and dynamics of changes in concentration of the elements studied in effluents from a municipal waste dump at Maślice near the city of Wrocław, and in underground waters of the adjacent land. Deposition of waste in this area began in the late 1960s. The ground conditions provide for an easy contact between underground water and dumped waste, and transport of the washed-out pollutants. Only part of the dump has sealing and drainage that conducts the effluents to a reservoir, where samples for this study were taken. At the turn of 1999 and 2000 the utilization of the dump was terminated and its reclamation began. Thus, the slopes of the refuse heap were fortified with reinforced ground, the cap sealed with synthetic-mineral material, and from the side of underground water inflow a shield was made (in 2002) that reached down to the impermeable ground layer in order to stop the inflowing waters. In 2004 the reservoir for effluents was filled in.

The results, presented in this report, on the content of calcium and magnesium in underground waters flowing into the dump did not show any other extra contamination. In dump effluents the relations between calcium and magnesium concentration remained on similar levels. Like for other dumps, in the first years of study calcium concentration

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prevailed, whereas effluents from older dumps contained greater amounts of magnesium. Increased contents of calcium and magnesium in underground waters flowing under the unsealed part of the dump indicated at continuous inflow of contaminations, that were not eliminated by the technical means applied during reclamation of the installation. Variations in the properties of waters flowing out of the dump depended mainly on the composition of the inflowing waters (max. concentrations occurred concurrently) and the amount of contaminants emitted into the ground from the dump (relations between mean contents of calcium and magnesium varied in them like in the dump effluents).

Key words: municipal waste dump, underground waters, dump effluents, calcium, magnesium.

WAPŃ I MAGNEZ W WODACH PODZIEMNYCH NA TERENACH OTACZAJĄCYCH SKŁADOWISKO ODPADÓW KOMUNALNYCH

Abstrakt

Zanieczyszczenia przenoszone przez odcieki ze składowisk odpadów komunalnych są poważnym zagrożeniem dla wód podziemnych. Mogą zawierać substancje rozpuszczone, wymywane przez opady atmosferyczne, a także substancje organiczne i mineralne powstające w trakcie beztlenowego rozkładu odpadów. Oprócz substancji uznawanych za szkodliwe dla środowiska (jak np. metale ciężkie), odcieki mogą zawierać duże ilości pierwiastków występujących powszechnie w przyrodzie, które w naturalnych stężeniach nie są uznawane za niebezpieczne. W odciekach z „młodych" składowisk, na których odpady podlegają głównie procesom fermentacji kwaśnej, stężenie wapnia może przekraczać 3000 mg·m^{-3}, a magnezu dochodzić do 1500 mg·dm^{-3}. Odcieki ze „starych" składowisk, z dominacją procesów fermentacji metanowej, najczęściej zawierają do 400 mg·dm^{-3} wapnia i do 200 mg·dm^{-3} magnezu.

Celem pracy było wykazanie charakteru i dynamiki zmian stężeń badanych pierwiastków w odciekach ze składowiska odpadów komunalnych „Maślice" we Wrocławiu oraz w wodach podziemnych terenów przyległych. Deponowanie odpadów na tym terenie rozpoczęto pod koniec lat sześćdziesiątych XX wieku. Warunki gruntowe ułatwiają kontakt wód podziemnych ze składowanymi odpadami oraz transport wymywanych zanieczyszczeń. Tylko część składowiska ma uszczelnienie i drenaż odprowadzający odcieki do zbiornika, z którego pobierano próby do badań. Na przełomie lat 1999-2000 zakończono eksploatację składowiska i rozpoczęto jego rekultywację. W ramach tego procesu wzmocniono zbocza hałdy odpadów gruntem zbrojonym, czaszę uszczelniono materiałem syntetyczno-mineralnym, a od strony dopływu wód podziemnych (w 2002 r.) wykonano ekran sięgający do warstwy nieprzepuszczalnej, mający zatrzymywać dopływające wody podziemne. W 2004 r. zasypano zbiornik na odcieki.

Analizując zawartości wapnia i magnezu w wodach podziemnych dopływających do składowiska, nie wykazano innego źródła zanieczyszczenia. W odciekach składowiskowych proporcje między stężeniami wapnia i magnezu utrzymywały się na zbliżonym poziomie. Podobnie jak na innych składowiskach, w pierwszych latach badań wykazano większe stężenia wapnia, odcieki z dłużej składowanych odpadów zawierały większe ilości magnezu. Podwyższone zawartości wapnia i magnezu w wodach podziemnych przepływających pod nieuszczelnioną częścią składowiska wskazywały na ciągły dopływ zanieczyszczeń, nie zahamowany przez zabiegi techniczne zastosowane w trakcie rekultywacji obiektu. Zmiany właściwości wód odpływających za składowiskiem zależały głównie od składu wód dopływających do obiektu (maksymalne stężenia wystąpiły w podobnym czasie) oraz ilości zanieczyszczeń emitowanych do podłoża ze złoża odpadów (proporcje między średnimi zawartościami wapnia i magnezu zmieniały się w nich podobnie jak w odciekach ze składowiska).

Słowa kluczowe: składowisko odpadów komunalnych, wody podziemne, odcieki składowiskowe, wapń, magnez.

INTRODUCTION

Calcium and magnesium are two elements which are chemically similar and common in the environment. In underground waters calcium concentrations do not usually exceed 100 mg·dm^{-3}, and those of magnesium 50 mg·dm^{-3}. The ratio Ca/Mg in slightly mineralized waters has most often the value 2-6 (MACIOSZCZYK, DOBRZYŃSKI 2002).

Contaminations carried by effluents from communal waste dumps are a serious danger to underground waters. They can contain solutes washed away by atmospheric precipitation, and also organic and mineral substances that are produced in aerobic decomposition of waste. The greatest amounts of contaminants are found in effluents that appear during the first few years of dumping. With oncoming stabilization of the decomposition processes, concentrations of most contaminants in effluents decrease. Aside of substances known to be harmful to the environment (e.g., heavy metals), effluents may contain large amounts of elements commonly occurring in nature, which are regarded not dangerous at natural concentrations. In effluents from "young" dumps, where the waste undergoes acidic fermentation mainly, calcium concentrations may exceed 3,000 mg·dm^{-3} and that of magnesium up to 1,500 mg·dm^{-3}. Effluents from "old" dumps, where methane fermentation dominates, most often contain up to 400 mg·dm^{-3} calcium and 200 mg·dm^{-3} magnesium (THORNTON et al. 2005, PAPADOPOPULOU et al. 2007).

The aim of the work was to find out the character and dynamics of changes in concentrations of the elements studied in effluents from a communal waste dump at Maślice near Wrocław and in underground waters in its vicinity.

MATERIAL AND METHODS

The investigations were carried out in the area around the communal waste dump at Maslice near Wrocław. Dumping of waste on this spot began in the late 1960s, utilizing for that purpose an excavation (of 7 ha area) that remained after sand exploitation. The ground under the dump is formed of sand-gravel formations, and the underground water surface is found at 1-2 m above the dump bottom. Such conditions facilitate contact between underground waters and the dumped waste, and transport of washed-out contaminants. The direction of underground water flow is from south-west to north-east towards the Odra river (SZYMAŃSKA-PULIKOWSKA 2001). Only part of the dump has sealing and drainage that directs the effluents to a reservoir, where the study samples were taken. At the turn of 1999-2000 the dump exploitation was terminated and its reclamation started. Consequently, the slopes of the refuse heap were fortified with reinforced ground, the cap sealed with synthetic-mineral material, and from the side of underground water inflow a shield was made (in 2002) that reached down to the impermeable ground layer in order to stop the inflowing waters. In 2004 the reservoir for effluents was filled in (SZYMAŃSKA-PULIKOWSKA 2005).

The paper presents the results of research on the content of calcium and magnesium in underground waters flowing into the dump, in dump effluents and in underground waters flowing out of the dump. The investigation was conduced in 1995-2007, while the investigations on the dump effluents were terminated when the reservoir was filled in. The samples were taken 3 times a year – the effluents from the reservoir and underground waters from four piezometers localized on the inflow (2) and outflow sides (2). Before sampling the water stagnant in the piezometric well was pumped out twice. Calcium and magnesium contents in the samples taken were determined according to methods described in the literature (NAMIEŚNIK et al. 1998, HERMANOWICZ et al. 1999). Statistical analysis of the results was conducted using the Statistica 7.1 program.

RESULTS AND DISCUSSION

Table 1 presents the characteristic values (mean, standard deviation, variance coefficient) and mean calcium to magnesium ratios of concentration in successive years of investigation on underground waters flowing into the dump.

Calcium content in the samples assayed exhibited great variation, being in the range 4.803-154.3 mg$\cdot$dm^{-3} and with maximum in the years 1998--2000. Magnesium contents varied similarly, the mean being in the range 6.683-87.20 mg$\cdot$dm^{-3} and culminating in 1998-2000. Large differentiation was also shown by the relation between mean calcium and magnesium concentrations (from 0.435 to 7.260), exceeding slightly the range determined for natural conditions. In spite of the large variation, the contents of calcium and magnesium observed in waters flowing into the dump did not diverge (aside of 1998-2000) from values that were regarded natural (MACIOSZCZYK, DOBRZYŃSKI 2002).

Table 2 shows the characteristic values (mean, standard deviation, variance coefficient) and means calcium to magnesium ratios of concentrations in successive years of investigation on the dump effluents at Maślice (the years 1995-2003, without 1998).

The highest values occurred in the beginning of the study period in 1995. The effluents then contained, on average, 480.7 mg$\cdot$dm^{-3} calcium and 280.0 mg$\cdot$dm^{-3} magnesium. In the successive years the concentrations did not reach such high values. Since 2000 the mean contents of both elements

Table 1

Characteristic values and mean calcium to magnesium ratios
in waters coming to the dump

Years		μ ($mg \cdot dm^{-3}$)	Ca/Mg	δ	ν (%)
1995	Ca	35.58	3.881	16.71	46.95
	Mg	9.167		2.251	24.56
1996	Ca	31.58	4.725	17.13	54.24
	Mg	6.683		3.543	53.01
1997	Ca	79.13	7.260	47.21	59.66
	Mg	10.90		7.034	64.54
1998	Ca	129.9	1.881	39.58	30.48
	Mg	69.05		73.53	106.5
1999	Ca	117.8	1.351	76.92	65.33
	Mg	87.20		91.01	104.4
2000	Ca	154.3	6.674	55.53	36.00
	Mg	23.12		28.47	123.1
2001	Ca	55.83	1.794	22.60	40.47
	Mg	31.12		43.37	139.3
2002	Ca	38.57	4.838	30.55	79.21
	Mg	7.973		6.905	86.60
2003	Ca	18.22	2.240	13.98	76.73
	Mg	8.133		4.955	60.92
2004	Ca	19.57	2.082	14.42	73.68
	Mg	9.400		6.232	66.30
2005	Ca	4.803	0.435	2.854	59.43
	Mg	11.05		7.656	69.29
2006	Ca	74.98	4.403	73.71	98.30
	Mg	17.03		18.00	105.7
2007	Ca	77.38	3.726	44.30	57.25
	Mg	20.77		10.59	51.00

Explanations: μ – mean, δ – standard deviation, ν – variance coefficient

systematically decreased, which may indicate a depletion of the "resources" accumulated in the dump. Studies conducted on Dyer Boulevard Landfill (Florida, USA) found that effluent samples (taken after dump closure) contained 176.13 $mg \cdot dm^{-3}$ Ca and 53.75 $mg \cdot dm^{-3}$ Mg (STATOM et al. 2004) – values only slightly higher than those for the Maślice dump after closure.

Table 2

Characteristic values and mean calcium to magnesium ratios in dump run-offs

Years		μ (mg·dm^{-3})	Ca/Mg	δ	ν (%)
1995	Ca	480.7	1.717	160.1	33.29
	Mg	280.0		20.00	7.143
1996	Ca	131.7	1.289	100.1	75.99
	Mg	102.2		76.24	74.59
1997	Ca	117.8	1.758	40.51	34.38
	Mg	67.00		24.62	36.75
1999	Ca	121.1	0.590	130.6	107.9
	Mg	205.3		15.14	7.375
2000	Ca	137.1	1.023	49.81	36.32
	Mg	134.6		95.02	70.57
2001	Ca	93.33	1.150	11.55	12.37
	Mg	81.17		52.98	65.27
2002	Ca	66.43	0.840	16.99	25.57
	Mg	79.00		40.95	51.84
2003	Ca	60.67	0.851	44.76	73.78
	Mg	71.33		44.24	62.02

Explanations: μ – mean, δ – standard deviation, ν – variance coefficient

Relations between calcium and magnesium concentration in the dump effluents varied from 0.590 to 1.758, departing markedly form the values found in waters flowing to the dump. During all the study period the values observed showed large variation. In the first years of the study calcium concentrations prevailed. After the dump closure the concentrations of both the elements reached a similar level, with magnesium concentration even starting to prevail. This tendency could be confirmed by the research done by Williams (2002). He reported that effluents arising in the phase of acidic fermentation may contain 270-6240 (151 on average) mg Ca·dm^{-3} and 25--820 (384 on average) mg Mg·dm^{-3}; whereas concentration ranges for the phase of methane fermentation are: 20-501 (151 on average) mg Ca·dm^{-3} and 40-1580 (250 on average) mg Mg·dm^{-3}. A similar trend in the changes of calcium and magnesium concentrations in dump effluents was shown in an investigation conducted on a dump in Sieraków (Meller et al. 2001). The highest concentrations of calcium and magnesium were found in effluents from the youngest quarter of the dump, with calcium concentration prevailing. Effluents from older quarters contained concentrations of the elements that were several times lower, with magnesium concentration prevailing.

Table 3 shows the characteristic values (mean, standard deviation, variance coefficient) and ratio of mean concentrations of calcium and magnesium in successive years of research on underground waters flowing out of the dump. Contents of calcium and magnesium were markedly higher than those in waters flowing into the dump, with large variance. Mean calcium concen-

Table 3

Characteristic values and mean calcium to magnesium ratios in waters flowing from the dump

Years		μ (mg·dm^{-3})	Ca/Mg	δ	ν (%)
1995	Ca	177.0	5.836	37.26	21.06
	Mg	30.33		7.250	23.90
1996	Ca	122.6	8.212	72.15	58.86
	Mg	14.93		3.000	20.10
1997	Ca	201.1	4.428	84.05	41.79
	Mg	45.42		29.38	64.70
1998	Ca	254.8	0.879	96.43	37.85
	Mg	290.0		171.5	59.15
1999	Ca	415.7	1.488	106.6	25.64
	Mg	279.3		78.28	28.03
2000	Ca	624.3	3.315	205.3	32.86
	Mg	188.3		179.9	95.54
2001	Ca	422.5	2.809	293.5	69.46
	Mg	150.4		73.86	49.10
2002	Ca	156.4	1.185	79.24	50.67
	Mg	132.0		23.26	17.62
2003	Ca	204.8	1.476	166.0	81.11
	Mg	138.8		34.46	24.84
2004	Ca	212.9	1.476	141.9	66.64
	Mg	144.2		49.18	34.11
2005	Ca	49.61	0.404	33.53	67.59
	Mg	122.8		70.72	57.61
2006	Ca	293.9	3.016	271.8	92.50
	Mg	97.43		62.71	64.50
2007	Ca	118.4	1.611	72.15	60.95
	Mg	73.48		61.19	83.27

Explanations: μ – mean, δ – standard deviation, ν – variance coefficient trations were from 49.61 to 624.3 mg□dm^{-3}, and those of magnesium 14.93 to 290.0 mg□dm^{-3}. The highest contents of the elements discussed occurred in underground waters flowing out of the dump in the years 1998-2001. At the beginning of the study period (1995-1997) in the waters analyzed calcium prevailed, in later years the prevalence was not so distinct. A high and distinct differentiation in concentrations of the elements was also noticed in studies on a dump in Radiowo (PACHUTA, KODA 2001). Underground waters around the dump contained from 68.25 to 329.75 mg Ca·dm^{-3}, and from 14.02 to 193.87 mg Mg·dm^{-3}. Similar results were obtained in investigations in the vicinity of an unsealed communal dump in Gazipur (Delhi). Underground waters contained from 43 to 447 mg Ca·dm^{-3} and up to 220 mg Mg·dm^{-3} (MOR et al. 2006). On the other hand, investigation of underground waters from dug wells near a communal waste dump situated in the Green Region of Poland (TAŁAŁAJ 2001) showed lower calcium concentrations (73.4 mg·dm^{-3} on average) and that of magnesium (34.1 mg·dm^{-3} on average), with high variations.

Increased contents of calcium and magnesium in underground waters under the unsealed part of the communal waste dump indicated a continuous inflow of contaminants, not eliminated by the technical means applied during the reclamation of the site. Changes in the composition of waters flowing out of the dump depended mainly on two factors: composition of incoming waters (max. concentrations occurred concurrently) and contaminants emitted into the ground from the dump (relations between mean contents of calcium and magnesium varied in them like in effluents from the dump).

CONCLUSIONS

1. Calcium and magnesium contents in underground waters flowing out of the dump did not indicate other sources of contamination.

2. In spite of the variation in mean concentrations of calcium and magnesium in the dump effluents in the successive years of study, relations between contents of the elements remained at a similar level (the ratio Ca/Mg was from 0.590 to 1.758). Like in other dumps, in the first years of study calcium concentrations prevailed, whereas effluents from old dumps contained more magnesium.

3. The content of calcium and magnesium in underground waters flowing out of dump depended on both quality of incoming waters and composition of effluents to the ground.

REFERENCES

HERMANOWICZ W., DOJLIDO J., DOŻAŃSKA W., KOZIOROWSKI B., ZERBE J. 1999. *Fizyczno-chemiczne badanie wody i ścieków*. Arkady, Warszawa, 555 ss.

MACIOSZCZYK A., DOBRZYŃSKI D. 2002. *Hydrogeochemia strefy aktywnej wymiany wód podziemnych*. Wyd. Nauk. PWN, Warszawa, 448 ss.

MELLER E., NIEDŹWIECKI E., WOJCIESZCZUK T. 2001. *Koncentracja makroelementów i pierwiastków śladowych w odciekach pochodzących z trzech kwater wysypiska odpadów komunalnych w Sierakowie*. Zesz. Probl. Post. Nauk Rol., 477: 405-410.

MOR S., RAVINDRA K., DAHIYA R. P., CHANDRA A. 2006. *Leachate charakterization and assessment of groundwater pollution near municipal solid waste landfill site*. Environ. Monit. Assess., 118(1-3): 435-456.

NAMIEŚNIK J., JAMRÓGIEWICZ Z. (red.) 1998. *Fizykochemiczne metody kontroli zanieczyszczeń środowiska.* Wyd. Nauk.-Tech., Warszawa, 462 ss.

PACHUTA K., KODA E. 2001. *Stan środowiska i samoistne kształtowanie się pokrywy roślinnej na terenie wysypiska „Radiowo" koło Warszawy*. Zesz. Probl. Post. Nauk Rol., 478: 487-493.

PAPADOPOULOU M. P., KARATZAS G. P., BOUGIOUKOU G. G. 2007. *Numerical modelling of the environmental impact of landfill leachate leakage on groundwater quality – a field application*. Environ. Model. Assess., 12(1): 43-54.

STATOM R. A., THYNE G. D., MCCRAY J. E. 2004. *Temporal changes in leachate chemistry of a municipal solid waste landfill cell in Florida, USA*. Environ. Geol., 45(7): 982-991.

SZYMAŃSKA-PULIKOWSKA A. 2001. *Wpływ wysypiska odpadów komunalnych Maślice na środowisko*. Zesz. Nauk. AR we Wrocławiu, 413: 31-47.

SZYMAŃSKA-PULIKOWSKA A. 2005. *Zanieczyszczenie wód podziemnych w otoczeniu starego składowiska odpadów komunalnych*. Zesz. Probl. Post. Nauk Rol., 505: 439-444.

TAŁAŁAJ I. A. 2001. *Jakość wód gruntowych w studniach kopanych w pobliżu składowisk odpadów komunalnych*. Zesz. Probl. Post. Nauk Rol., 475: 497-504.

THORNTON S. F., TELLAM J. H., LERNER D. N. 2005. *Experimental and modelling approaches for the assessment of chemical impacts of leachate migration from landfills: A case study of a site on the Triassic sandstone aquifer in the UK East Midlands*. Geotech. Geolog. Engin., 23 (6): 811-829.

WILLIAMS P. T. 2002. *Emissions from solid waste management activities*. Environ. Sci. Technol., 18: 141-170.