Review

Physico-Chemical and Toxicological Characteristics of Leachates from MSW Landfills

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Abstract

This article contains a review of literature on the quantity and physico – chemical characteristics of leachates from municipal solid waste (MSW) landfills. The state of knowledge on estimation of hazard landfills through toxicity testing of leachates by use of aquatic organisms is also presented. There is little information in Poland regarding the harmful effects of leachate waters on aquatic biocenoses.

Keywords: municipal solid waste (MSW) landfills, MSW landfill leachates, physico-chemical composition, toxicity

Introduction

In accordance with art. 3.3 of the Act on Waste from April 27, 2001 (Law Gazette 2001 no. 62, item 628) as municipal wastes are regarded those wastes that arise in households, as well as wastes that do not contain hazardous materials originating from other producers, whose nature or composition resembles wastes arising in households.

Waste landfilling continues to be the main and most common method of disposal of municipal solid wastes (MSW) in Poland. Wastes generated in our country basically differ with regard to composition from those generated in the European Union countries. They contain fewer plastic materials but a lot of organic components, paper, metal and also hazardous components. This is caused by the inadequately developed selection of waste materials. Even though the Act on Waste makes the initial selection of scrap materials appropriated for composting or thermal processing obligatory, these requirements do not, however, concern their deposition on landfills.

Incorrectly secured and improperly operated municipal solid waste (MSW) landfills pose a serious threat to the environment, mainly to surface and ground waters. The need to protect ground waters as a valuable source of pure water for human use resulted in the 1960s in the introduction of the obligation to dump wastes on landfills with leak-tight bases. The elimination of the hazard related to the pollution of ground and surface waters is closely tied to the piping, storage and disposal of leachates generated during the exploitation of MSW landfills and frequently also after their closure. The scale of this threat depends on the quantity and composition of the leachates and the distance of a landfill from waters [1, 2]. Knowledge of the quantity and composition of leachates is necessery when designing treatment facilities and is important in determining raw leachate pollution effect on the environment. MSW landfill leachates can be considered as highly concentrated complex effluents which may contain mineral and organic compounds (humic substances, fatty acids, aromatic compounds), heavy metals and many other hazardous chemicals. Bioassays using different organisms are useful tools and provide essential information on the toxicological effects of leachate waters on aquatic biocenoses [3,4,5].

Quantity of MSW Landfill Leachates

The quantity of leachate waters generated in landfills depends mainly on the climatic factors in its vicinity, that is the above all on the water balance in the layer

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covering wastes. The volume of leachates is also affected by: initial moisture content of the wastes, solid waste composition, biochemical and physical transformations taking place in them and causing changes in their humidity and by the inflow of water from outside a landfill [1, 2]. The amount of leachates in the scale of a year is not constant. They are formed most frequently in the period from November to April, with the maximum usually occurring in December. The dry period when leachates practically do not form usually lasts from May to October. The nonuniform leachate generation factors adopt values from 2.6 to 3.5 [6].

Systematic studies on the quantity of leachates have not yet been carried out in practically any of the landfills in Poland. During the exploitation of landfills no observations of their water balance are made and the quantity and quality of leachates is analysed only sporadically as part of the overall monitoring of landfills. For some landfills there are data relating to the amounts of leachates removed to municipal wastewater treatment plants. The practical use of many mathematical models elaborated for forecasting the water balance of landfills and quantity of leachates that can arise over many years of operation is hindered by the lack of appropriate output data, and the results of calculations considerably depart from the actual exploitation data [7 after 8].

The age of a landfill also significantly affects the quantity of leachates formed. The ageing of a landfill is accompanied by increased quantity of leachates, which according to Szpadt [7] should be ascribed to the water-retaining capacity of wastes with simultaneous reduction of their water capacity as a result of the mineralization of organic substances. In effect, the amount of leachates in older landfills being exploited over longer periods of times without a cover layer may increase to even 25-30% of total precipitation. These data concern landfills that are strongly condensed by compactors that are used in Poland at most large sites. For small landfills that are usually poorly compacted with the use of bulldozers, higher quantities of leachates, of the order of ca 40% of total precipitation, are assumed for the balances [7].

Physico-Chemical Composition of MSW Landfill Leachates

Leachates arise as a result of the infiltration of precipitation to the interior of landfills, but at the same time water present in the wastes and released in different processes taking place in a landfill also contributes to the generation of leachates. There are several factors affecting the composition of leachates and their production. According to Johansen and Carlson [1] the most important of these are: solid wastes composition, operation mode of a landfill, climate and hydrogeological conditions as well as those inside the landfill (biochemical activity, moisture, temperature, pH and age of landfill). The above-mentioned factors vary considerably from landfill to landfill.

The breakdown of organic compounds in wastes may occur under aerobic, anaerobic or mixed aerobic-anaerobic conditions. Degradation in aerobic or aerobic-anaerobic conditions leads to the rapid stabilization of organic components and relatively low concentrations of organic and inorganic substances in the leachates [2]. This occurs in most landfills in Poland, especially not very large ones that are characterized by lack of regular compacting or poor compacting and deposition in thin layers on a large surface [7]. In the opinion of the same author the strong condensation of wastes leads to anaerobic conditions inside a landfill and subsequent development of methane fermentation. This process occurs in two stages: acidogenic, characteristic for "young" landfills (hydrolysis, formation of organic acids, hydrogen and carbon dioxide) and methanogenic, proper to "old" landfills (formation of methane, carbon dioxide etc.). Other authors [9, 2, 10, 11] emphasize, however, the considerable fluctuations in the physico-chemical composition of the leachates, depending on atmospheric conditions, technology for depositing waste materials and age of landfill.

Leachates generated in the initial period of waste deposition (up to 5 years) on landfills have pH 3.7-6.5 that reflects the presence of carboxylic acids and bicarbonate ions. With time the leachates become neutral or weakly alkaline (pH 7.0-7.6). Landfills exploited for a long period of time give rise to alkaline leachates (pH 8.0--8.5) [12]. However, according to Szpadt [7], otherwise than in the case of foreign landfills, leachates from Polish ones usually do not show an acidic pH, even in the course of acidogenic fermentation, this being due to the high alkalinity of municipal wastes that contain ashes and slag from the combustion of stone coal and coke in household furnaces.

The early comprehensive paper by Johansen and Carlson [1] deals with the identification of the composition of leachates from six landfills in the Oslo region in Norway and two in the Seattle region in the USA. Leachate samples were taken during dry and rainy weather. The composition of the leachates is presented in Table 1. Considerable fluctuations in the composition of the leachates, related mainly to the efficiency with which water penetrated into the landfills, were observed. For the high strength leachates 90% of the total content of organic compounds was accounted for by organic acids, mainly acetic, propionic and butyric. The high concentrations of the acids reflect the high efficiency of the first two stages of anaerobic degradation in which complex organic compounds are converted to organic acids that are easily water soluble; low concentrations of acids point, however, to the low effectiveness of the degradation or stabilization of organic compounds as occur in the second stage of anaerobic degradation. In the view of the authors the remaining part consisted of such unidentified compounds as humic acids, lignins and other cellulose-like materials. All leachate samples were found to contain high concentrations of nitrogen, mainly in the form of ammonium (NH_4-N),

Table 1. Leachate analysis from some landfills in Norway and the Pacific Northwest, USA [1].

Parameter / Fill			Norway						USA	
			Grønmo	Brånåsdalen	Yggeseth	Isi I	Isi II	Taranrød	Cedar Hills	Kent Highland
Dry weather analysis	COD	mg O_2/l	470	1080	9425	825	110	3455	38800	3800
	BOD total	mg O_2/l	320	870	5250	590	50	2300	24500	2460
	TOC	mg C/l	100	250	1700	180	30	800		
	Total N	mg N/l	182	254	250	155	16.6	156	630	56
	NH_4-N	mg N/l	120	225	227	141	10.2	84		
	NO_3-N	mg N/l	0.04	0.01	0.04	0.02	0.79	0.68		
	Organic N 1)	mg N/l	62	29	23	14	6	71		
	Total P	mg P/l	0.6	1.7	7.7	3.3	0.1	1.6	11.3	5.9
	Suspended solids	mg/l	140	397	466	270	68	1079	310	220
	Volatile suspen. solids	mg/l	85	98	182	229	11	602	170	90
	Total solids	mg /	2960	2730	4160	3880	610	3160		
	Total volatile solids	mg/l	760	1005	2180	890	145	1670		
	pH		6.8	6.9	5.9	7.0	6.4	6.2	5.4	6.4
	Alkalinity	meq/l	30	41	39	31	6.2	21.6	130	26
	Spec. conductance	mS/cm	3310	3210	3380	3050	655	2370		
	Ca	mg Ca/l	188	198	400	173	99	218		
	Mg	mg Mg/l	66	96	54	58	13	40		
	Na	mg Na/l	462	229	206	312	34.8	197		
	K	mg K/l	200	172	187	219	21.3	214		
	Chloride	mg Cl/l	680	280	370	590	68	340		
	Sulphate	mg SO_4/l	30	10	100	37	41	100		
	Fe	mg Fe/l	67.6	78.0	234	37.7	11.5	68.9	810	245
	Zn	mg Zn/l	0.055	0.095	0.65	0.085	0.12	2.65	155.0	5.3
	Cr	mg Cr/l	0.023	0.035	0.06	0.027	0.002	0.17	1.05	0.05
	Ni	mg Ni/l	<0.1	0.02	0.03	0.015	0.005	0.12	1.20	0.10
	Cu	mg Cu/l	0.085	0.011	0.022	0.009	0.008	0.021	1.30	0.18
	Cd	mg Cd/l	0.0005	0.0001	0.0009	0.002	0.0005	0.0008	0.03	0.01
	Pb	mgPb/l	0.004	0.001	0.01	0.001	0.001	0.015	1.40	<0.1
	Co	mg Co/l	-	0.009	0.07	0.018	0.004	0.033	-	-
Wet weather analysis	COD	mg O_2/l	520	825	9730	215	145	245	9100	455
	Total N	mg N/l	155	255	305	80	12	24	172	31
	Fe	mg Fe/l	84.3	42.7	258	10.2	6.8	10.3	215	38

1) Calculated as the difference between total N and NH_4-N

whereas the content of phosphates was low. As for metals, high concentrations of iron in the leachates, followed by zinc, were determined. The concentrations of chromium, nickel, copper, cadmium and lead were low and ranged from 0.01 to 1.4 mg/l.

The regularities regarding the low content of organic compounds and concentrations of sulphates and small BOD_5/COD ratio in leachates from landfills with long operation time (5-10 years) and with active methanogenesis, and on the other hand the high content of organic compounds with domination of fatty acids and high BOD_5/COD ratio in leachates from the acidogenic phase of degradation, presented by Johansen and Carlson [1] and Ehrig [13], were confirmed by the results obtained by Schultz and Kjeldsen [9] from Danish landfills.

Tałałaj [12] presents changes in the composition of leachates, depending on the duration of exploitation on the example of landfills in Hryniewicze near Białystok (Table 2). The new field of this landfill is in its acidogenic stage and hence the leachates contain high concentrations of volatile fatty acids. They are also characterized by relatively low pH values varying from 6.4 to 7.9 and at the same time high BOD_5 and COD values ranging from 5,000 to 13,000 mg/l and 19,000-21,000 mg/l, respectively. With the ageing of the landfills the processes of the biological degradation of organic substances slow down and the susceptibility of leachates to biological degradation declines. In effect, leachates from old deposition sites are characterized by smaller BOD_5 and COD values of the order of several hundred to several thousand mg/l O_2 and approximately 3,000 to 7,000 mg/l O_2, respectively, and even very low ones in both cases, approximately several hundred mg/l O_2. The BOD_5/N-NH_4 ratio that is quite frequently encountered in the literature [14] is useful for the characterization of leachates. For young leachates this ratio is considerably larger than 1, whereas for older ones it is lower than 1 or close to it. In the case of the landfill in Hryniewicze, the BOD_5/N-NH_4 ratio for its younger parts ranges from 9.7 to 24.0 and for the older ones is in the 0.8-2.0 range.

Similarly, Jędrczak and Haziak [2] after Thomanetz [15] present the chemical composition of leachates from municipal landfills in Germany from "young" (2-4 years) wastes in which the acidogenic phase of methane fermentation dominates and from "old" wastes (over 5 years) in which methane fermentation takes place (Table 3A). The development of methane fermentation is accompanied by the stabilization of organic compounds in the wastes and their concentrations in the leachates drop. Consequently, the value of the BOD_5/COD ratio drops from 0.7 to below 0.1, pH of the leachates increases and the concentration of heavy metals declines. In Table 3B and 3C is presented range of values and mean chemical composition of leachate waters in this country.

The data obtained by various authors, compiled by Kulikowska [16], indicate that in the case of landfills exploited less than five years the BOD_5/COD ratio averages 0.54, with the range of values from 0.22 to 0.7. In the case of landfills operating longer than five years the ratio was lower and averages 0.31, with values ranging from 0.08 to 0.7. The relatively high BOD_5/COD ratio in leachates from older landfills can be explained not only by exploitation conditions but also by the type of wastes deposited.

The high content of dissolved organic carbon (DOC) is the result of anaerobic degradation processes in a landfill. Even in old landfills characterized by extensive

Table 2. Changes in the composition of leachates depending on duration of landfill exploitation [12].

Parameter	Units	Range of value			
		New field of deposition of solid waste		Old field of deposition of solid waste	
		1997	1998	1997	1998
pH	-	6.40 – 6.51	7.9- 8.04	7.49 – 7.60	7.85 – 8.50
BOD_5	mg O_2/l	5140 – 12818	-	664 - 3218	-
COD_{Cr}	mgO_2/l	18907 - 20534	420 - 3610	3234 - 6727	648 - 720
Chlorides	mg Cl/l	260 - 2400	850 - 2650	5000 - 7000	1350 - 3250
COD_{Mn}	mg O_2/l	750 - 1000	-	1150 - 2150	-
Total N	mg N/l	705 - 832	-	1300 - 2400	-
NH_4 - N	mg N/l	686-700	400-3400	1055 - 2290	1750 - 4500
NH_3 -N	mg N/l	532 - 543	310 - 2637	820 - 1775	1357 - 3490
Total P	mg P/l	3.9 – 12.7	-	5.2 – 21.9	-
Total suspended solids	mg/l	100 - 1100	-	125 - 400	-
BOD_5/ NH_3 -N	-	9.7 – 24.0	-	0.8 – 2.0	-
BOD_5/ Total P	-	1.318 - 1009	-	128 - 147	-

Investigations in 1997 carried out by the Water Supply System of Białystok

Table 3A. Chemical composition of municipal landfill leachates in Germany [2 after 15].

Parameters		Acidogenic phase		Methanogenesis phase	
		Range of value	Mean value	Range of value	Mean value
pH		-	<7		>7
COD_{Cr}	mg O_2/l	6000 - 60000	22000	500 - 4500	3000
BOD_5	mg O_2/l	4000 - 40000	13000	20 - 550	180
BOD_5/ COD_{Cr}		0.5 - 0.7	0.6	0.04 - 0.1	0.06
Sulphates	mg/l	70 - 1750	500	10 - 420	80
Ca	mg/l	10 - 2500	1200	20 - 600	60
Mg	mg/l	50 - 1150	470	40 - 350	180
Fe (total)	mg/l	20 - 2100	780	3 - 280	15
Mn	mg/l	0.3 - 65	25	0.03 - 45	0.7
Zn	mg/l	0.1 - 120	5	0.03 - 4	0.6

Table 3B. Chemical composition of municipal landfill leachates in Germany [2 after 15].

Parameters		Range of value	Mean value
Total dissolved solids	mg/l	300 - 50000	8000
NH_4 -N	mg N/l	30 - 3000	750
NO_2 - N	mg N/l	0.001 - 25	0.5
NO_3 - N	mg N/l	0.1 - 50	3
Organic N	mg N/l	10 - 4250	600
Total N	mg N/l	50 - 45000	1500
Total P	mg P/l	0.1 - 30	6
Chlorides	mg Cl/l	100 - 45000	1500
Na	mg/l	50 - 4000	1350
K	mg/l	10 - 2500	1100
F	mg/l	0.05 - 6	3
Cyanides	mg/l	0.001 - 2	0.01
AOX	mg/l	0.3 – 3.4	2

Table 3C. Chemical composition of municipal landfill leachates in Germany [2 after 15].

Parameters		Range of value	Mean value
Arsenic	mg/l	0.0 - 1.0	0.02
Barium	mg/l	0.3 - 0.9	0.7
Boron	mg/l	4 - 9	5
Chromium (total)	mg/l	0.02 - 15	0.2
Aluminium	mg/l	0.3 - 28	2
Cadmium	mg/l	0.001 – 0.1	0.005
Copper	mg/l	0.01 - 1	0.05
Molybdenium	mg/l	-	0.01
Nickel	mg/l	0.02 - 2	0.2
Lead	mg/l	0.02 - 1	0.05
Mercury	mg/l	0.001 – 0.05	0.01
Selenium	mg/l	0.00 – 0.01	
Vanadium	mg/l	0.01 – 0.03	0.01

methanogenesis, leachates tens of years later may contain dissolved organic carbon at the level of thousands of milligrams per litre [13]. The studies of Harmsen [17] demonstrated that approximately 33% of the DOC content in leachates from landfills being in the methanogenesis phase consisted of poorly degradable compounds with mass greater than 1000 Da. According to Artiola-Fortuny and Fuller [18] over 60% of DOC content in anaerobic leachates was accounted for by components with structure resembling that of humic compounds. These authors also suggested that fulvic acids are formed before humic acids. Hence, the "ageing" of leachates and their dilution is accompanied by a change in the ratio of humic acids to fulvic acids from below one to above 1. However, Chian [19] and Chian and de Walle [20] observed the opposite tendency in time.

In general, literature reports point to the presence of the above-mentioned types of acids in old leachates which, however, were characterized in but a few cases. On the other hand, there is no information at all about the participation of fractions not belonging to humic and fulvic compounds. According to Christensen et al. [21] the fraction called hydrophilic can be expected to account for a significant part of dissolved organic carbon.

Studies on leachates from municipal waste landfills in Poland where industrial wastes were also deposited revealed the presence of different specific components such as a series of petroleum derivative compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls as well as heavy metals [22, 23]. Szymański [22] observed in leachates from landfills near Koszalin, on which wastes from the electrochemical industry and agricultural and food-processing industries were also deposited, the domination of fluoranthene and the occurrence of carcinogenic benzo(a)pyrene and toxic PCB 52, whose concentration reached 1.152μg/l. Similarly, Słomczyńska and Wojtkowska [23] in leachates from Łubna landfill noted the periodic occurrence of considerable heavy metal content, that is chromium, zinc, cadmium, copper, manganese, nickel, lead and iron, exceeding the values recorded for other municipal landfills and on occasion being close to the values for leachates from landfills containing industrial wastes. Wastewater sludges have also periodically been deposited on this landfill and wastes particularly hazardous for the environment, such as paint sludge, galvanic wastewaters, cullet contaminated with mercury and spent picture tubes, are also disposed of there. At the same time it should be stressed that thus far in Poland there have been no systematic studies on the composition of leachates.

Toxicity of MSW Landfill Leachates

From among the four main groups of procedures embracing the following tests [24]:

1. survival with invertebrates and fishes,
2. survival with the use of juvenile forms of invertebrates of the Toxkit type,
3. growth inhibition,
4. enzymatic various authors have used with good results several kinds of tests for the evaluation of the toxicity of leachates from municipal waste landfills.

These tests were conducted according to standard procedures elaborated in their respective countries.

In the 1980s the Canadian researchers Atawater et al. [25] and their American colleagues Plotkin and Ram [3] used survival tests with crustaceans (*Daphnia pulex, Daphnia magna)* and fishes (*Salmo gairdneri, Oncorhynchus nerka*, *Pimephales promelas)* to evaluate the toxicity of leachates from municipal waste landfills from Vancouver Lower Mainland (Canada) and Fitchburg in the state of Massachusetts (USA). Tests with crustaceans taking 48 or 96 hours were carried out according to the procedures described by Peltier [26], Standard Methods [27] and Weber [28]. To prepare solutions of leachates, lake water filtered through a 0.45 μm glass fibre filter or reconstituted water with known physical and chemical characteristics was used. At the same time the authors stressed the need to ensure an appropriate water supply to obtain reproducible results. Studies on the toxicity of leachates using *Daphnia* tests revealed that in many cases the period of 24 hours was too short for manifestation of the acute toxic effect in these organisms. Not until after 48, and in some cases even after 96 hours, was the high mortality of the organisms observed. Hence, the value LC50-48h proved to be a better indicator of the toxicity of leachates than LC50-24h (Table 4). In addition, the phenomenon of the floating of the organisms to the surface of the leachate solutions as a result of air filled of their carapaxes impeded the determination of their viability in the first 24 hours of the test.

Atwater et al. [25] conducted 96 hour tests with the fishes *Salmo gairdneri* and *Oncorynchus nerka* according to the procedure elaborated by the Canadian Federal Government Standardization Program [29] in 45 l aquariums in which the pH, temperature and oxygen content in solutions of leachates with appropriate concentration were continuously monitored and kept at constant values. The authors found a significant correlation (n=12, R^2=0.87 at confidence level 1%) between the LC50-96h results obtained with tests using the fish *Salmo gairdneri* and tests employing the crustacean *Daphnia magna*. Taking into account the generally high sensitivity of survival tests with *Daphnia magna*, in this case it proved comparable to the sensitivity of parallel tests with fishes.

Plotkin and Ram [3] carried out 96 hour tests with the fish *Pimephales promelas* according to the procedure described by Peltier [26] on both filtered and unfiltered leachates. For the dilutions, reconstituted water characterized by low hardness was used. The tests embraced young specimens with average weight 0.6 g. Besides the crustaceans and fishes mentioned above, the authors also employed the alga *Selenastrum capricornutum* for evaluation of the toxicity of leachates in a test according to the modified procedure of Miller et al. [30] and the luminescent bacterium *Photobacterium phosphoreum* in the Microtox test according to the instructions of Beckman Instruments Inc. [31].

The battery of tests presented above used by Plotkin and Ram [3] demonstrated the high toxicity of the leachates for the alga *Selenastrum capricornutum* and luminescent bacterium *Photobacterium phosphoreum*, moderate toxicity for *Daphnia pulex*, and low toxicity for the fish *Pimephales promelas* (Table 4). Considerable differences in the results obtained for the four employed organisms prove the significance of carrying out tests with organisms representing different trophic levels for estimating the potential toxic effect of leachates on the aquatic ecosystem.

At present, toxicological studies prefer to employ the sublethal response of organisms (sublethal end points) for the evaluation of the deleterious effect of wastewaters/leachates. Janssen [32] and Persoone [33] recently conducted a survey of microbiotests involving invertebrates as the test organisms. These include 24 and 48 hour standard tests with larval stages of invertebrates (so-called Toxkits) and short (1-2 hours) tests determining toxicity *in vivo* based on inhibition of the activity of such enzymes as β-galactosidase and esterase. Also short (1 hour) tests with invertebrates based on measurements of suppression

Table 4. Toxicity results [LC(EC)50-t] for leachates from MSW landfills using different types of tests.

Organisms/type of test	LC(EC)50-t [%]	References
Daphnia magna survival test (crustacean) *Oncorhynchus nerka* survival test (fish)	LC50-48h = 4.8 – 89 LC50-96h = 3.8 – 86 LC50-96h = 3.2 - 56	Atawater et.al. [25]
Daphnia magna survival test (crustacean) *Pimephales promelas* survival test (fish) *Selenastrum capricornutum* growth inhibition test (alga) *Photobacterium phosphoreum* Microtox test (bacteria)	LC50-48h = 62 – 66 LC15- 96h = 100 (values based solely upon survival in 100 percent leachate after 96 hrs) 1 < EC50-13 days<10 EC50-5min = 17 All above values for filtered leachates	Plotkin and Ram [3]
 Ceriodaphnia dubia survival test (crustacean) *Ceriodaphnia dubia* CerioFAST (crustacean) *Ceriodaphnia dubia* survival test (crustacean) Chronic *Selenastrum capricornutum* test (alga) *Vibrio fischeri* Microtox test (bacteria)	The most toxic and the least toxic leachates : LC5-48h = 1.7 – 3.4; LC50-48h = 2.4 – 35.3 EC50-1h = 3.4 – 7.3; EC50-1h = 13.5 – 90.7 EC50-48h=1.4 – 17.1 EC50-96h=0.8 - 23.2 6.1<EC50-15 min > 90.0 All above values for filtered leachates	Ward et al. [36] Ward et. al.[5]
Brachydanio rerio survival test (fish)	Raw leachates: LC50-24h = 2.2 – 5.7 LC50-48h = 2.2 – 5.7 Leachates treated with 2 g $Al_2(SO_4)_3$ /l: LC50-24h = 13.2 LC50-48h = 13.2 Leachates treated with 4g $Al_2(SO_4)_3$ /l: LC50-24h = 32.6 LC50-48h = 32.6	Sisinno et al. [42]
Daphnia magna survival test (crustacean) *Daphnia magna* IQ Toxicity Test (crustacean) *Daphnia magna* Daphtoxkit F (crustacean) *Artemia franciscana* Artoxkit M (crustacean) *Thamnocephalus platyurus* Thamnotoxkit F (crustacean) *Scenedesmus quadricauda* growth inhibition test (alga)	LC50-24h = 4.4 – 23.4 EC50-1h = 2.8 – 12.8 LC50-24h = 3.8 – 20.2 LC50-24h = 13.8 – 42.4 LC50-24h = 5.4 – 22.3 EC50-72h = 3.0 – 14.8	Słomczyńska and Słomczyński [46]

of their feeding activity are used to study the toxicity of leachates. These include the recently described by Bitton et al. [34, 35] test CerioFAST with *Ceriodaphnia dubia* used by Ward et al. [36] for the toxicity testing of leachates from three MSW landfills in Florida (Alachua, Citrus, Levy). It is based on observations of the feeding behaviour of these organisms with the use of yeast cells stained with a fluorescent marker as food. After exposing the animals to solutions of leachates they were fed yeast cells stained with 5-([4,6-dichlorotriazin-2–yl] amino) fluorescein (DTAF). After 20 min. feeding period the animals were removed from the test chambers, placed on a glass slide and observed under fluorescent microscope. Specimens not demonstrating gut fluorescence were considered damaged. The results of the CerioFAST test were expressed as EC50-1h, that is the concentration resulting in reduced food uptake or absence of food uptake in 50% of the tested organisms. The results obtained with the use of this method and those from the survival tests with *Ceriodaphnia dubia* demonstrated the considerable toxicity of leachates from Citrus and Levy landfills, and the particularly high toxicity of leachates from Alachua (Table 4). The results of studies conducted by Ward et al. [36] were within the range of lethal and effective concentrations obtained by other authors who studied the toxicity of leachates from municipal waste landfills with the use of tests involving fish, invertebrates and plants [37, 3, 38]. Such high toxicity shown by CerioFAST and survival *Ceriodaphnia* test was most probably due to organic substances and ammonia content since parallel tests for the presence of metals (MetPLATE) indicated the very low toxicity or absence of heavy metal toxicity. At the same time analysis of toxicity data revealed that the EC50-1h values from CerioFAST tests were higher than the LC50-48h values obtained in the survival tests, which indicates their lower sensitivity.

In the view of the authors CerioFAST test has, however, important advantages since it may be a tool allowing the rapid determination of the toxicity of leachate samples as well as serve as a screening test, particularly in the case when wastewaters with unknown toxicity are introduced into wastewater treatment plant. At the same time it should be stressed that in their earlier studies Bitton et al. [35] and Jung and Bitton [39] demonstrated a significant correlation between the results of the CerioFAST test and 48 hour *Ceriodaphnia dubia* survival test with the use of pure compounds and industrial wastewaters.

Ward et al. [5] studied the harmful effects of MSW landfill leachates from six sites in north and north-central Florida, using a battery of tests. Toxicity of filtered leachate waters was assayed with survival *Ceriodaphnia dubia* test, chronic *Selenastrum capricornutum* test and Microtox test with *Vibrio fischeri* according to procedures recommended by the US EPA [40, 41] and Beckman Instruments [31]. The EC50 values for both *Ceriodaphnia dubia* (1.4%-17.1%) and *Selenastrum capricornutum* (0.8%-23.2%) showed that the leachates were highly toxic (Table 4). A significant relationship was found between total ammonia content of the leachates and toxicity as determined by crustacean and algal tests. For un-ionized ammonia (NH_3) content of the leachates the relationship was not as strong with either the *Ceriodaphnia dubia* or the *Selenastrum capricornutum* toxicity data. The alkalinity of the leachates assayed was relatively high. The major role of alkalinity in leachate toxicity appears related to its buffering capacity and its effect on ammonia (NH_3) concentrations. Alkalinity showed a significant relationship with the EC50 results for *Selenastrum capricornutum* and *Ceriodaphnia dubia*, but relationship with Microtox was weaker. The authors concluded that Microtox test was not as effective as the other bioassays for determining the toxicity of MSW landfill leachates.

To evaluate the toxicity of raw leachates from the Brazilian landfill Morro do Ceu and leachates pre-treated using various methods Sisinno et al. [42] employed a survival test with the fish *Brachydanio rerio* according to the Brazilian standards [43]. The pre-treatment methods involved the action of EDTA and the coagulant $Al_2(SO_4)_3$:

1. EDTA 0.1 M 5% v/v in 2000 ml of leachates;
2. EDTA 0.1 M with aeration;
3. $Al_2(SO_4)_3$ in amount of 2g/l and 4g/l;
4. $Al_2(SO_4)_3$ 4g/l with aeration;
5. combined action of $Al_2(SO_4)_3$ 4g/l and EDTA 0.1 M with aeration.

The obtained LC50-24h values proved the high toxicity of raw leachates. The LC50-48h values were identical as for LC50-24h, which indicates that acute toxicity is manifested within the first 24 hours of the test. It is probable that toxic compounds are subject to degradation or transformation in tests exceeding 24 hours. These results are incompatible with those obtained earlier by Atwater et al. [25] with the use of the *Daphnia magna* test. In this case the period of 24 hours was too short to allow the manifestation of the toxic effect. Of the employed pre-treatment methods only the use of the coagulant $Al_2(SO_4)_3$ in amount of 2 g/l or 4 g/l, combined with aeration, resulted in significantly reduced toxicity (Table 4).

To evaluate the acute and chronic toxicity of eluates from municipal wastes after their processing with the use of mechanical and biological methods over various periods of time Latif and Zach [44] employed conventional survival tests and Toxkits. Estimations of the acute toxicity of eluates were made with the use of tests involving the crustacean *Daphnia magna* (survival and Daphtoxkit F) and luminescent bacteria *Vibrio fischeri*, whereas the chronic toxicity tests employed the alga *Selenastrum capricornutum* (conventional and Algaltoxkit F) as well as a test determining the growth of the roots of the cress *Lepidium sativum*. Eluates from four waste disposal plants in Austria after different composting times were found to be characterized by differentiated toxicity. It was high with regard to algae, cress and luminescent bacteria, especially in the case of eluates from wastes with short composting times. The varied sensitivity of the four test organisms used was also observed. *Daphnia* proved less sensitive that the other organisms except for one case. It was also shown that Daphtoxkit tests were just as sensitive as conventional ones except for two cases when microbiotests were found to be more sensitive. Similarly, Algaltoxkit F was found to be a test with similar sensitivity to the conventional test with algae, except for two cases in which it proved more sensitive. The conventional growth inhibition test involving algae was found to be the more sensitive test for the evaluation of the toxicity of eluates from wastes following their processing, demonstrating particularly significantly reduced toxicity following the process of the composting of wastes over prolonged periods of time.

The results obtained by Latif and Zach [44] indicate that both Daphtoxkit F and Algaltoxkit may be successfully employed for monitoring the hazard posed to the environment by wastes. Both tests gave reliable and reproducible results for all tested samples with high correlation with conventional tests employing these organisms, which points to the possibility of their use as an alternative to commonly known conventional tests. These results seem promising for the use of this type of tests also for toxicity studies of leachates from municipal waste landfills.

In Poland there is little information regarding the harmful effect of leachates on aquatic biocenoses. Recently Słomczyńska and Słomczyński [45, 46] studied the toxicity of leachates from Łubna landfill with the use of *Daphnia magna* survival tests, microbiotests of the Toxkit type with larvae of the crustaceans *Artemia franciscana*, *Daphnia magna* and *Thamnocephalus platyurus* and enzymatic tests of the IQ Toxicity Test type with *Daphnia magna.* To this end they also used algal growth inhibition tests with *Scenedesmus quadricauda*. All the tests demonstrated the high toxicity of the studied leachates (Table 4). The values of lethal (LC50-24h) and effective (EC50-1h) concentrations obtained with Toxkits and the IQ Toxicity Tests were generally low and ranged from 2.8 to 42.4%, depending on type of test and the test organism. Also, low were the values of effective concentrations (EC50-72h) obtained in tests with algae, ranging from 3.0 to 14.8%. As shown by the results of the above-mentioned authors the possibility of the more widespread use for such evaluation of three used so far with positive results for evaluating the toxicity of substances and wastewaters seems very promising. The low values of the coefficient of variation (less than 20%) obtained for the individual tests indicate the good intralaboratory repeatability of the methods used. Microbiotests, because of their simplicity and reproducibility, as well as sensitivity and relatively low cost of execution, can be used singly for the initial evaluation of the toxicity of leachates (screening tests) and also constitute an important element of the so-called battery of toxicological tests embracing producers, consumers and decomposers. The fairly significant differences in the values of lethal and effective concentrations of leachates for various test organisms found in the quoted work and also recorded by foreign authors [3,5,44] also point to the need to use the mentioned battery of tests for evaluating the harmfulness of leachates.

A review of the literature presented in this article brings examples of the use of various tests methods for the evaluation of the toxicity of leachates. Conventional survival tests with *Daphnia magna* and algal growth inhibition tests with *Selenastrum capricornutum* are currently based on the methodology presented in International standards, OECD protocols and tests of the Toxkit type according to standard procedures for each kind of test [47-52]. The test with luminescent bacteria (Microtox and LUMIStox) is carried out according to procedures recommended by Beckman Instruments, USA [31] and Dr Lange Corporation, Germany [53], respectively. This ensures the high precision and reproducibility of toxicological studies.

Summary

Leachate waters are formed as a result of the penetration of rainfall inside a landfill and the subsequent leaching of soluble organic and mineral compounds. As shown by the presented studies, physico-chemical characteristics of leachates change over the course of a landfill's life. On so-called young landfills, the concentrations of pollutants in the leachates are high but as they age the value of BOD_5/ COD ratio decreases. This phenomenon results from the fact that young landfills contain many organic compounds that readily succumb to biodegradation, giving rise to refractory compounds that accumulate with the exploitation of landfill and are resistant to biochemical degradation.

In the case of leachates characterized by high values of BOD_5, COD, TOC and considerable concentrations of ammonium nitrogen, with pH values in the range of 6.7-8.7, high toxicity for crustaceans, fishes and algae was observed. The reason for the harmfulness of these leachates for bioindicators used was the high content of ammonium nitrogen, which under the conditions that lean towards alkaline values give rise to non-ionized toxic ammonia.

A survey of the literature data regarding methods used in toxicological studies indicates a tendency to use standardized tests according to ISO, CEN, OECD and above all to introduce cost-effective Toxkit tests, developed at the University of Ghent, Belgium. A method that has become particularly widespread is determination of the inhibition of bioluminescence of the bacterium *Vibrio fischeri* by components contributing to the toxicity of leachates (Microtox/LUMIStox test). The use of precise and highly reproducible methods involving organisms representing the food chain of an ecosystem is justified ecologically and guarantees proper interpretation of the results of studies. Consequently, in the last decade the conception of a "battery" of tests involving the use of producers, consumers, decomposers as model ecotoxicological relationships studies has been introduced.

In Poland there is scant information on deleterious effect of leachates on aquatic biocenoses. Consequently, it is absolutely necessary to introduce the large scale monitoring of toxicity of leachates flowing from municipal landfills with regard to aquatic organisms. This problem is directly related to the need to employ adequate standardized toxicity tests in parallel with determination of such specific components of leachates as, for instance, heavy metals, pesticides, PCB, and crude oil derivatives.

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