Chapter 2

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The Influence of Waste Landfills on Ground and Water Environment

1. Introduction

In Poland's legal system, the superior act governing the rules of conduct in the area of waste management is the "Waste Act" implementing relevant directives of the European Union (Council Directives 1999/31/EC and 75/442/EEC). The Act regulates general issues of the waste management in scope of preventing generation, utilization, neutralization and disposal of waste. According to its provision, neutralization consist in subjecting wastes to processes of biological, physical or chemical transformations aimed to bringing them to a state in which they no longer pose any hazard neither to human life or health nor to the natural environment.

According to the Statistical Yearbook 2010, about 12 million tons of municipal solid waste is generated annually in Poland (12,052 thousand tons in the year 2009), of which the most in Mazowieckie (15%) and Śląskie (13.7%) provinces, and the less (2%) in Świętokrzyskie. In the year 2009 alone, 10,053 thousand tons of waste were collected, of which 84% was subject to neutralization (of which 78% by means of landfilling). Wastes are collected on 803 landfills with total surface area of 2,821 ha. Depending on categorization, waste can be subject to neutralization in one of three landfill types: for hazardous, inert, or other than hazardous or inert waste. According to Ordinance of the Board of Ministers of 9 October 2004 (J. Laws No. 257, Item 2573), waste landfill sites are considered objects that can have a significant effect on natural environment. In view of the risks posed, the structures are classified as category three geotechnical objects (J. Laws No. 126, Item 839).

Currently, the most important issue concerning construction of waste landfill sites consists in minimization of their environmental impact. In the first place, proper location is being selected; next, adequate engineering solutions are adopted such as construction of complex systems isolating the landfill allowing to discharge the resulting emissions in a controlled way, with permanent and systematic monitoring of the surrounding environment (Szymańska-Pulikowska 2009).

A waste landfill can be considered a reactor in which liquid, solid and gaseous substances interact with each other, resulting in origination of leachates and biogas (Cossu 2010). Biological, physical and chemical processes and transformation occurring in the mass of the disposed waste result not only in changes of physical form of the wastes, but also lead to creation of numerous hazardous compounds that, penetrating the environment, may pose a substantial hazard to surface waters, underground waters, and the soil.

Decomposition of municipal wastes in a landfill site proceeds in several stages (Fig. 1). Each of the stages is characterized by specific changes in population of individual groups of bacteria and creation and utilization of products of their metabolism, while different fragments of a landfill (even if located close to each other) may coexist in different stages of the decomposition process.



Fig. 1. Stages of organic compounds decomposition in waste landfill (Kaczorek, Ledakowicz 2005)

Throughout the whole operation period, but also after its termination, a landfill is exposed to contact with waters, the source of which is mainly precipitation. A portion of precipitation water reaching the area of the disposed waste is subject to surface runoff, some part evaporates, and the remaining portion migrates through the landfill volume leaching soluble solids, liquid and gaseous substances out from it and resulting in occurrence of leachates. Potential contamination of the water-soil environment by a landfill may depend on many factors, the most important of which are: the type of dumped waste, amount of leachates migrating outside the landfill, insulating properties and self-cleaning capabilities of the substrate. Leachates infiltrating deep into the ground result not only in its chemical and microbiological contamination but may also results in a change of its geological and engineering parameters.

Many factors are decisive for the quantity of leachates generated, in particular climatic and hydrogeological conditions. Average annual atmospheric precipitation, amount of snowmelt water and intrusion of ground waters are of special importance in this case. Other factors considered particularly important include also; the waste preparation methods (segregation, compacting), landfill structure and operating condition of the waste disposal process (shields, side walls, watering, recirculation, vegetation mantle), as well as parameters characterizing the landfill bed, including particle size, density and moisture content. Other effects result from the processes occurring in the landfill and related to the organic matter decomposition degree, gas generation effectiveness, or settlement (Øygard *et al.* 2004, Ozkaya 2005, El-Fadel *et al.* 2002).

Water accumulated in the waste bed may appear both in the free state, filling empty spaces between waste particles and moving gravitationally towards the drainage, and in the bound form, moistening such materials as paper, cardboard, kitchen waste, greenery waste and earth. Usually, waste dumped to a landfill contains about 40% water in its mass. As a result of compacting processes, water is partly squeezed and freed from the waste becoming thus a leachate, partly used in biological transformation processes, or subject to evaporation; the remaining part is still bound with the waste. Water losses are supplemented with atmospheric precipitation, however, with the passage of time, the waste bed is gradually drying off. The delay time between rainfall and occurrence of leachates may be as long as 1-2 months (Bendz et al. 1997). When designing landfill drainage systems it is usually assumed that 0.01-0.1 dm³·s⁻¹·ha⁻¹ of leachates is generated from atmospheric precipitation; the quantity added to water contained in waste and this created as a result of biochemical decomposition gives $1.5-1.8 \text{ m}^3 \cdot \text{d}^{-1} \cdot \text{ha}^{-1}$ leachates in total (Łuniewski 2000).

The inflow of contaminants in the form of landfill leachates disturbs the natural processes determining composition of underground waters. The processes may include: infiltration feeding, flora and evapotranspiration effect, the processes occurring in the soil and in the aeration zone, including, inter alia, chemical weathering of minerals, dissolving, biodegradation, oxidation, reduction, ion

exchange; processes occurring in the saturation zone, including, among other things, oxidation, reduction, sorption, membrane processes; and hydrogeological conditions. From among waters existing in the saturation zone, subsurface waters and ground waters are most exposed to contamination.

From the point of view of its location, municipal waste landfill site represent a point-like sources of contamination. One feature determining the possibility of degradation of underground waters is their susceptibility to contamination. This represents a natural property of the natural environment determining the risk of migration of hazardous substances of anthropogenic origin from the earth surface to the aquiferous level. Among the most frequent symptoms of underground water contamination caused by municipal waste landfills, one can count: increase of mineralization, hardness and permanganate value of water; organoleptic changes; presence of carbon dioxide, methane, hydrogen sulfide and ammonia; occurrence of sulfur, chlorine and iron(II) ions, organic compounds, aldehvdes, alcohols, phosphorus compounds; increase of organic substances content expressed as COD (Chemical Oxygen Demand) and BOD (Biochemical Oxygen Demand); and presence of numerous bacteria. Among micro-components derived from decomposition of organic substances and mixes of wastes and industrial wastewaters one can number: boron, cadmium, chromium, copper, mercury, nickel, lead, selenium, zinc as well as silver, gold, barium, beryllium, bismuth, bromine, fluorine, germanium, indium, lanthanons, molybdenum and thallium. As a result of long time spent by waste in the landfill bed, the contaminants are subject to partial degradation and, as a consequence, a number of potentially hazardous compounds appears in leachates. A significant part of contaminants are of xenobiotic character (Szymańska-Pulikowska 2009, Aziz et al. 2010).

Up to now, attention of authors examining presence of hazardous substances in leachates was focused on volatile hydrophobic compounds such as e.g. benzene, toluene, ethylbenzene, and xylenes (BTEX) or chlorinated aliphatic and aromatic compounds; non-volatile compounds were also considered, such as polychlorinated biphenyls (PCBs), or polycyclic aromatic hydrocarbons (PAHs). Moreover, occurrence of compounds with polar nature and having function groups demonstrating ionic character, such as: phtalates, phenols, pesticides as well as aliphatic, alicyclic and aromatic organic acids, was also analyzed (Christensen et al. 1998, Baun et al. 2003). It have been demonstrated in the course of studies that the highest concentrations in leachates were observed for benzene, toluene, ethylbenzene and xylenes. Compounds of this group are most commonly used as solvents in household practice and industrial technological processes and include tetrachloroethylene, trichloroethylene and dichloroethane. Another strongly represented group of chemical substances are phthalates, the main source of which in waste are plasticizers. Phthalic acid degradation products are frequently detected in leachates, reaching levels as high as $14 \text{ mg} \cdot \text{dm}^{-3}$ (Slack *et al.* 2005).

Up to date, more than 200 organic substances have been identified in leachates from municipal landfills, including 35 substances considered potentially hazardous.

However, in ground waters in the vicinity of landfills, more than 1,000 of substances of different types were detected. This means that transformation and/or partial degradation of hazardous substances of different types leads to release of intermediate products and may cause contamination of ground waters. In samples taken from ten selected landfills in Denmark, 55 types of xenobiotic substances have been identified, of which 10 were products of transformation processes. The group structure of the compounds was as follows (Baun *et al.* 2003, 2004):

- aromatic compounds (toluene, alkyltoluenes, alkylbenzenes, xylens, naphthalene and methylnaphthalene) 18 types, including 1 degradation product (benzyl-succinic acid constituting a product of anaerobic degradation of toluene). Aromatic compounds were detected within the concentration range from 0 to 200 μ g·dm⁻³;
- chlorinated aliphatic compounds (1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene);
- phenol and its derivatives 14 types, including cresols and xylenols in concentrations 0-61 µg·dm⁻³, chlorinated phenols including 3,5-dichlorophenol, a degradation product;
- phthalates 8 types, including 5 degradation products: monoesters of *o*-phthalic acids, phthalic acid (260 μg·dm⁻³) and monoethyl phthalate (340 μg·dm⁻³);
- pesticides 21 types, including 3 products of their partial degradation.

A source of refraction substances may consists also in high molecular weight substances of natural origin occurring in wastes, such as lignins, celluloses and hemicelluloses. As a result of biochemical transformations of these compounds, aromatic acids, phenols and terpenes are released to leachates (Leenheer *et al.* 2003).

Leachates, flowing through a landfill's ground substrate, mix with underground waters. In the course of flow of the leachates through substrate (aeration zone), contaminants present in leachates are being partly removed. That is why concentration of contaminants reaching underground waters is usually less than this in leachates. In some cases, mainly as a result of denitrification, concentration of NH₄⁺ ions in underground waters may be higher than this observed in landfill leachates. Similarly, increase of concentration of NO₃⁻ ions in underground waters may be a result of predominance of nitrification over denitrification processes. Occurrence of these processes depends mainly on aerobic conditions, underground waters delivery and permeability of the soil layer located above the underground table. Another factor resulting in periodical increase of content of individual contaminants in underground waters, can be leaching of contaminants adsorbed earlier by the landfill substrate. Given concentration of individual contaminants at a determined distance, one can calculate efficiency of the process of removal of contaminants in the course of their flow through the landfill substrate and in the aquiferous layer. In some cases, effectiveness of the processes may exceed 90%. Szymański et al. (2007), analyzing the decrease of concentration of contaminants with increasing distance from a landfill, have found the highest removal ratio (about 90%) in the case of COD, BOD₅, volatile organic acids, residues after

drying and roasting, and some heavy metals. At a distance exceeding 300 meters, compounds of organic, ammonia and nitrite (III) nitrogen as well as chlorides and phosphates were effectively removed. To less extent, nitrogen (V), calcium and magnesium compounds, sulfates and total iron were also removed. Compared to others, ions of these compounds demonstrated migration capabilities in the water-soil medium increasing with the facility operating time.

Szymański *et al.* (2007) report that effectiveness of elimination of heavy metals from in the aquiferous layer increases with increasing distance from landfill leachates and amounts to 93-99% at a distance of 400 m. The authors proved that there is a close correlation between certain heavy metals. Correlation coefficients between copper, zinc, manganese and lead are all close to the unity. Another groups of strongly correlated metals include cadmium and nickel as well as iron and chromium with COD. All of the above-mentioned heavy metals occur in constant negative correlation with the environment's pH.

Depending on geological conditions, the contamination zone may by as deep as from 20 meters to even 40 meters, while the horizontal contamination spread range may be many times larger. The highest concentration of contaminants are observed in direct neighborhood of landfills, but traces of these substances can be found as deep as 1-2 kilometers. The process of leaching contaminants from a landfill may last as long as a several dozen years.

The natural ground conditions prevailing in the landfill substrate and the underground waters area as well as the form in which individual ions occur, determine the spreading potential of the contaminants in the water-soil environment. The processes are determined by content and type of organic substances, mainly humic compounds, sedimented on the leachates reservoir bottom. Humic compounds contained in bottom sediments may form permanent bonds with copper, lead, cadmium and zinc. It is also believed that presence of illite and montmorillonite in the ground facilitates creation of bonds with lead, copper and zinc. In elimination of heavy metals in aqueous environment, certain role is also played by iron and aluminum oxides showing sorption properties with respect to copper, lead, zinc and nickel. One of factors limiting durability of organometallic bonds can be high concentration of chloride and nitrate ions. Chloride ions occurring in leachates in amounts higher than 2,000 mg·dm⁻³ and in underground waters in concentration of about 900 mg·dm⁻³ facilitate creation of soluble forms of heavy metals compounds with said ions and thus facilitate spreading of the micro-contaminants in the water-soil environment (Ziyang et al. 2009. Laner et al. 2011).

Mechanical treatment consisting in retention of solid phase in pores of the ground, proceeds most effectively in the aeration zone. On the other hand, physicochemical processes dominate in the aquiferous layer, where phenomena involving dissolving and mixing of inflowing contaminants occur. Ions of alkali and heavy metals as well as the ammonium cation are subject to sorption, interaction and ion exchange processes, while iron, manganese, lead and zinc ions are susceptible to hydrolysis (Matura *et al.* 2010). The natural biological treatment processes are related mainly to organic substances, nitrogen compounds and heavy metals compounds. Intensity of the processes depends mainly on aerobic conditions, reaction value and temperature. This path of contamination removal is related to chemical treatment. Ammonia nitrogen compounds, coming mainly from biochemical decomposition of organic substances, may develop also as a result of reduction of nitrates (III) and (V) by hydrogen sulfide and pyrites. The resulting ammonia ions may then migrate to underground waters in the form of soluble ammonium salts (Eggen *et al.* 2010).

The leachate degradation processes occurring in the water-soil environment change with increasing landfill age. In the initial period, the aeration zone demonstrates relatively good treatment properties. With the passage of time, the processes of mechanical retention of contaminants become weaker and the processes of leaching organic and mineral substances adsorbed in earlier stages begin to dominate.

2. Experimental metods

A research project has been undertaken concerning contamination of landfill leachates with polycyclic aromatic hydrocarbons and volatile aromatic hydrocarbons. The research work was carried out on the municipal waste landfill located in Wysieka near Bartoszyce in north-western Poland (Fig. 2), operated for 7 years and not equipped with any technological line for waste segregation.



Fig. 2. Retention reservoir of leachates and localization of investigated waste landfill (*phot. J. Koc-Jurczyk*)

The percentage structure of individual waste groups in the total mass was as follows: organic waste of animal and vegetable origin -25.3%, glass -14%, paper and cardboard -12.2%, plastics -4.4%, metals -3.07%, and textiles -2.75%. Other waste groups, not listed above, contributed for the remaining organic (6.65%) and inorganic (31.6%) matter. No liquid waste, sanitary sewage, hazardous substances, radioactive or toxic waste were disposed to the landfill.

Samples with total volume of 2 dm^3 were taken on one-time basis from the leachate retention tanks in November. Then, leachates were stored at 4°C and analyzed within 3 days. Determination procedure was repeated three times in each case.

Among hazardous volatile organic substances, the following were determined: (benzene, toluene, ethylbenzene, xylenes); organic compounds BTEX (dichloromethane, chloroform, trichloroethylene, tetrachloroethylene) and alkylbenzenes (styrene, methylethylbenzene, trimethylbenzene). The abovementioned compounds were isolated from the sample matrix by means of gas scrubbing, with simultaneous interception in the sorption trap filled with Tenax GC sorbent, and then desorbed in the countercurrent process at temperature 250°C to the chromatographic column.

Among non-volatile organic compounds, the following were analyzed: PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-cd)pyrene, dibenz(*a*,*h*)-anthracene, benzo(*g*,*h*,*i*)perylene); and PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB1 53, PCB 180). Leachate samples were extracted in the liquid-liquid system. The organic phase was collected, and the extract evaporated down to volume of 300 µL. Samples prepared that way were analyzed by means of gas chromatography with mass detection.

3. Results

Average BTEX concentration determined in raw leachates amounted to 20.4 μ g·dm⁻³ (Fig. 3). The highest concentration was found for xylenes (13.8 μ g·dm⁻³) and benzene (4.6 μ g·dm⁻³). Among organic volatile compounds, methylbenzene and trimethylbenzene occurred in concentrations 2.9 μ g·dm⁻³ and 6.2 μ g·dm⁻³, respectively.

Concentration of volatile organochlorides in raw leachates (determined as a total) amounted to $40 \ \mu g \cdot dm^{-3}$ (Fig. 4).



Fig. 3. The concentration of hazardous organic pollutants in leachate (volatile alkylbenzenes, including BTEX)



Fig. 4. The concentration of hazardous organic pollutants in the leachate

In the leachates, presence of all 16 conventionally determined PAHs was detected (Fig. 5). The series, sorted by decreasing concentrations, is as follows: phenanthrene, fluoranthene, pyrene, naphthalene, anthracene, chrysene, benz(*a*)anthracene, benzo(*b*)fluoranthene, benzo(g,h,i)terylene, fluorene, acenaphthylene, benzo(*a*)pyrene, indeno(1,2,3-cd)pyrene, acenaphthene, benzo(k)fluoranthene and benzo(g,h,i)perylene.



Fig. 5. PAHs concentrations in the leachate

In view of their decomposition time and products, aromatic hydrocarbons occurring in leachates are very dangerous for the water-soil environment. Biodegradation of aromatic hydrocarbons occurs both in aerobic and anaerobic conditions. With limited availability of oxygen or in purely anaerobic conditions, the process proceeds much slower, and the final products are not CO₂, water and biomass, but also transformation products, frequently much more toxic than the substrates. The resulting products of biochemical transformations may penetrate ground waters, contaminating the ground environment. Szymański *et al.* (2007) have carried out studies on content of volatile aromatic hydrocarbons (BTEX) and 16 US EPA-listed PAHs in ground waters of the first aquiferous layer of the landfill area and in underground waters. They found that concentration of most of PAHs in the leachates did not exceed 50 μ g·dm⁻³. Naphthalene was not detected, and concentration of benzo(*g*,*h*,*i*)perylene and *o*-xylene amounted to about 100 μ g·dm⁻³. The highest concentration in the examined samples was noted

for toluene (about 500 μ g·dm⁻³). In most of the examined samples, the total concentration of PAHs did not exceed 200 μ g·dm⁻³, while the sum of monoaromatic hydrocarbons amounted to about 500 μ g·dm⁻³. In the underground waters of the landfill area, presence of PAHs was detected. The average value of the total of 16 PAHs amounted from 14.64 to 15.27 μ g·dm⁻³. PAH content in ground waters ranged from 2.02 to 27.14 μ g·dm⁻³. In the case of landfill leachates, concentration of aromatic hydrocarbons depends strongly on the season, because of seasonal nature of precipitation.

4. Summary

Leachates from municipal waste landfills without sealed substrate represent a potential hazard to underground waters. Continuous increase of contamination is observed in underground waters occurring within the landfill interaction area. The majority of contaminants contained in landfill leachates is being removed in the course of migration through the aeration zone. In view of presence of aromatic hydrocarbons in leachates, including polycyclic aromatic hydrocarbons and volatile aromatic hydrocarbons, landfill leachates must not be discharged directly to the water-soil environment. Concentration of polycyclic aromatic hydrocarbons in leachates depends strongly on the season of the year and the related precipitation intensity. In leachates from the examined municipal waste landfill, the highest concentrations were observed for such organic hazardous substances as: volatile aromatic hydrocarbons, tetrachloroethylene, and among the polycyclic aromatic hydrocarbons – naphthalene, phenanthrene, fluoranthene and pyrene.

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