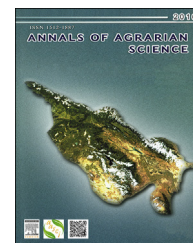


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Biochemical processes in soil and groundwater contaminated by leachates from municipal landfills (Mini review)

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ABSTRACT

World clean water deficit grows by increasing pollution on the planet. Landfill of solid domestic waste is one of the most important sources of pollution, where the leachate seeping through soil, gets into the soil and groundwater. Area of landfills of solid household waste, reaches tens of hectares and the mass of waste reaches millions of tones. The specificity of the leachate is the high content of soluble organic substances, providing reduction conditions in contaminated soil and groundwater. Reduction environment is defines biogeochemical processes under landfills with the participation of: ammonium, iron, manganese, bicarbonate, sulfate, methane. The main processes in polluted soil stream are including: biological degradation of organic matter and a variety of biological and abiotic processes. Wide discrimination of the most diverse groups of microorganisms in the polluted leachate is occurs, overlay neighboring redox zones. Microbial population is identifies specific redox zones more contaminated leachate nucleus than on the borders of the leachate with oxygen-enriched by the background thread. Biological reduction processes in the leachate are developing at different speeds: fast evolving and denitrification reduction of iron, slow – methanogenesis.

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Introduction

In recent years, composition of substances polluting environment is changing. Another 20–30 years ago, attracted universal attention was air emission of heavy metals. Now the problem has shifted to the East: to China, India, and Iran, where the development of industry and energy has not been accompanied by adequate measures of air protection [1]. But in the West, these air emissions have ceased, and in Russia have stabilized and are declining.

At the same time on the planet is grow shortage of clean water. At the World Economic Forum in Davos (Switzerland) in 2016 year risks global stability, the third highest ranked hazard problem was “water crisis” [2]. Pollutants in water are comes from natural and anthropogenic sources. As a natural example, it should be noted the widespread arsenic contamination of groundwater in East and South-East Asia.

There are many anthropogenic sources of water pollution. First of all, it is untreated effluents of industrial enterprises in the water. A striking example of regional pollution can serve as North Western Siberia, where the water is polluted by oil

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and drilling solutions in the field of oil production. Finally, there are the local, targeted sources of contamination of soil and groundwater in municipal solid waste storage sites where the leachate seeping through soil, gets into the soil and groundwater. Despite the locality of such pollution, it is very dangerous. Firstly, the concentration of pollutants in the water reaches very high values. Secondly, the pollutants are poisoned water a long time, even decades after closure of waste storage. Thirdly, the landfill is placed near major cities, posing a risk to supply.

Landfills of municipal solid waste, commercial and industrial services have become the main source of pollution of soil and groundwater in many parts of the world [3,4]. The volume of solid waste landfills as waste disposal sites is growing along with the population of the planet [5]. For 20 years (from 1988 to 2009) actively engaged in clearing the dumps in US: total number of landfills dramatically decreased with the 7900 before 1900, but their mean size increased. Given the small landfills in the United States the number of solid waste landfills is more 100 000 [4,6]. Despite the successes in reusing resources, reduce consumption and large-scale composting measures for 15 years (from 1985 to 2010) the annual amount of waste in the US was increased from 150 to 165 million tons.

In Russia the main path utilization of solid domestic waste-dumping is construction of specially designated landfills. This is the cheapest way, but far from the most harmless. In Russia sanitary-protective zone is limited to 1000 m in diameter [7,8]. If landfills in a hill, the filtrate flow is covers the soil and groundwater. If dumps are located in lowland, leachate drainage ditches is caught. It is thus the filtrate spreads from major solid waste landfill near Moscow [7,8].

Any landfills are may spread contaminated leachate beyond sanitary-protective zone. This is determining the need for monitoring leachate from landfills. The second question is about the timing of the actions adopted sanitary-protective zone. It can be assumed that, over the years, flow of pollutants will begin to shrink, but real data about the rate of pollution reduction in specific landfills with very little. Usually limited to observation 4–5 years, but this gives an idea of the extent of temporary only variation of a given pollutant [7,8].

Because of leaching of heavy metals from municipal solid waste landfills, the soil and groundwater become dirty, in particular, wells for drinking water. Area of dumps of solid household waste may be tens of hectares and the mass of waste – millions of tones. Volume of water filter from large landfills may be significant and reach more than 45,000 m³/year, or >123 m³/day [5]. This applies in particular to large landfills in humid regions with high rainfall. So, the landfill in Perm had accumulated more than 2 million tons of municipal solid waste, the average annual volume of contaminated leachate – 68,000 m³, or 186 m³/day [9].

By filtering out the rain and snow water, moisture is get through the soil into the groundwater, contaminating the drinking water wells, as well as ponds, where water is discharged.

The main pollutants of landfills are organic residues acting as reluctant on biogeochemical processes. In addition to large quantities of dissolved organic carbon leachate are contains salts, ammonium, as well as specific organic compounds and heavy metals and metalloids. The processes of decomposition

of organic pollutants are studying in landfill leachate primarily. The temporal and spatial variation of biogeochemical conditions is necessary to study that determine the different rate of degradation of organic pollutants. The processes of degradation are strongly influenced by the availability of electron acceptors in the leachate. All these issues are of paramount importance.

The aim of this work is to organize the data on biogeochemical processes in soil and groundwater contaminated by leachates from municipal landfills restored.

The sources and composition of the leachate from landfills

Such important properties of solid waste landfills are excreting [10]:

1. Dumps are heterogeneous, both in area and volume,
2. Landfills contain a mixture of inorganic and organic pollutants,
3. The landfill can allocate pollutants for tens and hundreds of years.

Landfill size usually varies from a few hectares to more than 50 ha [11]. The value of landfill can vary from 100,000 to 5,000,000 m³. Water soluble pollutants from municipal landfills can be divided into four groups [12].

1. Water-soluble and oxidable by oxygen, organic substances including methane and volatile fatty acids.
2. Inorganic macro components: Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, Fe²⁺, Mn²⁺, Cl⁻, SO₄²⁻, HCO₃⁻.
3. Heavy metals: cadmium (Cd²⁺), chromium (Cr³⁺), copper (Cu²⁺), lead (Pb²⁺), nickel (Ni²⁺), zinc (Zn²⁺).
4. Organic xenobiotics, falling from household and industrial chemicals. The concentration of each of them is less than 1 mg/l. They are represented by different aromatic hydrocarbons, phenols, Cl-aliphatic hydrocarbons, pesticides, medicines.

Most often the organic and inorganic gross pollutants presented in paragraphs 1 and 2 are researched in landfill leachate. At the same time organic and inorganic pollutants as described in clauses 3 and 4 are contained in smaller concentrations. They are dangerous, but their impact on biogeochemical processes in soil-groundwater is small. We emphasize that the contamination of soil and groundwater with heavy metals and organic xenobiotics are devoted to individual reviews [13]. We therefore concentrated on the analysis of gross pollutant that has a major effect on soil biogeochemistry and groundwater contaminated by leachates from landfills.

The study of the composition of the leachate is often limited to the analysis of one or some samples under each of the landfills. This is clearly insufficient for understanding the nature of contamination of soil and ground water [14]. For example, because of a considerable spatial heterogeneity in the composition of the leachate is could show no contamination of soil and groundwater in single analysis. This

situation was in the area of large landfills Grinstead, Denmark, because of 60–70% of wells had no discernible exceeded content pollutants. But in 10% of samples taken over an area of 10 ha is received the high concentration of pollutants in the 20–100 times higher than on background. Detailed information is needed to monitor large landfills, even after prolonged their conservation.

In the Table 1 shows the interval content of pollutants in landfill leachate, obtained through a large number of literary data on landfill sites younger than 25 years [15]. As can be seen from the Table 1, contents of dissolved organic matter and inorganic pollutants can reach very high values: 10–500 times above background values.

Similar results were obtained in the analysis of leachate, which entering in the drainage ditches around a solid waste landfill near Moscow [7]. Priority pollutants here: mercury, chromium, manganese and magnesium. The MAC values for household water were exceeded up to 520 times for mercury, to 143 times for ammonium, to 24 times for chromium and up to 14 times for manganese. Trend of temporary pollution over four years (2005–2008) observations is not detected, due to the heavy dependence of the composition of leachate because of from rainfall [7].

Degradation of organic matter in landfills has resulted in changes in leachate pollution. At the beginning of the fermentation of organic matter reduces the leachate pH and content of many substances increases, especially the organic compounds, such as volatile fatty acids. Then, when products of fermentation were turn into methane, pH leachate was increases and organic matter degradation in the filtrate slows down [10].

In 2011, 19 large landfills were studied in 16 US states, with 12 municipal and 7 private landfills among them [5]. These dumps are intended for the collection of urban and construction waste, sewage sludge and solid non-toxic commercial waste. Leachate pH close to neutral: 6.0–7.6. Main anions of pollutants: chloride and sulphates. The concentration of Cl^-

ranged from 167 to 3040 mg/l, SO_4^{2-} concentration ranging from 0.4 to 3430 mg/l.

The content of dissolved organic carbon in effluents varied greatly: from 13 to 6110 mg/l. In the semiarid area the average annual mass filtrate was only $2.2 \cdot 10^{-6}$ gallons or 8300 m^3 (23 m^3/day) and in the humid zone it reaches $39 \cdot 10^{-6}$ gallons or 148,000 m^3 (404 m^3/day). Characteristically, the highest concentrations of dissolved organic carbon in landfills which are located in humid regions with the amount of annual precipitation >50 cm.

At each test site content of any pollutant varies in space. To characterize the contamination of soil and groundwater at a landfill can be maximum content of pollutant in the water. Detailed studies were conducted at Grinstead, Denmark. Here the maximum content of main redox-sensitive substances is nonvolatile fatty acids up to 75 mg/l, Fe(II) – up to 200–250 mg/l, sulfate – up to 100 mg/l, of ammonium – up to 75 mg/l, Mn(II) – up to 25 mg/l, nitrate – up to 1 mg/l, oxygen – up to 3 mg/l [16]. As can be seen, among the natural electron acceptors is clearly dominated by iron (III) reduction of which enriches the soil water up to 250 mgFe (II)/l. In leachate of landfills large part of nitrate is restored for ammonium.

Redox conditions in soil and groundwater

Native, usually oxidized groundwater flow change redox conditions strongly after entry from landfill leachate. The main processes in polluted soil stream include: biological degradation of organic matter, a variety of biological and abiotic redox processes of dissolution/precipitation of minerals, complex formation, ion exchange and sorption [10]. New reductive conditions determine the processes of biogeochemical transformations of inorganic and organic pollutants, so these conditions require special attention by researchers.

Characteristic of redox conditions in polluted stream given in the review [17]. Redox conditions are characterized by the following indicators:

1. Redox potential (Eh).
2. Redox sensitive components in soil and dirt water.
3. The value of pH in the soil and dirt water.
4. The content of volatile fatty acids
5. Characteristics of the soil solid phase primer.
6. Composition of the microorganisms.

It must be borne in mind that the information is varying not only in space but also in time [18]. Changing redox conditions in the flow of contaminated leachate responds according to the following simplified schema. Directly beneath the dump situated area of methane formation of the dirt water. Below the gradient flow is formed sulfate reduction zone, although usually it partly occupies area of methane formation. More below of flow is formed less reductive conditions favoring for Fe^{3+} reduction. Sufficient quantities of manganese on the area add Mn^{4+} reduction. Finally, outside of the contaminated flow recovery saved aerobic (background) conditions when content of dissolved oxygen in excess of 1 mg/l [10].

Table 1 – Composition of leachate from the landfills for domestic solid waste [15].

Parameter	Range
pH	4.5–9
Conductivity (MS/sm)	2500–35000
Solid residue	2000–60000
Total content C org	30–29000
Organic nitrogen	14–2500
Total content P	0.1–23
Chlorides	150–4500
Sulfates	8–7750
Bicarbonate	610–7320
Na	70–7700
K	50–3700
Ammonium (N)	50–2200
Fe	3–5500
Mn	0.03–1400
Cu	0.005–10
Pb	0.001–5
Ni	0.015–13
Zn	0.03–1000

Note: dimension in mg/g except for pH and conductivity.

Along a gradient of contaminated stream the contents of the recovered particles (organic matter and ammonia) are falling. In the same direction, the magnitude of the redox potential (Eh) is gradually increasing, as well as the content of dissolved acceptors of electrons. Occur following transformation: due to sulfate reduction formed sulphides; at some distance in the solution reaches a maximum content of ions Fe^{2+} and Mn^{2+} .

In the Table 2 present the most common redox reaction with the change in Gibbs free energy ΔG_0 at standard conditions. Low, the negative values of ΔG_0 is the most energetically favorable reactions. Oxidation of methane with oxygen is accompanied by changes $\Delta G_0 = -196$ kcal/mol. Organic matter (in the form CH_2O) is oxidized by oxygen and gives $\Delta G_0 = -120$ kcal/mol. Then in a row of declining activity are nitrate, manganese, iron oxides and sulfates. Finally, when the electron acceptors were used up, it is beginning the formation of methane.

The real rate of different redox reactions in the leachate were measured at Grindsted, Denmark. These rates of reaction are divided into three groups. The fastest reactions are: denitrification up to 20 nmol N_2/g per day and iron reduction up to 20 nmol $\text{Fe(II)}/\text{g}$ per day. This second reaction is more important, because the stocks of iron in the soil are usually higher than nitrate. Average rates were noted in reduction of manganese – up to 2 nmol $\text{Mn(II)}/\text{g}$ per day and sulfate reduction up to 1 nmol/g per day. Low rate is formation of methane – up to 0.1 nmol CH_4/g per day [16].

Properties of electron donor

Detailed research was conducted on the oldest landfill Norman, Oklahoma, US [4]. Dump took waste in 60 years and was mothballed in 1985. In the area of the Norman landfill were drilled many wells, they are equipped with different sensors; the landfill was created for prolonged monitoring behavior of restored filtrate in groundwater. It is studied the behavior of both donors and acceptors of electrons.

In landfill filtrate of Norton municipal solid waste was studied in detail by organic matter in 1999 and 2006. Landfill filtrate of solid waste organic matter has been studied in detail. Besides total content of organic matter was analyzed non-volatile fraction of organic matter [10]. The monitoring showed that pollutants are migrating along a gradient of an

underground stream. In filtrate in border landfill the concentration of non-volatile organic substance reaches its maximum 113 mg/l, compared to 3.3 mg/l in the above thread dumps [19]. The high concentration of non-volatile organic substances is the result of dissolution and partial degradation of organic waste in landfill. The content of non-volatile organic substances in the landfill is some more higher and reaches 300 mg/l. Non-volatile organic substances is a heterogeneous mixture of nonvolatile organic compounds and protein fragments, lignin, cellulose, polysaccharides, lipids and waxes, which were formed because of biological and chemical reactions in a landfill [20,21].

Periodically was increasing the content of nitrate in the filtrate. Increasing the content of nitrate is accounted for by the top part of the flow, when the dirt water comes fresh, oxygen-enriched rainfall. It is a transitional area where there are hydrological conditions the oxidation of NH_4^+ and formation of NO_3^- .

Properties of electron acceptors

One of the most important acceptors of electrons in reduction filtrate is Fe hydroxides. The role of the Fe hydroxides is high in conditions of low solubility of oxygen and low content of other acceptors of oxygen: nitrates and sulfates. In the Table 2 Fe hydroxides are presented in the form of Fe(OH)_3 .

But the electron acceptor can be not only the Fe (III)-hydroxide: effective electron acceptor is also Fe (III) in clay minerals [22]. Although compared to the (hydr)oxides of iron layered silicates belong to low Fe-minerals. There is a certain correlation between the degree of Fe in clay minerals and their response to the reduction of Fe(III). Unstable hydroxides have high concentrations of Fe(III) within 58–70% and therefore hydroxides are dissolved completely by the reduction [22]. Minerals with high concentrations of Fe(III), including the Fe layered silicates with the content of Fe(III) = 4–58%, at first losing iron and other elements, and then dissolve. Layered silicates with the content of Fe (III) < 4% are reduced as solid phase change and their particles persist despite the reduction conditions. Second, that strongly influences the destruction of clay minerals is an acid reaction.

Microbial structural reduction of Fe(III) of clay minerals in recent years has received reliable evidence [23–26]. Reduction of Fe(III) in clay minerals involved bacteria species *Geobacter*

Table 2 – Basic redox reactions in landfill leachate [3].

Reactions	Processes	ΔG_0 (Kcal/mol)
Methanogenesis/mineralization of organic matter	$2\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$	-22
Sulfate-reduction/OOM	$2\text{CH}_2\text{O} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow 2\text{CO}_2 + \text{HS}^- + 2\text{H}_2\text{O}$	-25
Reduction of iron/OOM	$\text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + 4\text{Fe}^{2+} + 11\text{H}_2\text{O}$	-28
Reduction of manganese/OOM	$\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$	-81
Denitrification/OOM	$5\text{CH}_2\text{O} + 4\text{NO}_3 + 4\text{H}^+ \rightarrow \text{CO}_2 + 2\text{N}_2 + 7\text{H}_2\text{O}$	-114
Aerobic oxidation/OOM	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	-120
Reduction of CO_2	$\text{HCO}_3^- + \text{H}^+ + 4\text{H}_2 \rightarrow \text{CH}_4 + 3\text{H}_2\text{O}$	-55
Ammonium oxidation	$\text{NH}_3^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$	-72
Oxidation of methane	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	-196

Note: OOM – oxidation of organic matter.

and *Shewanella*. Fe(III)-silicate in soils with a low content of iron hydroxide contribute to reduction especially noticeable.

Let us back to the monitoring data of landfill Norman, US. Accumulation of Fe^{2+} in filtrate (over 23 mg/l) is due to microbial reduction of iron oxides, which provide ubiquitous red-brown soil. Naturally, the content of iron oxides within the restored zone was decreased [27]. Fe^{2+} was formed, whose contents in water varied greatly in time and space. The content of the Fe^{2+} is consistent with the amount of non-volatile organic substances, but not consistent with the methane or sulfate content. Variation of content of Fe^{2+} may be the result of secondary deposition Fe-hydroxides. Over time, the remaining particles of iron oxides in soil become less soluble and rate of reduction in the filtrate decreases.

Sulfates are another type of electron acceptors. Their formation most often in dirt water is due to the action of oxygen saturated groundwater on natural iron sulphides: FeS and FeS_2 [28]. In the area of the reductive filtrate under Norman landfill content of sulfates are reduced gradually; for 7 years the content of sulphate significantly decreased [29–31]. Isotope analysis showed that sulphates play an important role in the biological oxidation of organic matter.

Barite BaSO_4 from rock is the second source of sulfates at Norton. The particles of barite are dissolved in solution of sulphate if sulphate content is low (<1 mg/l). Low content of sulfate occurs in the center of the reduction stream, where barite slowly is decays to barium and sulfate. As shown by scanning electron microscopy, the barite particles surface has corrosion heavily, where sulfate content from <10 mg/l and has not corrosion at the site, which contains ~100 mg sulfate/l [31].

On the edges of filtrate flow redox conditions are defined mode by entering acceptors of electrons from the background groundwater. But in the center (nuclei) of leachate, the main source of electron acceptors is a solid phase.

Microbial activity and redox processes

The high content of dissolved organic matter in leachate depends not only on organic substances from landfill of solid waste, but also from the intense activity of microbes in a polluted stream. The composition of the microbial population in polluted leachate is differing from the population in the background.

In microbial populations are dominate prokaryotes: bacteria and archaea. The total number of prokaryotes in polluted leachate varies very strongly: from $4 \cdot 10^4$ to $1.5 \cdot 10^9$ cells per gram of dry matter. The number of living cells is run up $(1-60) \cdot 10^7$ KOE/g [3]. But a variety of studied methods and a wide range of groundwater cloaked distinction among bacteria in contaminated and background threads. On landfill leachate Grindsted (Denmark) the total number of bacteria and the number of living cells practically does not depend on the distance to landfill [32]. Analysis of the number of living cells by the method of fatty acids phospholipids showed more of them in polluted leachate than background dirt water [32].

Changing the structure of microbial communities was studied at Norman, Oklahoma, US [4]. Microbial indicators at a distance of 250 m from the landfill differed from those that

were in place the expiration of leachate. On this place the diversity of microbial community has increased (Shannon index rose from 5.88 to 6.62) and the number of genes has increased: from 458 to 1600. Change of microbial indicators was not linear; some extremes were at an intermediate distance from the landfill. Discriminating analysis showed that the microbial community structure was dependent on the distance from the landfill, but the little: only 13% [4]. The first place was left geochemical factors: content of dissolved ammonia, methane, hydrogen sulfide, sulfate, chloride, organic carbon. Exactly they identified 53% of microbial community structure which were determining the effectiveness of the biological treatment of leachate from organic pollutants.

In the area of the landfill of municipal solid waste in Benisvelde (Netherlands) were clarified the impact of filtrate on the chemical properties of microbial community structure [33]. Using genetic analysis, prokaryotes were divided in the 2 group: bacteria and archaea. Statistical analysis showed different force of their connection to hydrochemical indicators: stronger were associated archaea than bacteria. In particular, this affected the connection of microorganisms with a simple indicator of the filtrate contamination – its electrical conductivity. The correlation coefficient of electrical conductivity with bacteria was only $R^2 = 0.54$, but it grew when the conductivity with archaea $R^2 = 0.64$. The reason for the differences – the archaea domain includes a variety of methanogens, responsible for the formation of methane in the landfill and leachate.

At the same landfill was investigated the ability of microbial populations to recycle various forms of organic compounds [34]. In the dirty samples the microorganisms are able to use a larger set of organic compounds than in the baseline sample.

At the solid waste landfill Grindsted (Denmark) the distribution of micro-organisms along a gradient flow of filtrate was studied [32]. Methanogens and reduction of sulfate are dominated near landfills, but their number decreases when to move away from the source of pollution. Distribution of reduce-bacteria of iron, manganese and nitrate were other; the number of cells was great and it remained such throughout all along the flow of filtrate. The abundance of these groups of microorganisms was unexpected; it guarantees the possibility of development of different redox processes. Thus, the dominance of any process depends more from geochemical environment and availability of appropriate acceptors of electrons than from the composition of the microbial population.

A detailed study of the biogeochemistry of soil and groundwater in two landfills: Norton (US) and Grindsten (Denmark) showed how the similarity of redox processes and its difference [10]. In effluents on both landfills identified three redox processes: reduction of iron and sulfate and synthesis of methane. But apart from them on the Grindsten landfill have two additional redox processes: processes of denitrification and reduction of manganese.

This variety of redox processes due to the abundance of nitrates, as well as important Mn oxides as acceptors of electrons. Several different redox processes go simultaneously in these microbial communities and various

biochemical processes are not mutually exclusive. In fact, in polluted leachate occurred the combination of overlay neighboring redox zones. Specifically, synthesis of methane combine with sulfate reduction and reduction of manganese on the one hand combined with reduction of iron and with nitrate reduction on the other hand. Dimensions of those or other redox zones are varying greatly even in neighboring transects [15].

There are important features of redox zones. Microbial population is peculiar specific redox zones more contaminated leachate in the kernel, but on the borders of filtrate formed complex microbial community and it is formed strong redox gradient.

Stabilization process in landfill leachate

In the world of canned dumps is controlled over about 30 years. During this period has increased our understanding of the complex combination of chemical and biological reactions, which gradually is changed in the leachate. The basic geochemical zones in soil and groundwater are changed with time.

In the leachate are dominated aerobic and anaerobic acidic zone at the beginning of pollution. But with time, the situation is changing: primary and stable methane zones are dominance (Table 3).

Geochemical situation varies considerably in these zones [15]. Oxygen consumption is reached peak at the initial acidic phase of organic substances fermentation: as biological oxygen demand (BOD) and chemical oxygen demand (COD). At a later methanogenic phase, leachate average pH is increases from 3.8 to 8.0, and oxygen consumption is decreased by 1–2 order. The ratio BOD/COD is reduced 10 times. Contamination of the filtrate with metals and sulphate was reduced sharply.

Detailed studies of the dynamics of leachate were conducted under landfill Norton. For seven years the content of non-volatile organic substances and chloride in filtrate on the center has not changed, but other changes were occurred [10]. The degradation of organic matter in polluted stream leads to a reduction oxidized particles such as O_2 and SO_4^- and the accumulation of products of reduction, for example, Fe^{2+} .

Polluted water is contains less than 0.2 mg O_2/l , and dominated reaction is reduction. But narrow aerobic zones enriched with oxygen are formed on the border of a level of subsoil waters, where contaminated water is mixed with rainwater [15,28].

Another donor electron in filtrate – ammonium, the concentrations in the center of the stream is reached 150 mg N/l compared with the background 1–2 mg N/l [10]. Ammonium accumulates downstream flow resulting from the fermentation of organic matter outside the dump. Ammonium concentration in the flow decreases sharply, forming a distinctive front with 75 mg N/l concentration. Front for 7 years ammonium moved down the gradient to 35 m, i.e. at a rate of approximately 5 m/year. Its movement was much slower chloride, which was moving at a velocity of 15 m/year [19]. Slow migration of ammonium explains its gradual arrival due to desorption, as well as the biodegradation of organic substance in the filtrate. This is confirms the data analysis of the isotopic ammonium [19].

Conclusion

World clean water deficit grows by increasing pollution on the planet. Solid domestic waste is one of the most important sources of pollution landfills, where the leachate seeping through soil, gets into the soil and groundwater. Despite the locality of such pollution, it is extremely dangerous: the concentration of pollutants in the water reaches very high values; dumps poisoned the water for many years. The number of contaminated leachate depends both on the amount of stockpiled wastes and from geographical location: from dumps in humid region is leached significantly more leachate than in the arid region.

The specificity of the leachate is the high content of soluble organic substances, providing reduction conditions in contaminated soil and groundwater. It is reduction conditions determine the biogeochemical processes under landfills. The main processes in polluted soil stream include: biological degradation of organic matter and a variety of biological and abiotic processes.

Table 3 – Comparison of chemical composition of leach ate at the initial stage of the domination of the acidic phase and at a late stage of the domination of methane formation phase [15].

Parameter	Initial, acid phase leachate		Late, methanogenic phaseleachate	
	Average	Range	Average	Range
pH	6.1	4.5–7.5	8.0	7.5–9.0
Biologicoxygendemand (BOD)	13,000	4000–40000	180	20–550
Chemicaloxygendemand (COD)	22, 000	6000–60000	3000	500–4500
Ratio BOD/COD	0.58		0.06	
Sulfate	500	70–1750	80	10–420
Ca	1200	10–2500	60	20–600
Mg	470	55–150	180	40–350
Fe	780	20–21200	15	3–280
Mn	25	0.3–65	0.7	0.03–45

Note: dimension in mg/g besides pH and ratio BOD/COD.

In contaminated soils microbial reaction depends on the chemical composition of leachate: dissolved methane, ammonium, hydrogen sulfide, sulfate, chloride, organic carbon. With these settings the stronger associated archaea than bacteria. Wide dissemination of the most diverse groups of microorganisms in the polluted leachate leads to overlay neighboring redox zones. So, synthesis of methane combine with sulfate reduction and reduction of manganese on the one hand combined with reduction of iron and with nitrate reduction on the other hand. Microbial population affect specific redox zones more in contaminated leachate kernel than on the borders of the leachate with oxygen-enriched by the background thread.

Biological reductive processes in the leachate are developing at different rates. The fastest rates are denitrification and reduction of iron, the lowest rate is methane formation.

In the leachate are dominated aerobic and anaerobic acidic zone at the beginning of pollution. But with time, the situation is changing: primary and stable methane zones are dominance.

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