A STUDY ON THE LANDFILL LEACHATE AND ITS IMPACT ON THE GROUNDWATER QUALITY OF THE GREATER AREA

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Abstract. Characterisation of the leachate originating from the Ano Liosia landfill (situated in Attica region, Greece) as well as assessment on the quality of the local aquifer were carried out. The experimental results showed that most of the parameters examined in the leachate samples such as colour, conductivity, TS, COD, NH₃–N, PO₄–P, SO₄^{2–}, Cl[–], K⁺, Fe and Pb were found in high levels. The organic load was quite high since the COD concentrations were in the range of 3250–6125 mg L⁻¹. In addition, the low BOD/COD ratio (0.096–0.195), confirmed that the majority of this organic matter is not easily biodegradable. The groundwater near the landfill site was characterised as not potable and not suitable for irrigation water, since most of the physical and chemical parameters examined – such as colour, conductivity, DS, hardness, Cl[–], NH₃–N, COD, K⁺, Na⁺, Ca²⁺, Fe, Ni and Pb exceeded the permissible limits given by EE, EPA and the Greek Ministry of Agriculture. Furthermore, this study presents the application of the hydrologic evaluation of landfill performance (HELP) model for the determination of the yearly leakage from the base of the landfill after the final capping.

Key words: groundwater pollution, landfill, leachate quality and quantity

1. Introduction

The storage of any waste material in a landfill poses potential problems. One problem is the possible contamination of soil, groundwater and surface water that may occur as leachate produced by water or liquid wastes moving into, through and out of the landfill, migrates into adjacent areas. This problem is important especially when industrial wastes are involved because many of these substances are resistant to biological or chemical degradation and, thus, are expected to persist in their original form for many years, perhaps even for centuries.

The chemical quality of leachate varies as a function of a number of factors including the original nature of the buried waste materials and the various chemical and biochemical reactions that may occur as the waste materials decompose. The spatial variations in leachate composition mainly reflect differences in waste composition and infiltration of water through the top cover of the landfill (Kjeldsen et al., 1993). In the absence of evidence to the contrary, most regulatory agencies prefer to assume that any leachate produced will contaminate either ground or sur-



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face waters (Schroeder et al., 1994). The leachate composition for a given landfill cannot be predicted from literature data since the parameters influencing its quality are not easy to justify. Research has shown that the composition of landfill leachate from the same source as well as from different sources, is extremely variable (Chian and DeWalle, 1976; Bolton and Evans, 1991). The composition of leachate and its emission rates differ between the old and the new areas of the fill. This was confirmed by a leachate study which was conducted at a large, operating, regional municipal solid waste landfill near Seattle, Washington (Ragle et al., 1995).

The adverse impacts of landfill leachates on adjacent surface and groundwater have prompted a great number of studies since 1980. This includes studies of the constituents in leachate, such as those of Flyhammar (1995) who examined the leachate quality of several active Swedish landfills, and Sanchez Ledesma et al. (1993) who investigated the leachates generated by two different landfills located in the municipality of Madrid. It also includes studies of the leachate intrusion in the groundwater, such as Zheng et al. (1991) who investigated the impacts on groundwater of the leachate originating from the Lone Pine landfill situated in Monmouth County, New Jersey, Gailey, and Gorelick (1993), who developed and applied a groundwater quality management tool for the Gloucester landfill site near Ottawa in Canada, and Blight (1995) who examined the pollution of the groundwater downstream of an unlined landfill in South Africa.

The qualitative and quantitative characteristics of leachates are very important in the design and management of landfills. This was demonstrated by Tejero et al. (1993) from results obtained at the Meruelo landfill in Spain and by analysing the control measures and the treatment of liquids.

In order to assess the pollution of the groundwater, either experimental determination or estimation through mathematical modelling can be followed. A mathematical model that simulates leaching from solid waste landfills and the solute transport into the aquifer is presented by Lu and Bai (1991). Bütow et al. (1989) describe the transport of groundwater contaminants from a closed domestic landfill in Berlin. In the present study, the first procedure was chosen in order to estimate the extent of the leachate adverse impacts on the groundwater of the area, where the landfill is situated, and the pollution level of the aquifer. In a later stage mathematical modelling will be enforced. Modelling was used to estimate the leakage from the base of the landfill through the application of hydrological balance model.

2. Study area

This study examines the Ano Liosia landfill site in Greece (Attica region) (Figure 1). The landfill has been in operation since 1973 and currently receives the domestic wastes from an urban population of nearly 3,500,000 inhabitants. It has a total area of 173 ha, of which 88 ha are actually covered by deposited wastes.



Figure 1. Ano Liosia landfill – the location of the wells 1–6.

The average quantity of wastes deposited daily is 3500 t. The production of wastes is estimated at approximately 0.875 kg per capita per day with an annual increase rate of 1.5–2.5% (ACMAR, 1996). The composition given for the domestic waste produced in the Attica region is 52% organic material, 20% paper, 9% plastics, 4% metals, 4% glass, 3% textiles, wood and leather, 4% inert and 4% others. Worth noting is the high percentage of the organic material.

The landfill is located in a moderately steep, semi-arid area, covered by wild vegetation consisting of low plants and grasses. The prevailing geological formation is limestone of the Triassic and Jurassic ages. The formations are characterised as permeable, with a percolation rate of 8–10 m/day. The bottom of the landfill is not lined and there is no provision for the collection of leachate apart from a system of surface trenches dug along the bottom contours of the deposits that collect leachates mixed with surface run off and divert them to a pond, with a capacity of 1000 m³. The wastes are compacted on site mechanically, deposited in layers of 150–350 cm and are covered by 50–200 cm of soil, sand gravel and clay materials. The depth of deposition in the centre of the landfill body exceeds 20 m (Stournas et al. 1990).

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3. Methods

This study includes an evaluation of the hydrologic balance of the Ano Liosia landfill site, situated in Attica region, characterisation of the landfill leachate as well as determination of the pollution level of the groundwater.

3.1. HYDROLOGIC BALANCE EVALUATION

Generally, the parameters involved in a hydrologic balance are precipitation, surface runoff, evapotranspiration and infiltration. In the framework of the present study, the hydrologic balance was estimated through the application of the hydrologic evaluation of landfill performance (HELP) model developed by the US EPA (Schroeder et al., 1994), the objective being to estimate the quantity of the leachate production. This model is a quasi-two-dimensional hydrologic model of water movement across, into, through and out of landfills. The model accepts weather, soil and design data and uses solution techniques that account for the effects of surface storage, snowmelt, runoff, infiltration, evapotranspiration, vegetative growth, soil moisture storage, lateral subsurface drainage, leachate recirculation, unsaturated vertical drainage and leakage through soil, geomembrane or composite liners (Schroeder et al., 1994). The weather data required in the HELP model are classified into four groups: evapotranspiration, precipitation, temperature and solar radiation. Meteorological data for 1973-1995 were entered into the model. The model output covers the period of 23 years by giving yearly values for every parameter that is involved in the hydrologic balance. The various layer characteristics data used in the present simulation are shown in Table I. This layer sequence is considered to be a representative structure for the landfill body and it was based on 14 boreholes that were drilled with continuous sampling in the waste body and continuous coring in the limestone formation (Coumoulos et al., 1995).

In this simulation, the infiltration of precipitation into the landfill and the surrounding land is assumed to be the only source of recharge to the whole aquifer system. Runoff is computed using the SCS (Soil Conservation Service) Curve Number method based on daily amounts of rainfall and snowmelt (USDA, Soil Conservation Service, 1985). The program assumes that areas adjacent to the landfill do not drain on to the landfill. The time distribution of rainfall intensity is not considered. Therefore, the program cannot be expected to give accurate estimates of runoff volumes for individual storm events on the basis of daily rainfall data. However, because the SCS rainfall-runoff relationship is based on considerable daily field data, long-term estimates of runoff should be reasonable. Potential evapotranspiration is modelled by an energy-based Penman method. The vegetation data are generated by a vegetative growth model. The HELP program assumes Darcian flow for vertical drainage through homogeneous, temporally uniform soil and waste layers (Darcy, 1856). As such, the program will tend to overestimate the time

No of layer	Type of layer	Layer	Hydraulic
		thickness (cm)	conductivity (cm s ^{-1})
1 (Top layer)	Fine sandy loam	15	$0.52 \times 10E - 03$
2	Silty clay	100	$0.33 \times 10E - 04$
3	Waste	350	$0.10 \times 10E-02$
4	Silty clay	50	$0.33 \times 10E - 04$
5	Waste	300	$0.10 \times 10E-02$
6	Silty clay	140	$0.33 \times 10E - 04$
7	Waste	260	$0.899 \times 10E - 03$
8	Silty clay	100	$0.319 \times 10E - 04$
9	Waste	150	$0.899 \times 10E - 03$
10	Silty clay	50	$0.319 \times 10E - 04$
11	Waste	250	$0.899 \times 10E - 03$
12	Silty clay	200	$0.319 \times 10E - 04$
13 (Bottom layer)	Waste	300	$0.899 \times 10E - 03$

TABLE I Landfill layer structure

required for leachate to be generated. The effects of these limitations are minimised since the program increases the effective saturated hydraulic conductivity and decrease the field capacity. Percolation through soil liners is modelled by Darcy's law, assuming free drainage from the bottom of the liner. The liners are assumed to be saturated at all times, but leakage occurs only when the soil moisture of the layer above the liner is greater than the field capacity.

As mentioned above, the landfill under study is not lined. Twelve layers (an alternation of soil liners and waste material that account for a depth of 22.5 m) were taken into account for the simulation (Table I). This is a representative structure and it is in accordance with what Stournas et al. (1990) report in respect with the landfill structure. A vertical percolation layer is a layer of moderate to high permeability material that drains vertically, primarily as unsaturated flow, as long as it is not underlain by a liner with a lateral drainage collection and removal system. Its primary purpose is to provide moisture storage; top soil layer and waste layers are classified as such. A layer of low permeability soil designed to limit percolation/leakage is classified as a barrier soil liner. The layer drains only vertically as a saturated flow.

3.2. SAMPLING AND EXPERIMENTAL ANALYSIS

The leachate samples were collected from two leachate trenches; one near the disposal site and other one near the pond. Samples were collected on a monthly basis covering the period from May 1995 to November 1996. Over this period 19 samples were taken from each leachate trench. For statistical purposes samples

Well no.	Location (m)	Depth (m)
1	50 (at the entrance of the disposal site)	80
2	300 (east of the landfill)	140
3	400 (southeast of the landfill)	80
4	800 (south of the landfill)	75
5	2000 (southwest of the landfill)	68
6	3000 (southwest of the landfill)	80

TABLE II Characteristics of the wells

were collected in triplicate. Therefore, 57 samples were collected from each leachate trench.

In order to assess the state of quality of the groundwater in the vicinity of the landfill, six testing wells were chosen. The various locations of the wells and depths are given in Table II and shown in Figure 1. The sampling covered the period between November 1995 and November 1996. Samples were taken every month from all wells. For statistical purposes samples were collected in triplicate. Therefore, 39 samples were collected from each well.

The samples were collected in 1L high density polyethylene (HDPE) bottles and they were analysed immediately lest changes in the various parameters occur. When this was not possible, they were preserved, refrigerated and analysed within 24 h (Chian and DeWalle, 1976).

The parameters measured were pH (using WTV Wissenschaftlich Technische Wekstatten pH 537), colour (Spectrophotometric method), total solids, suspended solids, dissolved solids, BOD, COD, alkalinity (Standard Methods APHA, AWWA, WPCF, 1995), conductivity (using Hanna Instrument HI 8819N), PO_4^{3-} (stannous chloride method), SO_4^{2-} Turbidimetric method), NH_3 -N (Kjelndahl method), chlorides (argentometric method), sodium, potassium, calcium (flame photometric method) and heavy metals Cd, Cr, Cu, Fe, Ni, Pb, Zn, (atomic absorption spectroscopy – Perkin-Elmer 2380 and ICP-AES, Jobin Yvon). Nitrates (cadmium reduction method), nitrites (diazotization method) and hardness (Standard Methods APHA, AWWA, WPCF, 1995) were also measured in water samples.

4. Results and discussion

4.1. HYDROLOGIC BALANCE EVALUATION

The results that were obtained through the application of HELP model are shown in Table III in which the average annual values of the parameters involved in the hydrological balance and the standard deviations for the years 1–23 are given.

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Water balance parameters and SD for years 1–23 (results from the application of HELP model)

	%	mm	m ³	SD
Precipitation	100	390	175742	109.9
Surface runoff	1.1	4.4	1976	7.7
Evapotranspiration	55.6	217	97708	56.4
Percolation/leakage through the	42.8	167	75153	65.3
landfill's base				



Figure 2. Precipitation–percolation from the base of the landfill (results from the application of HELP model).

The average annual leakage from the landfill base was 42.76% of the average annual total precipitation. Evapotranspiration was 55.59% and surface runoff was 1.125%. Figure 2 demonstrates the relation between the precipitation and the percolation/leakage from the base of the landfill for the years 1–23. The peaks and valleys of the graph may not coincide exactly but it is obvious that the leakage from the landfill base is greatly influenced by precipitation. As found in literature, for other disposal sites in Europe (Hjelmar 1989; Ehrig, 1991), the yearly leakage from the base of the site, after the final capping, usually fluctuates between 70 and 400 mm, evapotranspiration between 30% and 70% and surface runoff between 25% and 40%. These quantities are of course depended on the local climatic conditions and on the design characteristics of the disposal site. Therefore, the results of the present study (leakage 167 mm), were at normal and expected levels compared with the aforementioned literature data.

4.2. LEACHATE CHARACTERISATION

The experimental results obtained for the leachate are summarised in Tables IV and V. The pHvalues of the leachate ranged between 8.07 and 8.63. These alkaline values were expected since the landfill is an old one. These values indicated that the biochemical activity in the landfill body was in its final stage and the organic load was biologically stabilised. During the initial stage the pH values were quite low due to acid formation but during the methanogenic stage the pH was mainly in the alkaline region. The colour of the leachate was dark brown to black which indicated the presence of humic compounds. The colour appeared to be less intense during winter months because of the attenuation with the rain water. The measured values for colour were in the range of 4900–10,000 Pt units, (APHA, AWWA, WPCF, 1995). The concentrations of the total solids were in the range of 8334–

Parameter	Min	Max	Mean	SD
pH-value	8.30	8.63	8.44	0.118
Colour	5800	10,000	7268	1353
Total solids (mg L^{-1})	8334	13,546	11,850	1619
Suspended solids (mg L^{-1})	110	400	245	124
Dissolved solids (mg L^{-1})	7934	13,115	11,618	1638
$BOD_5(mg L^{-1})$	520	865	665	138
$COD (mg L^{-1})$	4250	6100	5086	655
Conductivity ($\mu s \ cm^{-1}$)	23,000	26,900	24,038	1228
Alkalinity (as $CaCO_3$) (mg L ⁻¹)	2300	3170	2685	369
Sulphate (SO_4^{2-}) (mg L ⁻¹)	192	758	356	232
Phosphate (PO ₄ –P) (mg L^{-1})	9.71	16.8	13.6	2.23
Ammonia (NH ₃ –N) (mg L^{-1})	1030	1350	1216	110
Chloride (Cl ^{$-$}) (mg L ^{-1})	3424	5100	4149	580
Potassium (mg L^{-1})	1499	2094	1676	199
Sodium (mg L^{-1})	1440	3322	1984	690
Calcium (mg L^{-1})	45.4	63.4	57.1	5.52
Iron (mg L^{-1})	6.35	7.19	6.76	0.314
Zinc (mg L^{-1})	0.36	0.79	0.53	0.144
Lead (mg L^{-1})	0.24	0.42	0.32	0.062
Chromium (mg L^{-1})	1.20	2.44	1.45	0.420
Cadmium (mg L^{-1})	0.02	0.04	0.03	0.006
Copper (mg L^{-1})	0.16	0.31	0.22	0.045
Nickel (mg L^{-1})	0.24	0.97	0.67	0.287
BOD ₅ /COD	0.096	0.174	0.130	0.025

TABLE IV Physical-chemical characteristics of the leachate: Trench 1

Parameter	Min	Max	Mean	SD
pH-value	8.07	8.51	8.34	0.139
Colour	4900	9500	7400	1862
Total solids (mg L^{-1})	8467	17,000	12,208	3061
Suspended solids (mg L ⁻¹)	130	660	331	215
Dissolved solids (mg L^{-1})	7997	16,340	11,877	2916
$BOD_5(mg L^{-1})$	540	1196	718	225
$COD (mg L^{-1})$	3812	6125	5173	851
Conductivity ($\mu s \ cm^{-1}$)	22,200	26,900	23,850	1737
Alkalinity (as $CaCO_3$) (mg L ⁻¹)	2130	3255	2721	418
Sulphate (SO_4^{2-}) (mg L ⁻¹)	200	658	392	174
Phosphate (PO ₄ –P) (mg L^{-1})	13.2	17.8	15.5	1.67
Ammonia (NH ₃ –N) (mg L^{-1})	1000	1280	1131	103
Chloride (Cl^{-}) (mg L^{-1})	3074	5375	4322	814
Potassium (mg L^{-1})	1287	2927	1868	596
Sodium (mg L^{-1})	1438	3290	2148	910
Calcium (mg L^{-1})	43.7	70.1	55.8	10.2
Iron (mg L^{-1})	5.17	8.27	6.42	0.885
Zinc (mg L^{-1})	0.51	1.08	0.71	0.218
Lead (mg L^{-1})	0.43	0.57	0.50	0.043
Chromium (mg L^{-1})	0.80	1.95	4.45	0.339
Cadmium (mg L^{-1})	0.02	0.04	0.03	0.008
Copper (mg L^{-1})	0.16	0.23	0.20	0.027
Nickel (mg L^{-1})	0.46	0.81	0.67	0.135
BOD ₅ /COD	0.098	0.195	0.126	0.026

TABLE V
Physical-chemical characteristics of the leachate: Trench 2

17,000 mg L⁻¹. It is worth mentioning that the total solids were much higher than those reported for landfills that operate more than ten years (Chian and DeWalle, 1976; Loizidou and Kapetanios, 1993). The same observation stands for the suspended solids and dissolved solids. The conductivity values ranged in higher levels than those reported in literature (Tejero et al., 1993; Blight, 1995) with the values being in the range of 22,200–26,900 μ s cm⁻¹. These high values can be attributed to the high levels of the various anions. The alkalinity of the leachate samples expressed as CaCO₃ was in quite low levels in relation with reported values (Blight, 1995).

The BOD₅ values of the leachate were in the range of 520–1196 mg L⁻¹. The concentrations of COD exhibited a range of values between 3812 and 6489 mg L⁻¹. A very interesting observation was the low BOD₅/COD ratio (0.096–0.195) which indicated that the majority of the organic compounds present are not biodegradable.

Usually for landfills older than 10–15 years the BOD₅/COD ratio is lower than 0.1. The differentiation that was observed for the landfill under study, which has been operating since 1973, is mainly due to the high quantities of organic material that are disposed since municipal waste contains about 52% organics. Another important parameter that contributes to this differentiation is the time hysteresis of the initiation of the biological processes in the landfill body due to the lack of moisture which is related to the climatological conditions of the landfill area (e.g. low rainfall frequency).

The ammonia range was considered to be in high concentration (1000–1350 mg L⁻¹) due to the anaerobic conditions that prevailed in the landfill which in return contributed to nitrate reduction towards ammonia gas phase. These high concentrations are very toxic to the microorganisms that are responsible for the anaerobic processes. Consequently, the high level ammonia inhibits their growth and activity. The phosphates fluctuated between 9.71 and 17.8 mg L⁻¹. These values were higher than those mentioned in the literature for landfills that are in operation for more than 10 years, (Newell et al., 1990; Zheng et al., 1991; Gailey and Gorelick, 1993). These high levels can be attributed to the organic load of the refuse which contains prosphorus; this organic material, (mainly phospholipids and phosphoproteins), during its biodegradation release phosphorus and therefore increase phosphate concentrations. Sulphate concentrations were found to vary in concentrations higher than those expected for old landfills (Gailey and Gorelick, 1993). The values fluctuated between 185 and 758 mg L⁻¹.

Chloride is a conservative contaminant and is not affected either by the biochemical processes taking place in the landfill body or by the natural decontamination reactions in which the leachates are involved during their penetration in the vadose zone. Therefore the chlorides constitute a serious threat for the aquifer of the area, since their concentrations fluctuated to high levels ($3074-5375 \text{ mg L}^{-1}$). The concentrations of potassium ranged to higher concentrations ($1287-2927 \text{ mg L}^{-1}$) than those mentioned in the literature (Chian and DeWalle, 1976; Lu and Bai, 1991; Zheng et al., 1991; Gailey and Gorelick, 1993), while the concentrations of sodium ($1438-3322 \text{ mg L}^{-1}$) and calcium ($43.7-70.1 \text{ mg L}^{-1}$) appeared to be lower (Gailey and Gorelick, 1993).

The metals examined in this study were cadmium (0.02–0.04 mg L⁻¹), chromium (0.8–2.44 mg L⁻¹), copper (0.16–0.31 mg L⁻¹), iron (5.17–8.27 mg L⁻¹), nickel (0.24–0.97 mg L⁻¹), lead (0.24–0.57 mg L⁻¹) and zinc (0.36–1.08 mg L⁻¹). Generally, the concentrations of the metals (except Fe and Pb) were relatively low compared with those mentioned in the literature. This is due to the fact that the landfill receives mainly municipal solid waste and very low quantities of industrial waste. In addition, metals form insoluble sulphides since reductive conditions prevail in the landfill body.

4.3. GROUNDWATER QUALITY

The groundwater of the area under study is mainly used for industrial and irrigation purposes. Its use as potable water is very limited since the area is served by a central water supply system. The detailed examination of a large number of parameters would allow the characterisation of water and consequently its appropriate use. For comparison purposes, the limits for the various parameters in drinking water, according to the EE Directive 80/778 and EPA (1990), were taken into account. The mean values of the results obtained are shown in Tables VI and VII. From the experimental data the following observations can be reported.

	Mean value		
Parameter	Site 1	Site 2	Site 3
pH-value	7.23	7.30	7.16
Colour (Pt units)	272	20.7	226
Total solids (mg L^{-1})	2111	1323	2295
Suspended solids (mg L^{-1})	130	50	124
Dissolved solids (mg L^{-1})	1981	1273	2170
$BOD_5(mg L^{-1})$	4.17	1.17	_
$COD (mg L^{-1})$	78	35.8	37.8
Hardness (mg L^{-1})	807	727	786
Conductivity ($\mu s \ cm^{-1}$)	4470	2273	3893
Alkalinity (as $CaCO_3$) (mg L ⁻¹)	230	122	149
Sulphate (SO_4^{2-}) (mg L ⁻¹)	65.2	88.7	112
Phosphate (PO ₄ –P) (μ g L ⁻¹)	171	76.2	86.8
Ammonia (NH ₃ –N) (mg L^{-1})	67.8	6.35	18.2
Nitrate ($\mu g L^{-1}$)	211	885	395
Nitrite ($\mu g L^{-1}$)	26.7	296	7.83
Chloride (Cl ^{$-$}) (mg L ^{-1})	878	384	939
Potassium (mg L^{-1})	87.4	20	34.4
Sodium (mg L^{-1})	448	234	376
Calcium (mg L^{-1})	126	177	140
Iron (mg L^{-1})	1.92	0.56	0.86
Zinc (mg L^{-1})	0.05	0.07	0.16
Lead (mg L^{-1})	0.26	_	0.30
Nickel (mg L^{-1})	0.12	0.03	0.11

 TABLE VI

 Groundwater characteristics for sampling sites 1–3

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Groundwater characteristics for sampling sites 4-6.

	Mean value		
Parameter	Site 4	Site 5	Site 6
pH-value	7.29	7.49	7.37
Colour (Pt units)	18	5.17	10
Total Solids (mg L ⁻¹)	2012	369	819
Suspended Solids (mg L^{-1})	72.5	123	93.3
Dissolved Solids (mg L^{-1})	1940	246	725
$BOD_5 (mg L^{-1})$	4	_	_
$COD (mg L^{-1})$	10.4	_	_
Hardness (mg L^{-1})	807	618	560
Conductivity ($\mu s \ cm^{-1}$)	3977	723	1795
Alkalinity (as $CaCO_3$) (mg L ⁻¹)	142	52.2	53.3
Sulphate (SO_4^{2-}) (mg L ⁻¹)	96	4.17	15
Phosphate (PO ₄ –P) (μ g L ⁻¹)	103	103	11.3
Ammonia (NH ₃ –N) (mg L^{-1})	22.3	0.93	3.58
Nitrate ($\mu g L^{-1}$)	229	715	703
Nitrite ($\mu g L^{-1}$)	0.78	20.1	299
Chloride (Cl ^{$-$}) (mg L ^{-1})	866	47.2	316
Potassium (mg L^{-1})	42.1	3.20	3.83
Sodium (mg L^{-1})	426	50.8	271
Calcium (mg L^{-1})	161	93.2	260
Iron (mg L^{-1})	0.51	0.51	_
Zinc (mg L^{-1})	0.19	0.15	0.06
Lead (mg L^{-1})	_	_	_
Nickel (mg L^{-1})	0.12	_	0.02

The pH for all sampling sites was about neutral; the range being 6.91–7.60. The range of conductivity was between 700 and 4780 μ s cm⁻¹. Conductivity was found to be high, especially for sites 1, 2 and 4. These high conductivity values measured for the groundwater near the landfill is an indication of its effect on water quality. At all sites, conductivity values were above the EE suggested level (400 μ s cm⁻¹ at 20°C). Nevertheless, at site 5, water is suitable for irrigation according to the Greek legislation for irrigation waters (conductivity < 1000 μ s cm⁻¹ at 20°C) (Greek Ministry of Agriculture, 1991). The colour of the water samples at sites 1 (115–350 Pt units) and 3 (60–542 Pt units) was above the recommended EE limit (15–20 standard Pt units), at sites 2 (n.d–45 Pt units) and 4 (n.d–50 Pt units) fluctuated near the limit and at sites 5 (n.d–12 Pt units) and 6 (n.d–20 Pt units) was below the limit. For all sites under investigation, the range of dissolved solids was between 200 mg L⁻¹ (site 5) and 2685 mg L⁻¹ (site 3). All values except those measured at

site 5, in which the range was between 200 and 310 mg L^{-1} , were above the EPA, (1990) recommended limit for drinking waters (500 mg L^{-1}). The concentrations of suspended solids were also found to be in high levels, (n.d–380 mg L^{-1}). The hardness was very high, beyond the EE limit which is 120 mg L^{-1} CaCO₃.

High chloride concentrations were observed in particular at sites 1, 3 and 4 (810–1024 mg L⁻¹). The range at sites 2 and 6 was 325–434 mg L⁻¹. Site 5 exhibited lower chloride concentrations (40–52 mg L⁻¹) than the recommended limit (250 mg L⁻¹). Usually chlorides are considered as tracers but in this case it is difficult to assess the effect of the landfill since these high concentrations could be also attributed to the intrusion of seawater since the area is located in the vicinity of the Saronic Gulf. This phenomenon could possibly explain the fact that the most remote site (well 6) gave higher concentrations than site 5. Potassium was found in high concentrations at sites 1–4 (9.8–115 mg L⁻¹) while at sites 5 and 6 ranged between 1.6 and 6 mg L⁻¹; a fact which confirms once again the leachate effect. Sodium concentrations are also very high (30–590 mg L⁻¹). Calcium was found to be very high (79–283 mg L⁻¹) at all sampling sites and this can be attributed to the fact that the limestone soil of the area is mostly responsible for these increased levels.

Generally, phosphate concentrations measured were below the EE level of $400 \ \mu g \ L^{-1}$. For phosphates, the highest concentrations were found at site 1 (137–248 $\ \mu g \ L^{-1}$) while at site 6 phosphate traces were not detected. The effect of the landfill leachate was quite evident since ammonia concentrations were also found higher at site 1 (63–72 mg L⁻¹). At all sites ammonia concentrations were above the EE limit (0.05–0.5 mg L⁻¹). The nitrate and nitrite concentrations fluctuated on relatively normal levels (N–NO₃: 128–933 $\ \mu g \ L^{-1}$, N–NO₂: n.d–333 $\ \mu g \ L^{-1}$). The higher sulphate concentration was found at site 3 (141 mg L⁻¹). Nevertheless, all sites showed relatively low concentrations of sulphates and below the EE limit (maximum allowable level 250 mg L⁻¹).

At sites 1, 2 and 4 BOD₅ values were relatively low. BOD₅ ranged at these sites between 2 and 10 mg L⁻¹, while at sites 3 and 5 was not detected. According to Greek legislation the waters are suitable for irrigation, since the BOD₅ values are below the suggested limit of 40 mg L⁻¹. COD values ranged between n.d and 90 mg L⁻¹, with the highest value measured at site 1. Sites 5 and 6 gave zero COD values. It is quite evident that the groundwater is affected by the landfill leachates.

The metals, copper and zinc are characterised as undesirable substances (80/778/EE). Copper concentrations were not detected while zinc concentrations $(0.02-0.32 \text{ mg L}^{-1})$ were found to be below the EE limit (0.1 mg L^{-1}) at sites 1 and 6, $(0.02-0.09 \text{ mg L}^{-1})$ and above the limit at all other sites $(0.1-0.32 \text{ mg L}^{-1})$. Iron concentrations were above the limit (0.05 mg L^{-1}) at all sites and in particular at those in the closest proximity to the landfill (sites 1–4). In these four sites, the range was between 0.1 and 2.2 mg L⁻¹.

The metals lead, cadmium, chromium and nickel are characterised as toxic according to 80/778/EE. Cadmium and chromium were not detected. Nickel has

higher concentrations than the limiting value of 0.05 mg L⁻¹in sampling sites (sites 1, 3 and 4), located closer to the landfill. The range in these sites was between 0.08 and 0.15 mg L⁻¹. Lead concentrations were quite high at sites 1 and 3 (0.21–0.39 mg L⁻¹) and exceeded the limiting value (0.05 mg L⁻¹).

Assessing the water contamination in decreasing order, site 1 was characterised as the most polluted and this was expected since it is the closest one to the landfill. Sampling sites 3 and 4, though more remoted, were more polluted than site 2 which is closer to the landfill. This is an indication of the pollution transfer and the leachate movement. Site 6 (3 km) exhibited higher level pollution than site 5 (2 km). This most probably must be attributed to a local pollution source, or to the geological and hydrological characteristics of the area under study such as fractures or karstic cavities that influence the water movement.

5. Conclusions

The application of Hydrologic Evaluation of Landfill Performance model showed that the yearly leakage from the base of the landfill, after the placement of the final capping, is 42.76% of the total precipitation (167 mm). The results of the hydrologic balance obtained were at normal and expected levels.

The composition of the leachates under study showed a significant range for most of the parameters examined. The organic load appeared to be quite high and the low BOD₅/COD ratio confirmed the fact that the landfill operates in its last phase and, furthermore, the majority of the organic matter is not easily biodegradable. The high chloride concentrations constitute a serious threat for the aquifer of the area while heavy metals were in low levels with the exception of lead. For most of the sampling sites the groundwater quality is problematic, since most of the physical and chemical parameters examined exceeded the permissible limits.

Finally, the research showed that the pollution moves towards the southwestern side of the disposal site and it has also started to move towards the eastern part. Furthermore, the study confirmed the fact that the landfill leachates constitute a serious threat to the local aquifer.

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