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ENVIRONMENTAL ASSESSMENT OF CONTAMINANTS IN A DOWNSTREAM AREA OF A LANDFILL

Koutsopoulou E.[1], Katsanou K.[1], Papoulis D.[1], Zagana E.[1] and Tsolis-Katagas P.[1]

[1] University of Patras, Faculty of Natural Sciences, Department of Geology, ekoutsop@upatras.gr, katsanou@upatras.gr, papoulis@upatras.gr, zagana@upatras.gr, n.tsoli-kataga@upatras.gr

Abstract

Waste disposal poses a major pollution threat to public health and the environment. Therefore, the evaluation of environmental risks associated with a landfill and the effect of landfill surface runoff was investigated. Soil samples were collected in the downstream area of the waste disposal site and their mineralogy was studied. An appraisal of the heavy metal contamination in the area was attempted. Top layers of sediments seem to interact with chemically modified surface runoff waters from the landfill. Heavy metals such as As and Pb were in significant concentrations in the sediments within a distance of 200 m from the site. Anions such as chloride, sulphate and phosphate adsorbed on clay minerals suggest the interaction of sediments with surface runoff from the waste disposal site. Inorganic parameters NH_4^+ *and* NO_2^- *in surface water samples are above or slightly below the guidelines recommended by EE and WHO. The results indicated that environmental monitoring of the landfill is considered essential.*

Key words: *waste disposal site, clay minerals, stream sediments, surface water run-off, heavy metals.*

Περίληψη

Η διάθεση των απορριμμάτων αποτελεί τη μεγαλύτερη περιβαλλοντική απειλή για τη δημόσια υγεία και το περιβάλλον. Για το σκοπό αυτό η εκτίμηση των περιβαλλοντικών προβλημάτων που σχετίζονται με έναν χώρο απόθεσης απορριμμάτων και η επίδραση των υδάτων επιφανειακής απορροής προερχομένων από το χώρο θεωρήθηκε απαραίτητη. Εδαφικά δείγματα συλλέχθηκαν στην περιοχή κατάντη του χώρου και μελετήθηκε η ορυκτολογική τους σύσταση. Παράλληλα, επιχειρήθηκε μια εκτίμηση της ρύπανσης στην περιοχή. Τα επιφανειακά ιζήματα φαίνεται να αλληλεπιδρούν με τα χημικώς τροποποιημένα ύδατα επιφανειακών απορροών που προέρχονται από το χώρο απόθεσης απορριμμάτων. Παρατηρήθηκαν υψηλές συγκεντρώσεις σε As και Pb σε απόσταση 200 m από το χώρο απόθεσης. Οι αναλύσεις αργιλικών ορυκτών έδειξαν την παρουσία χλωρίου, θείου και φωσφόρου γεγονός που ενισχύει την αλληλεπίδραση τους με ύδατα απορροών από το χώρο απόθεσης. Παράμετροι όπως NH_4^+ *και* NO_2^- *στα ύδατα επιφανειακών απορροών βρίσκονται σε συγκεντρώσεις πάνω ή λίγο κάτω από τα όρια που προτείνονται από την ΕΕ και τον WHO γεγονός που υποδεικνύει ότι η περιβαλλοντική παρακολούθηση του χώρου απόθεσης θεωρείται απαραίτητη.*

Λέξεις κλειδιά: *χώρος απόθεσης απορριμμάτων, αργιλικά ορυκτά, επιφανειακά ιζήματα, επιφανειακή απορροή, βαρέα μέταλλα.*

1. Introduction

Rational waste management is a key issue in environmental engineering in order to minimize migration of pollutants and their potential effects on human health and the environment. Although significant efforts towards reduction of waste - through physical, chemical or biological methods - have been made in recent years, the disposal of waste in landfill sites is likely to continue (Department of the Environment, 1995, Hermanns Stengele and Plötze, 2000, EPA, 2010).

A number of requirements for landfills designed to ensure environmental protection have been established by the European legislation (e.g., 1999/31/EC, 1999, 2003/33/EC, 2002, 2008/1/EC, 2008 and 2008/98/EC, 2008). Landfill sites should comply with these standards and consist of a multi-barrier system comprising a geomembrane, a clay liner and a natural geological barrier are essential requirements to conserve the quality of the environment. In the case of pollutant escape the natural geological barrier is the final barrier to the migration of pollutants. Clay minerals are widely used as geological barriers in sanitary landfills because of their effective characteristics (Arch, 1998, Dubbin, 2000, Kugler et al., 2002, Du and Hayashi, 2006). These characteristics include their long-term compatibility with chemicals and the high sorption capacity for pollutants (Hermanns Stengele and Plötze, 2000, Volzone, 2004, Li et al., 2007). These properties depend on the mineralogy of the clay material used in the waste disposal site (Sezer et al., 2003). Therefore, the selection of the location for the landfill is one of the key parameters to ensure the retention of pollutants.

In the case of pollutant escape from the landfill site, enrichment of metals in stream sediments has been reported (Mantei and Coonrod 1989, Mantei and Foster 1991, Gonçalves et al., 2004). Surface runoff waters from the landfill site seem to affect the concentrations of metals in stream sediments. The potential pollution caused by runoff waters includes the release of ammonia, nitrates and nitrites, chlorinated and non-chlorinated compounds and heavy metal ions into the environment, all of which are toxic to living organisms (Baccini et al., 1987, Kjeldsen et al., 1998, Christensen et al., 2001).

The aim of this study is to evaluate the behaviour of the clay material down gradient of an operating waste disposal facility and its effectiveness for pollution control. The environmental impact of the landfill in the downstream area was evaluated. Stream sediments were examined for possible enrichment in heavy metals since they interact with chemically modified runoff waters from the landfill. The consequences of the disposal of waste and assessment of pollution on surface water downstream of the area were also investigated.

2. Materials and Methods

2.1. Site Characteristics and Sampling

The study area covers the landfill site and the surrounding area. This operating waste disposal facility is located at approximately 37°44΄37΄΄N and 20º55΄15΄΄E, West Greece (Fig.1). Two Pleiocene fine sediment sequences comprise the geology of the landfill area, the Upper and the Lower Horizon. The Upper Horizon consists of light grey to white sandstones with clay and marly intercalations and the Lower Horizon of blue marls and marly sandstones which do not host an aquifer (Monopolis and Bruneton, 1982, Skagias, 1986, Kamberis et al., 1998). The operations of the landfill commenced in 1992. The landfill area is about 90 acres and the mean waste load that receives is 22,484 ton/year (available data from 1997 to 2009). The landfill was constructed with a composite lining system according to the multi-barrier system and EU regulations (Hermanns Stengele and Plötze, 2000) and consists of a compacted clay liner, an overlying geomembrane (HDPE) and a geotextile. Samples were collected around the landfill and from top layers of sediments from a stream system, in the vicinity of the waste disposal site. Surface runoff water samples were collected downstream of the landfill and analysed to determine chemical parameters usually considered as indicators of pollution from solid waste disposal.

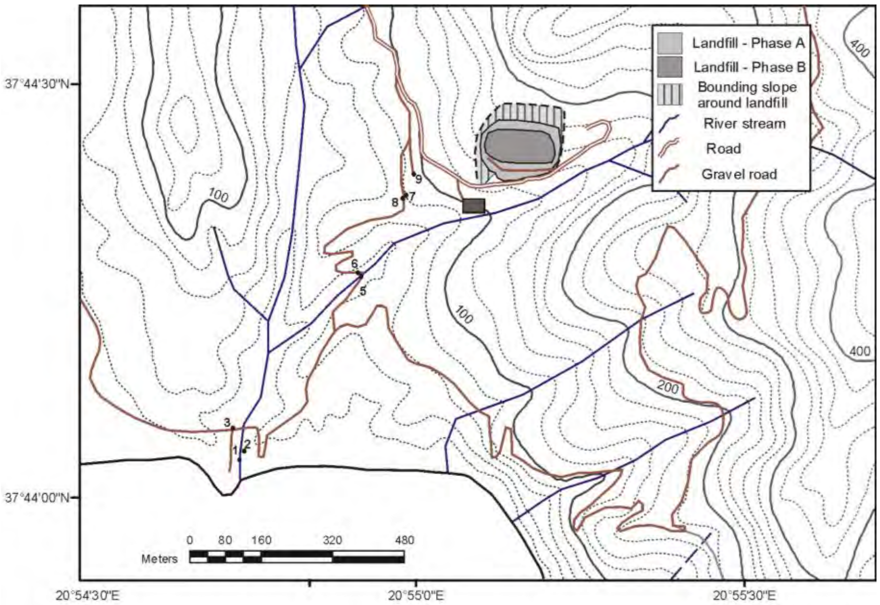

Figure 1 – Landfill site and sampling positions.

2.2. Experimental Methods

The bulk mineralogy of the samples was determined with X-Ray Diffraction, using a Bruker D8 Advance diffractometer, Ni-filtered CuKα radiation. The random powder mounts of bulk samples were scanned from 2 to 70º 2θ with a step increment of 0.015º 2θ and a count time of 0.3s per step. The <2 μm oriented specimens were prepared by sedimentation of the clay suspension onto glass slides and clay minerals were identified from three XRD patterns, after air-drying at 25 ºC, with ethylene glycol treatment, and after heating at 490 ºC for 2 hours.

The chemical composition of the minerals was determined using a Scanning Electron Microscope SEM JEOL 6300 equipped with an Energy Dispersive Spectrometer (EDS) with natural and synthetic standards and 20kV accelerating voltage, 10nA beam current. Microanalyses were performed on epoxy resin-impregnated polished and gold or carbon coated thin sections, and carbon coated sample powders mounted directly on the sample holder.

Chemical analyses were carried out in Activation Laboratories (Canada) by Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma (ICP) using a 4-acid (HF, HClO4, HNO3 and HCl) digestion technique. Bulk sample chemical analyses for major and trace elements were performed in all samples, using a Thermo Jarrell-Ash ENVIRO II ICP for INAA and a Perkin Elmer Optima 3000 ICP.

Chemical parameters of surface runoff water samples were determined by Flame Atomic Absorption Spectrometry (AAS) AVANTA P, GBC, by titration and by a DR 4000 HACH Spectrophotometer.

3. Results

3.1. Mineralogy

The X-ray diffraction patterns of random powder mounts are characterised by the presence of quartz, calcite, plagioclase and clay minerals in all samples. In some of the samples K-feldspar and dolomite are also present. The clay fraction (<2μm) is dominated by chlorite, smectite, vermiculite, illite, serpentine and mixed-layer chlorite-smectite. Chlorite is characterised by the presence of peaks at 14.2 Å, 7.1 Å, 4.74 Å and 3.55 Å which remain unaffected after ethylene glycol treatment and heating. Smectite is identified by the reflection at about 16.5 Å after ethylene glycol treatment which collapses to 10 Å after heating. Vermiculite is distinguished by the peak at 14.4 Å which is not affected by ethylene glycol treatment and collapses to10 Å after heating. Illite is identified by the peaks at10 Å, 5 Å and 3.3 which are not affected by ethylene glycol solvation and heating (Moore and Reynolds, 1989). The characteristic peaks of serpentine are observed at 7.30 Å, 3.65 Å which remain unaffected after heating treatment (Brindley and Brown, 1980). Mixed-layer chlorite-smectite is identified by the peak at 15.5 Å after treatment with ethylene glycol and at about 12 Å after heating (Thorez, 1975). Typical X-Ray Diffraction patterns of the <2 μm fraction of samples collected around the landfill and from stream sediments are shown in Figure 2.

3.2. Geochemistry

Bulk sample chemical analyses for major elements were performed in the samples and are shown in Table 1. Stream sediments (samples 1, 5 and 6, Fig.1) have the highest content in Al_2O_3, reflecting the abundance in clay minerals. Trace elements analyses (Table 2) showed that the content of As, Cu, Zn and Pb is higher in the stream sediments compared to the uncontaminated samples. Top layers of stream sediments are known to interact with runoff waters from the landfill. V and Rb are correlated with clay minerals whereas the high Ni and Cr contents reflect the presence of ultramafic components in the host rock.

Minerals present in the samples and the stream sediments were also examined by SEM-EDS for trace elements associated with pollution in waste disposal sites. SEM-EDS analyses showed traces of Cu and/or Zn in clay minerals. Anions such as chloride, sulphate and phosphate were also detected in clay minerals analyses.

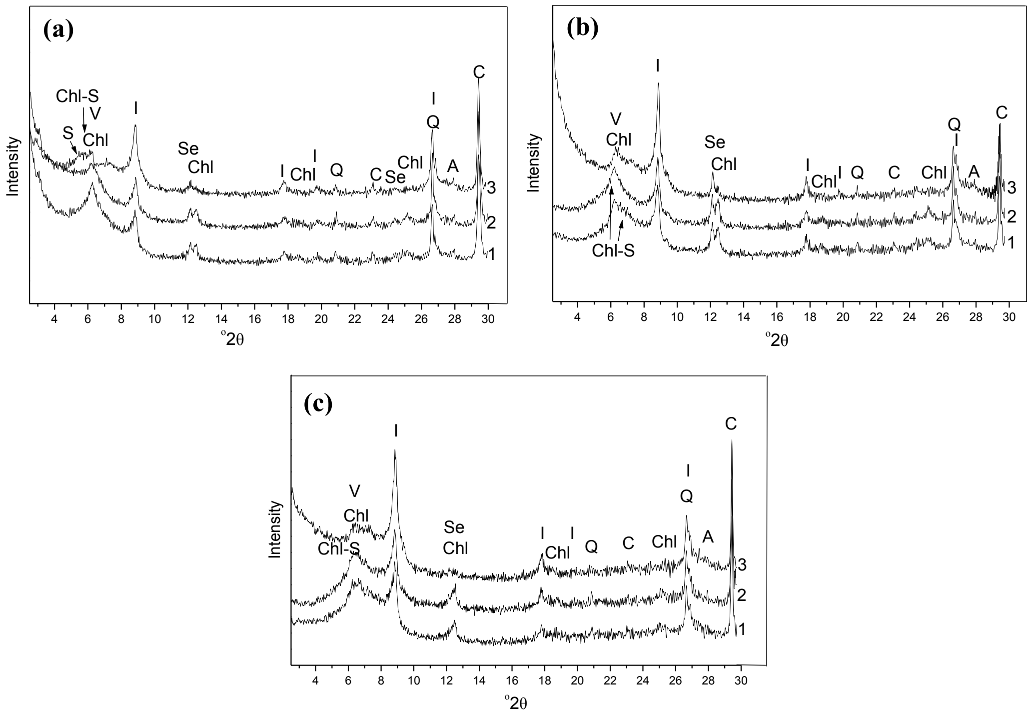

Figure 2 – X-Ray diffraction patterns of the <2 μm fraction. 1: air-dried sample, 2: glycolated, 3: heated. a) material collected downgradient of the landfill (sample 9), b) stream sediment (sample 1), c) stream sediment (sample 5). S: smectite, Chl-S: chlorite-smectite, I: illite, Chl: chlorite, V: vermiculite, Se: serpentine, Q: quartz, C: calcite, A: albite.

Table 1 - Bulk sample chemical analyses for major elements (wt %).

sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
1	52.68	8.20	3.65	0.05	3.62	13.16	1.39	1.56	0.48	0.09	14.98
2	59.30	4.01	1.66	0.05	3.74	13.09	1.36	0.98	0.30	0.06	14.82
3	57.21	6.25	2.75	0.05	3.52	13.41	1.25	1.26	0.41	0.07	14.20
5	53.39	8.05	3.42	0.06	2.15	14.36	1.22	1.56	0.46	0.08	15.71
6	46.72	8.95	4.60	0.07	4.37	13.93	1.09	1.76	0.51	0.10	17.19
7	50.43	4.03	1.30	0.04	1.40	24.54	1.05	0.81	0.36	0.07	15.30
8	55.60	4.76	1.51	0.04	1.67	14.48	1.19	1.12	0.29	0.04	18.80
9	53.65	6.60	2.61	0.05	2.35	15.50	1.33	1.27	0.43	0.08	15.56

Table 2 - Bulk sample chemical analyses for trace elements (ppm).

sample	As	Cu	Zn	Pb	Ni	Cr	V	Rb
1	4.6	16	48	11	173	386	67	57
2	5.0	4	28	<5	71	2350	25	26
3	4.9	11	35	6	157	847	48	43
5	6.6	18	44	12	133	455	67	57
6	9.4	20	57	11	192	437	87	74
7	3.1	5	18	<5	56	922	24	22
8	5.2	4	18	<5	86	773	30	30
9	6.3	11	34	8	120	532	50	39

3.3. Surface Water Quality

Surface runoff water samples were collected down gradient of the disposal site and analysed to determine chemical parameters usually considered as indicators of pollution from solid waste disposal. The mean chemical composition of surface runoff water samples collected after a rainy period was compared with the mean chemical composition of rainwater from the area and is shown in Figure 3. Most cations and anions analysed were quite low and range in concentrations below the recommended values and guidelines certified by EE (1998/83/EC, 1998). Ammonium concentration was above the guidelines recommended (0.5 mg/L) and nitrite was just below the guideline value of 0.1 mg/L.

4. Discussion

The greatest environmental concern in landfill sites is the generation of leachate from infiltrating surface water leading to the contamination of surface or groundwater supplies (Hermanns Stengele and Plötze, 2000). The mineralogy of the clay material used in a waste disposal site may influence the mobility of contaminants; therefore the determination of the types of clay minerals that are present in the landfill is of great importance for the assessment of their efficiency in the retention of pollutants.

Clay minerals and especially chlorite, smectite, illite and mixed layer chlorite-smectite identified by XRD, are abundant in the area the landfill was constructed and in the stream sediments. The specific clay minerals and especially smectite are widely used as natural clay barriers in waste disposal sites (Sezer et al., 2003). This is due to the sorption capacity of clay minerals for different metals and the anion and cation adsorption behaviour under various chemical conditions (Czurda and Wagner, 1991, Venema et al., 1996, Churchman et al., 2006, Chalermyanont et al., 2009, Koutsopoulou et al., 2010).

Geochemical analyses showed that the Al_2O_3 content is higher in the stream sediments compared to the rest of the samples. MgO and Fe_2O_3 content is related to the presence of chlorite and vermiculite. SEM-EDS analyses of trioctahedral chlorites in the samples showed Mg^{2+} and Fe^{2+} as the commonest divalent cations. The high MgO content in samples 2 and 3 is due to the presence of dolomite as revealed by the mineralogical analyses. Trace elements As, Cu, Zn and Pb showed elevated concentrations in the stream sediments. Enrichment of metals in stream sediments caused by various contamination sources have been reported (Ramamoorthy and Rust, 1978, Rule, 1986). Studies have shown elevated concentrations of Cu, Pb, Zn, Cd, Ag, and Ba in stream sediments affected by landfills and water treatment facilities (Mantei and Coonrod 1989, Mantei and Foster 1991). Stream sediments interact with runoff waters from landfills and show enrichment in metal concentrations. Clay minerals adsorption of heavy metals is strongly affected by the pH and the presence of anions in the solution since metal cations are known to form complexes with inorganic ligands (McLean and Bledsoe, 1992, Undabeytia et al., 2002, Churchman et al., 2006). The interaction between the metal ions and the complexing ligands could result in the formation of a complex that is either weakly adsorbed to the soil surface or more strongly adsorbed relative to the free metal ion (Benjamin and Leckie, 1982). The presence of Cl^-, SO_4^{2-} and PO_4^{3-} adsorbed on clay minerals in the stream sediments as revealed by SEM-EDS seems to have increased the negative charge of the surface and enhanced the adsorption of metals such as Cu and Zn from surface runoff waters from the waste disposal site.

Stream sediments also showed elevated lead and arsenic concentrations. Generally, Pb is accumulated near the soil surface. Sipos et al. (2005) suggested that soil organic matter plays a decisive role in the Pb adsorption, but the fixation by clay minerals is much stronger. Arsenite As(III) and arsenate As(V), are the main species in soils and sediments with the reduced state, arsenite being more toxic, soluble and mobile than arsenate (Bhattacharya et al., 2007). However, As mobility is usually limited due to the strong sorption by clays and Fe hydroxides (Kabata-Pendias, 2011). In general, the adsorption of arsenic in the form of arsenate is stronger than in the form of arsenite while Mn oxides are effective oxidants for the transformation of As(III) into As(V) (Dechamps et al., 2003).

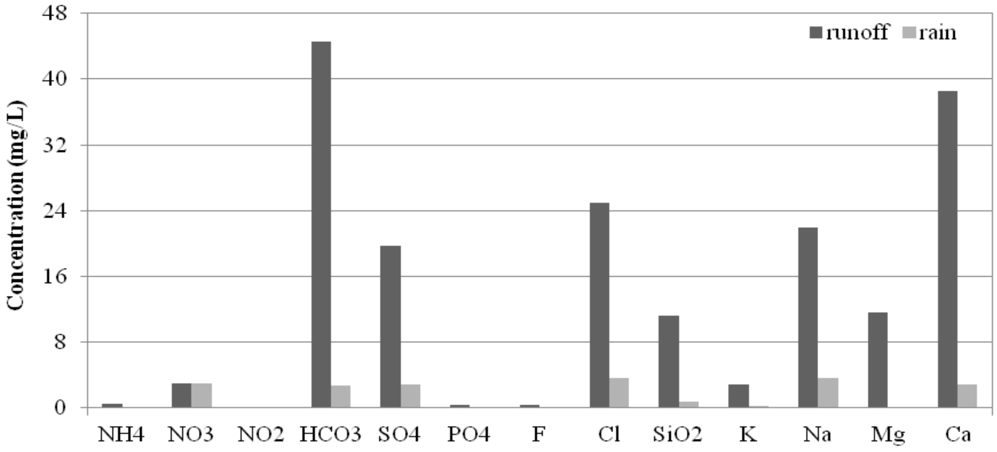

Figure 3 – Mean chemical composition of surface runoff water versus rainwater in mg/L.

The chemical composition of the surface runoff water samples showed concentrations below the maximum contaminant level (MCL) values given by European Council Directive (1998/83/EC, 1998) for the majority of the parameters. Rainwater is relatively free from impurities. However, landfill activities have the potential to deteriorate the quality of rainwater. The significance of the potential impacts will vary according to the phase of operation and the scale of the operations of the waste disposal facility. The comparison between surface runoff water and rainwater (Fig. 3) shows that the former is becoming enriched in most analysed parameters. Although the concentrations of chloride in surface runoff water are quite low, its presence in clay minerals analyses together with sulphates and phosphates could be attributed to contamination from the landfill. Chloride is usually considered as a tracer around landfill sites (Fatta et al., 1999). The ammonium concentration of the surface runoff water display elevated values that exceed the EE drinking water guidelines (1998/83/EC, 1998). Natural levels in groundwater and surface water are usually below 0.2 mg/L while anaerobic groundwaters may contain up to 3 mg/L (WHO, 2008, EPA, 2010). Ammonium in water is usually an indicator of possible bacterial, sewage or animal waste pollution and was attributed to contamination from the waste disposal site. Ammonium can also result in nitrite formation. The mean nitrite concentration (0.04 mg/L) was below the guideline value recommended (0.1 mg/L). However, its presence in the runoff water after an extended period of rainfall could only be of great concern for the operation conditions in the landfill.

5. Conclusions

The mineralogy of the naturally occurring clay material down gradient the landfill site and in the stream sediments is considered desirable in landfill sites.

Steam sediments are more abundant in clay minerals controlling the migration of pollutants. Trace elements analyses showed enrichment of As, Cu, Zn and Pb in the stream sediments compared to the uncontaminated samples. Since stream sediments are in contact with runoff waters from the landfill this could be an indication of contamination from the landfill. The presence of chloride, sulphate and phosphate adsorbed on clay minerals further contributes to the impact of clay mineralogy for pollution control.

The presence of ammonium and nitrite ions in surface runoff water is considered as human induced contamination from the landfill.

6. Acknowledgments

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7. References

1998/83/EC, O.J.L. 1998. *Council Directive of 3 November 1998 on the quality of water intended for human consumption*, European Union legislation.

1999/31/EC, O.J.L. 1999. *Council Directive of 26 April 1999 on the landfill of waste*, European Union legislation.

2003/33/EC, O.J.L. 2002. *Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC on the landfill of waste*, European Union legislation.

2008/1/EC, O.J.L. 2008. *Council Directive of 15 January 2008 concerning integrated pollution prevention and control*, European Union legislation.

2008/98/EC, O.J.L. 2008. *Council Directive of 19 November 2008 on waste and repealing certain directives*, European Union legislation.

Arch J. 1998. Clay Barriers in Landfills. Environmental Interactions of Clays. *Clays and the Environment*, in: Parker, A., Rae, J.E., (Eds.), Springer-Verlag, Berlin, 207-242 pp.

Baccini P., Henseler G., Figi R., and Belevi H. 1987, Water and element balances of municipal solid-waste landfills. *Waste management and Research*, 5, 483-499.

Benjamin M.M. and J.O. and Leckie. 1982. Effects of complexation by Cl, SO4, and S2O3 on adsorption behavior of Cd on oxide surfaces. *Environ. Sci. Technol*. 16, 162-170.

Bhattacharya P., Mukherjee, A.B., Bundschuh, J., Zevenhoven, R. and Loeppert, R.H. 2007. *Arsenic in Soils and Groundwater Environment*. Elsevier, Amsterdam. 640p.

Brindley G.W. and Brown G. 1980, *Crystal structures of clay minerals and their X- ray identification*. Mineralogical soc monograph No 5.

Chalermyanon T., Arrykul S. and Charoenthaisong N. 2009. Potential use of lateritic and marine clay soils as landfill liners to retain heavy metals, *Waste Management*, 29, 117-127.

Christensen T.H., Kjeldsen P., Bjerg P.L. Jensen, D.L. Christensen J.B., Baun A., Albrechtsen H.J. and Heron C. 2001. Biogeochemistry of landfill leachate plumes, *Applied Geochemistry*, 16, 659–718.

Churchman G.J., Gates W.P., Theng B.K.G., and Yuan G. 2006. Clays and Clay Minerals for Pollution Control, in: Developments in Clay Science Vol.1., *Handbook of Clay Science*, Bergaya F., Theng B.K.G. and Lagaly G. (Eds). 625-676pp.

Czurda K.A. and Wagner J.F. 1991. Cation-transport and retardation prossesses in view of the toxic-waste deposition problem in clay rocks and clay liner encapsulation, *Eng. Geol*., 30, 103-113.

Deschamps E., Ciminelli V.S.T., Weidler P. and Ramos A.Y. 2003. Arsenic sorption onto soils enriched in Mn and Fe minerals, *Clays and Clay Minerals*, 51, 197–204.

Department of the Environment, 1995. *Making waste work: a strategy for suitable waste management in England and Wales*, HMSO, London.

Du Y.J. and Hayashi S. 2006. A study on sorption properties of Cd^{+2} on Ariake clay for evaluating its potential use as a landfill barrier material, *Applied Clay Science*, 32, 14-24.

Dubbin W.E. 2000. Intercalation of organic and inorganic contaminants by expanding layer silicates, in: J.D. Cotter-Howells L.S., Campbell E., Valsami-Jones and M. Batchelder (eds) *Environmental Mineralogy: Microbial Interactions, Anthropogenic Influences, Contaminated Land and Waste Management*, Mineralogical Society Series, 9. Mineralogical Society, London. 227-244 pp.

EPA 2010. EPA Victoria. Siting, *Design, Operation and Rehabilitation of Landfills*. Publication 788.1, availiable at: http://www.epa.vic.gov.au/

Fatta D., Papadopoulos A. and Loizidou M. 1999. A study on the landfill leachate and its impact on the groundwater quality of the greater area, *Environmental Geochemistry and Health*, 21, 175-190.

Hermanns Stengele R. and Plötze M. 2000. Suitability of minerals for controlled landfill and containment, *Environmental Mineralogy*. EMU Notes in mineralogy, Vol. 2, Chapter 8, 291-331.

Gonçalves M.A., Nogueira J.M.F, Figueiras J., Putnis C.V. and Almeida C. 2004. Base-metals and organic content in stream sediments in the vicinity of a landfill, *Applied Geochemistry*, 19, 137-151.

Kabata-Pendias A. 2011. *Trace Elements in Soils and Plants*, 4th Edition. CRC Press. Taylor and Francis Group, LLC. 505p.

Kamberis E., Ioakim, Ch., Tsaila-Monopolis St., Marnelis F. and Sotiropoulos S. 1998. Geological and palaeogeographic evolution of western Greece, during the Neogene-Quaternary period in the geodynamic setting of the Hellenic Arc, *Roman J. Stratigraph*. 78, 63-74.

Kjeldsen P., Bjerg P.L., Rugge K., Christensen T.H. and Pedersen J.K. 1998. Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source. Landfill hydrology and leachate migration, *Waste Management and Research*, 16, 14–22.

Koutsopoulou E., Papoulis D., Tsolis-Katagas P. and Kornaros M. 2010. Clay minerals used in sanitary landfills for the retention of organic and inorganic pollutants, *Applied Clay Science*, 49, 372-382.

Kugler H., Ottner F., Froeschl H., Adamcova, R., and Schwaighofer B. 2002. Retention of inorganic pollutants in clayey base sealings of municipal landfills. *Applied Clay Science*, 21, 45-58.

Li L.Y., Ohtsubo M., Higashi T., Yamaoka S., Morishita T. 2007. Leachability of municipal solid waste ashes in simulated landfill conditions, *Waste Management*, 27, 932-945.

Mantei E.J. and Coonrod D.D. 1989. Heavy metal content in the stream sediments adjacent to a sanitary landfill, *Environmental Geology and Water Science*, 13(1), 51-58.

Mantei E.J. and Foster M.V. 1991. Heavy Metals in Stream Sediments: Effects of Human Activities, *Environmental Geology and Water Science*, 18, 2, 95-104

McLean J.E. and Bledsoe, B.E. 1992. Behavior of Metals in Soils, in: Boulding, J.R. (Ed.), EPA *Environmental Assessment Sourcebook*, pp. 19-56.

Monopolis D. and Bruneton A. 1982. Ionian Sea (Western Greece): its structural outline deduced from drilling and geophysical data, *Tectonophysics*, 83, 227-242.

Moore D.M. and Reynolds R.C.Jr. 1989. *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press. New York. 198-269 pp.

Ramamoorthy S. and Rust B.R. 1978. Heavy metal exchange processes in sediment water systems, *Environmental Geology*, 2(3), 165-172

Rule J. 1986. Assessment of trace element geochemistry of Hampton Roads Harbor and Lower Chesapeake Bay area sediments, *Environmental Geology,* 8(4):209-219

Sezer G.A., Türkmenoğlu A.G. and Göktürk E.H. 2003. Mineralogical and sorption characteristics of Ankara Clay as a landfill liner, *Applied Geochemistry*, 18, 711-717.

Sipos P., Nemeth T. and Mohai I. 2005. Distribution and possible immobilization of lead in a forest soil (Luvisol) profile. *Environ. Geochem. Health*, 27, 1–10.

Skagias S. 1986. *Hydrogeological Research of Zakynthos Island*. IGME, (Institute of Geology and Mineral Exploration), Athens.

Thorez J. 1975. *Phyllosilicates and clay minerals: A laboratory handbook for their X-Ray diffraction analysis*. Ed. G. Lelotte. B 4820 Dison, Belgique.

Undabeytia T., Nir S., Rytwo G., Serban C., Morillo E. and Maqueda C. 2002. Modeling Adsorption-Desorption Processes of Cu on Edge and Palnar Sites of montmorillonite, *Environ. Sci. Technol*. 36, 2677-2683.

Venema P., Hiemstra T., and van Riemsdijk W.H. 1996. Comparison of different site binding models for cation sorption: Description of pH dependency, salt dependency, and cation-proton exchange, *J. Colloid Interface Sci*., 181, 219-228.

Volzone C. 2004. Removal of Metals by Natural and Modified Clays, in: *Clay Surfaces: Fundamentals and Applications. Interface Science and Technology*. Vol. 1., F. Wypych and K.G. Satyanarayana (editors). Elsevier Academic Press. 291-320.

WHO, World Health Organization, 2008. *Guidelines for drinking-water quality*, 3rd ed. Vol. 1. incorporating 1st and 2nd addenda, Recommendations. Geneva.