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**CHARACTERIZATION OF LEACHATE FROM TWO MUNICIPAL WASTE
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ON NEARBY SOILS AND GROUNDWATER WELLS**

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UNIVERSIDAD DEL TURABO

CHARACTERIZATION OF LEACHATE FROM TWO MUNICIPAL WASTE DISPOSAL
LANDFILLS IN PUERTO RICO AND ITS POSSIBLE IMPACT
ON NEARBY SOILS AND GROUNDWATER WELLS

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DISSERTATION

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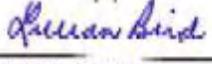
**Characterization of Leachate from Two Municipal Waste Disposal
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Nearby Soils and Groundwater Wells**

Luz Stella Betancourt Moreno

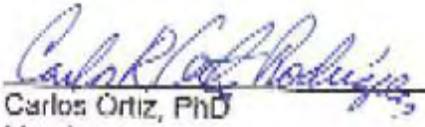
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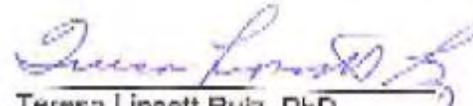
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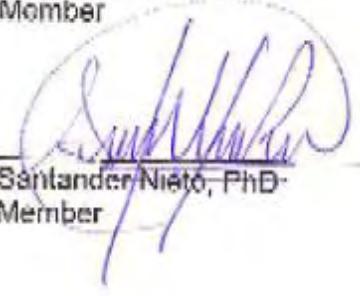
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Abstract

Luz Stella Betancourt Moreno. (PhD, Environmental Science)

Characterization of Leachate from Two Municipal Waste Disposal Landfills in Puerto Rico and its Possible Impact on Nearby Soils and Groundwater Wells (Mayo 2011)

Abstract of a doctoral dissertation at *Universidad del Turabo*.

Dissertation supervised by Professor César Lozano

No. of pages in text 192

Municipal solid waste landfills (MSWL) are currently the predominant solid waste disposal practice in Puerto Rico. In these landfills, runoff and rainwater combine with solid waste degradation products to produce leachate. Landfill leachate is rich in organic and inorganic substances, including heavy metal ions.

Although these chemical species represent a public health and environmental hazard, particularly when they reach surface and groundwater systems, no data regarding the type and concentration of heavy metals in leachates from landfills in Puerto Rico was available. At the time this study began, the PREQB did not have data on leachate composition and its impact on nearby soil and groundwater quality for any landfill in PR. Moreover, this agency used data from US landfills for decision-making with regards to landfill problems in Puerto Rico. It was thus a priority to document this information for optimal landfill operation, and to determine potential impact on nearby soil and groundwater wells. The results presented in this dissertation are aimed at addressing this need.

Through this study, the following goals were attained: (1) methods and procedures for sampling and analyzing metals in landfill leachates were designed and implemented; (2) a detailed analysis of selected parameters, using analytic techniques

approved by USEPA (U.S. Environmental Protection Agency) were performed; (3) the contribution of these parameters on leachate composition was assessed; (4) the leachate composition of samples obtained at two distinct locations within a specific landfill (one containing metal scraps and the other containing domestic wastes) was compared; (5) the metal composition of leachate from these two landfills was compared with that reported in other studies; and (6) the impact of the Toa Baja landfill leachate on nearby soil and groundwater quality was assessed.

Resumen

Luz Stella Betancourt Moreno. (PhD, Environmental Science)

Characterization of Leachate from Two Municipal Waste Disposal Landfills in Puerto Rico and its Possible Impact on Nearby Soils and Groundwater Wells (Mayo 2011)

Abstract of a doctoral dissertation at *Universidad del Turabo*.

Dissertation supervised by Professor César Lozano

No. of pages in text 192

Los sistemas de rellenos sanitarios (SRS) municipales son actualmente el principal método para el manejo de los desperdicios sólidos en Puerto Rico (PR). En los SRS, la escorrentía y el agua de lluvia se combinan con los productos de degradación de los desperdicios sólidos para producir el lixiviado. El lixiviado de los SRS es rico en sustancias orgánicas e inorgánicas, incluyendo los iones de metales pesados.

Aunque estas especies químicas pueden representar una amenaza a la salud pública y al ambiente, particularmente cuando llegan a los cuerpos de agua superficiales y subterráneos, en Puerto Rico no existen datos oficiales en cuanto al tipo y concentración de metales pesados en los lixiviados de SRS. Al momento de comenzar este estudio, la Junta de Calidad Ambiental de Puerto Rico (JCAPR) no disponía de datos concernientes a la composición de los lixiviados y de su impacto en los suelos y aguas cercanas a SRS en la isla. Más aún, para tomar decisiones relacionadas a los problemas de los SRS en PR esta agencia utilizaba datos provenientes de SRS de los Estados Unidos. Era, por tanto, prioritario documentar esta información para optimizar la operación de SRS y para determinar su posible impacto sobre suelos y aguas subterráneas cercanas. Los resultados presentados en esta disertación están dirigidos a atender esta necesidad.

Por medio de este estudio, las siguientes metas fueron alcanzadas: (1) se diseñaron e implementaron métodos y procedimientos para el muestreo y análisis de metales en lixiviados de SRS; (2) usando técnicas aprobadas por la Agencia de Protección Ambiental (USEPA, por sus siglas en inglés) se condujo un análisis detallado de parámetros específicos; (3) la contribución de cada uno de estos parámetros en la composición del lixiviado fue analizada; (4) la composición de muestras de lixiviado obtenidas en dos lugares diferentes de un mismo SRS (uno caracterizado por depósito de chatarra y el otro caracterizado por el depósito de desperdicios mayormente domésticos) fue comparada; (5) el contenido de metales y otros parámetros en dos SRS fue comparado con datos reportados en otros estudios; y (6) el impacto del lixiviado del SRS de Toa Baja en la calidad de suelos y aguas subterráneas cercanas fue evaluado.

Vita

Luz Stella Betancourt Moreno was born in Palmira, (Valle) a small and picturesque city in Colombia, South America. She's the sixth daughter of a family of seven children. She studied her elemental and intermediate education in San Vicente de Paul School. Its religious focus influenced her development. Her scientific interest was instilled at in Santiago de Cali University, where she got a bachelor of science in Biochemistry (1999). Then she decided to continue with her passion for Chemistry and came to Puerto Rico. In 2004 she obtained the Master's degree in chemistry at the University of Puerto Rico, Río Piedras and in 2011 she obtained the PhD in environmental science at *Universidad del Turabo*.

Dedications

I want to dedicate this thesis to my dear Lord, Rosa Elvira, my sweet mommy; Alfonso, Santiago, Enrique, Carlos, Martha and Joana, my brothers and sisters; Diego and Andres, my nephews, and Guadalupe, my friend.

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Chapter One

Introduction

Currently, the use of municipal waste disposal landfills (MWDL) is the predominant waste management practice in many countries. Puerto Rico (PR) is not an exception. However, there are potential public health and environmental implications associated with solid waste landfills.

The major concerns associated with waste management in PR are the high amount of municipal solid wastes generated on a daily basis and the inadequate management and disposal practices in landfills. Landfills in PR, due to an inappropriate design and management program, show several situations, such as generation of leachate, problems related to daily cover, and contribution to the greenhouse effect, among others, and pose harm to the environment as well as human health, including the potential to contaminate surrounding land and groundwater. Groundwater has been shown to be the primary contaminant release route at problematic landfills and its leachate the major cause (Mor et al. 2006).

The most important reason for the steady decline of landfills in PR, which have decreased from 61 in 1993 to 32 in 2004, is that they did not comply with the design requirements established in federal regulations (ADS 2003a). The lack of appropriate management has potential impact on environment and human health. In 2004, the Puerto Rico Environmental Quality Board (PREQB) reported a leachate problem in 53% of the 32 operating landfills in PR. (PREQB 2004). Leachate generation is an inevitable result of solid waste biodegradation in landfills. Its study is of relevance for an efficient landfill design and to control groundwater pollution. The leachate is produced as a result of rainfall percolation, which dissolves soluble components, such as hydrolyzed materials and degradation products from the waste. The leachate consists of different

organic and inorganic compounds that may be either dissolved or suspended in it. The composition of this leachate, which is related to factors such as climate and life style, is commonly characterized by measuring biological, chemical and physical parameters. In this study the characterization is limited to measuring inorganic macrocomponents, heavy metal contents (chemical parameter), pH and conductivity (physical parameters).

In relation to the impact that the landfills might produce in the environment, especially on groundwater quality, the leachate might be the main cause. Some of the components found in leachate, such heavy metal, could contribute to pollution of the groundwater if they migrate into surface water or groundwater, when appropriate collection and treatment procedures are not used prior to discharging this leachate.

The PREQB does not have official data on leachate composition including heavy metal chemical analysis and physical parameters such as its pH and conductivity for any landfill in PR. In addition, the PREQB does not have written procedures for sampling and analyzing landfill leachate. In order to understand the effect of improper landfill management practices on the environment and leachate to mitigate health consequences and adverse environmental effects, it is necessary to determine and understand the potential consequences of landfill leachate composition.

1.1.0 Statement of the Problem

MSW landfills in PR pose a potential risk of environmental contamination due to the lack of leachate collection systems and liners. As was previously indicated, the PREQB has no official data on leachate procedures (SOPs) for sampling and analysis of metals and other chemical parameters in landfill leachate. However the PREQB uses the chemical and physical parameters measured in United States landfills for decision-making related to the problems they face with landfills in PR and such practice might not be appropriate for the Island, for leachate varies from one landfill to another due to variations in climate, hydrogeology and waste composition. It's a priority to measure the

parameters mentioned earlier associated with the leachate, not only to evaluate their influence on the conditions of the landfills but also their possible influence in soil and groundwater quality nears the landfills.

1.2.0. Research Objectives

This study has three objectives .The first one is to provide valuable information of the leachate composition found in two of the Island's landfills by means of measuring the characterization parameters such as pH, conductivity, inorganic-macrocomponents and heavy metal. The second objective is to determine the possible influence of these landfill parameters on nearby groundwater quality for one of the two landfills. The third objective is to determine the possible influence of these landfill parameters on nearby soil quality for one of the two landfills.

The main hypotheses for this study are:

H1_o: The means of each quality parameter for the leachate landfills studied in Puerto Rico (Toa Alta and Toa Baja) will not differ among themselves.

H1_a: The means of each of the quality parameters for the leachate landfills studied in Puerto Rico, (Toa Alta and Toa Baja) will differ among themselves.

The second hypothesis is related to the potential impact to groundwater wells:

H2_o: The means of each of the quality parameters for groundwater wells close to the landfill are not the same as the mean values of the quality parameters for groundwater wells far from the landfill.

H2_a: The means of each of the quality parameters for groundwater wells close to the landfill are the same as the mean values of the quality parameters for groundwater wells far from the landfill.

The third hypothesis is related to the potential impact to soil quality:

H3_o: The means of each of the quality parameter for soil near the landfill are not the same as the away mean values.

H3_a: The means of each the quality parameter for soil near the landfill are the same as the away mean values.

1.3.0 Specific Aims

1. To design and implement procedures for parameter sampling of landfill leachate.
2. To correlate the results obtained between the two landfills in PR with data reported in other studies from the United States and other countries.
3. To correlate the two sampling points in Toa Baja landfills in terms of their composition based in the quality parameter, as well as type of waste deposited.
4. To investigate seasonal trends in the data and evaluate their effects on leachate composition.
5. To sample, analyze and compare the data obtained from samples taken far from the area of influence of the landfill leachate, with those inside the area of influence of the landfill (possible impact point) in order to establish the impact of leachate on groundwater quality.
6. To sample, analyze and compare the data obtained from soil far from the area of influence of the landfill leachate, with those in the area of influence of the landfill (possible impact point) in order to establish the impact of leachate on soil quality.

1.4.0 Significance

Puerto Rico has experienced a rapid population growth and economic development in the past decades (Hunter et al. 1995). This has led to an increase in the amount, generation of solid wastes and in the establishment of MSW landfills. The leachate generated may have adverse impact on the environment and affect the health of certain sectors of the population (Mor et al. 2006; Hunter et al. 1995; Vadillo et al. 1999). Most landfills in the Island do not comply with the design requirements established in federal regulations and, in consequence, most landfills pose a leachate problem. PREQB lacks official data on leachate composition from MSW landfills and its

impact on the environment. Therefore, an important area of research in PR is the study of landfill leachate in order to determine the presence and concentration of quality parameter and their impact on the environment. Characterization of leachate is an essential first step to understand the actual situation of landfills in the Island and to make decisions such as the implementation of programs aimed at minimizing the environmental impact of landfills through remediation and attenuation projects that could be coordinated between the academia and concerned agencies in the Island.

Through this study, the researcher proposes to sample and analyze the leachate of two landfills, as well as the groundwater wells and soil nearby in order to establish the quality parameters (pH, conductivity, inorganic macrocomponents and heavy metal), in the leachate of these landfills and determine the quality of groundwater and soil near these sites.

Chapter Two

Review of the Literature

2.1.0 Municipal Solid Waste Management

The appropriate management of municipal and industrial solid waste continues to be a major problem throughout the world. Municipal Solid Waste (MSW) management is to date one of the most critical concerns of our society as the production of waste is continuously increasing. The industrial and commercial growth in many countries around the world in the past decades has been accompanied by rapid increases in both the municipal and industrial solid waste generation (Lin and Chang 2000; Nczaj et al. 2005).

2.1.1 Generation of Solid Wastes

Over the years, the high population growth rates, as well as the rate of industrialization and urbanization, have contributed to environmental problems all over the world (Renou et al. 2008). Currently, solid waste generation and its disposal are two of the most significant problems. Modern lifestyle results in large quantities of solid waste generated every year. The amount of solid waste produced around the world is increasing at high rates. In Europe, more than 1.6 billion t are generated annually (EUC 2004).

According to the USEPA, in 2005, 222.9 million t of MSW were generated in the United States (USEPA 2006). Table 2.01 shows the MSW generated and disposed in the US from 1960 to 2005.

Table 2.01. Generation, materials recovery, composting, combustion with energy recovery, and discards of Municipal solid waste, 1960–2006 (in millions of t). (USEPA 2006).

Activity	1960	1970	1980	1990	2000	2003	2004	2005
Generation	88.1	121.1	151.6	205.2	237.6	240.4	247.3	245.7
Recovery for recycling	5.6	8	14.5	29	52.7	55.8	52.7	58.4
Recovery for composting*	Negligible	Negligible	Negligible	4.2	16.5	19.1	20.5	20.6
Total Materials Recovery	5.6	8	14.5	33.2	69.1	74.9	77.7	79
Combustion with Energy Recovery†	0	0.4	2.7	29.7	33.7	33.7	34.1	33.4
Discards to Landfill, Other Disposal‡	82.5	112.7	134.4	142.3	134.8	131.9	135.5	133.3

*Composting of yard trimmings, food scraps, and other MSW organic material. Does not include backyard composting.

† Includes combustion of MSW in mass burn or refuse-derived fuel form, and combustion with energy recovery of source separated materials in MSW (e.g., wood pallets and tire-derived fuel).

‡ Discards after recovery minus combustion with energy recovery. Details may not add to totals due to rounding.

In Puerto Rico, in 2003 the Solid Waste Management Authority hired the services of Wehran Puerto Rico Inc. to conduct a Waste Characterization Study at the 31 landfills and 2 transfer stations (ADS 2003b). They determined waste type, as well as amount of waste generated per day, week and year, among others. The results obtained in terms of the generation of solid waste, which were published by the Puerto Rico Solid Waste Management Authority (seeTable 2.02.).

Table 2.02. Waste measurements results in Puerto Rico (ADS 2003b).

Total Weekly Tonnage metric	62 787
Weeks Per Year	52
Estimated Tons metric Per Year	3 264 932.5
Average Daily Discard Rate Per Person (MSW and Yard Waste)	1 773.5 g
Average Daily Discard Rate Per Person (MSW & and Waste) in USA	1 773.5 g

2.1.2 Disposal of Solid Wastes

Landfill sites are currently the most common and dominant means of waste management practice in the USA and Europe (Reinhart et al. 2000; Lema et al. 1988; Baun and Christensen 2004; Kjeldsen et al. 2002). This is partly due to the low cost and easy management of the facilities located near almost all communities in the USA, factors that encourage their use as the predominant waste disposal option (Reinhart et al. 2000; Neczaj et al. 2005). Approximately 54% of the municipal solid waste generated in the US in 2005 was placed in MSW landfills, as reported by USEPA (USEPA 2006). New alternatives such as sorting, composting and recycling are promoted. However, while the percent of recycled solid waste is increasing, its rise has been very slow, and

at present there is no other alternative suggested more strongly than landfill disposal management. Therefore, landfills will continue to be the most common means of MSW disposal in the near future.

Municipal authorities are in charge of the municipal, commercial and domestic wastes generated in Puerto Rico and most of those wastes are disposed of in a final manner at the MSW landfills that exist in the Island. The ADS reported (ADS 2004) a weekly generation of 69 211 tons of solid waste, of which 69 200 were disposed on municipal landfills. Even though the MSW landfills currently have many deficiencies, to date it is the main way that PR has to dispose of its solid wastes, approximate the 85% municipal solid waste is disposed of through landfills.

2.2.0 Landfill

2.2.1 Definition

By definition, a landfill is a hole in the ground where solid waste is deposited and a municipal solid waste (MSW) landfill site is an engineered waste disposal site facility with specific pollution control technologies (Skultetyova 2009; Sabahi et al. 2009a). The large area of ground normally is lined to prevent material to escape to the ground. The landfill is used as a method of solid waste disposal in which the controlled deposit of waste to land is conducted with little or no pre-treatment. In the landfill, the waste is deposited in thin layers compacted to the smallest volume, and it is covered with soil at the end of the work day. MSW landfills may contain a mixture of household, commercial and industrial waste, as well as treatment sludges (semi-solid material left from industrial wastewater) (Baun et al. 2004).

2.2.2 Environmental Legislation

There is an increasing amount of government policy and legislation to reduce the environmental liabilities associated with MSW disposal in the US. Among the Federal regulations for the disposal of solid waste, one of the most important is the Resource

Conservation and Recovery Act (RCRA). These regulations, referred to as Subtitle D regulations of RCRA, address all aspects of landfill disposal, including siting, design, operation, closure, and post-closure (USEPA 2010).

Recently established landfills have been constructed with the new design established by RCRA regulation. Therefore, contamination is limited by multiple engineered liners (clay and/or geosynthetic liners are commonly used). Historically, most landfills (or open dumps) were built without liners or leachate collection systems, and leachate still continues to be discharged directly into the ground. The liner system is an important part of the leachate collection system (Meeroff 2006). The role of the collection system is to collect and remove the leachate from the base of the landfill. In PR, most of the landfills do not have the new design for leachate collection (PREQB 2004) (see Figure 2.01).

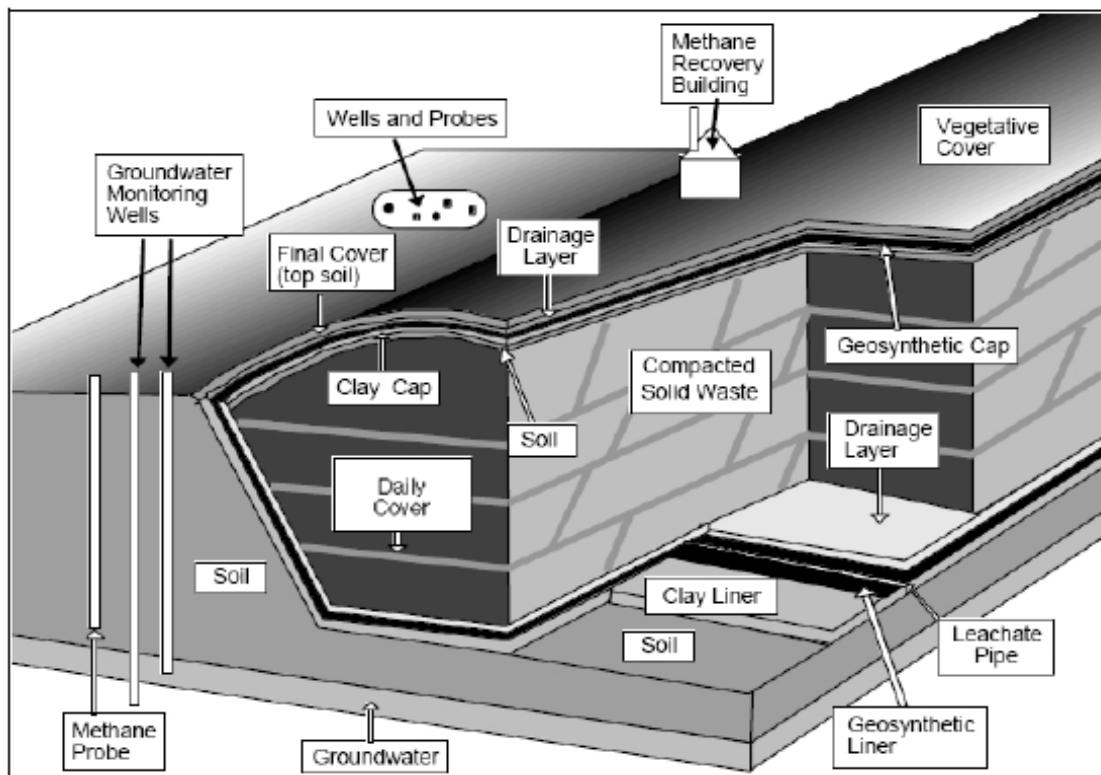


Figure 2.01. Illustration of cross-section of typical landfill (Meeroff 2006).

2.2.3 Potential Adverse Impacts of Landfills

Despite the regulation and measures implemented, municipal landfills can represent a widespread and significant threat to environment, wildlife and human health concern (Eggen et al. 2010).

2.2.3.1 Health Impacts from MSW Landfills

Usually it is not possible to determine which chemicals are responsible for the observed health effects in landfill sites because normally waste sites contain multiple chemical components. There are currently strong national and international concerns about the possible adverse health effects of living in the vicinity of MSW landfills. A great amount of research has been carried out to identify the possible adverse health effects of landfill sites on people living nearby. The main risks related to these adverse health effects include low birth weight, birth defects, and certain types of cancer (Elliott et al. 2001; Baibergenov et al. 2003). In Great Britain, Elliott et al. (2001), investigated the risk of adverse birth outcomes associated with residences near landfill sites. The findings included a small increase in the rate of congenital malformations and low birth weight (Elliott et al. 2001). In the United States, a study performed by Baibergenov et al. in 2003 in New York supports the hypothesis that living near a polychlorinated biphenyls (PCBs) contaminated site poses a risk of giving birth to low birth weight infants (Baibergenova et al. 2003).

Canadian researchers conducted a study to evaluate cancer incidence in populations living near the Miron Quarry landfill (Goldberg et al. 1999). The data from this study and from a previous research at the same site, suggests that men who lived near this landfill site may have been at excess risk of cancer. Cancer of the liver, kidney and pancreas are among the most incidences.

2.2.3.2 Environmental Impact

A wide variety of individual waste fractions such as paper, metals, glass, organic material and other combustible and non-combustible waste fractions, may be found at MSW landfills. Each of these categories or fractions may contribute to impact the environment in different ways. For example, the fraction deposited of solid waste than can undergo anaerobic decomposition will contribute to the greenhouse gas (GHG) effect due to the emission of landfill gases (such as methane and carbon dioxide) on the environment (Scheutz et al. 2004). In general, MSW Landfills may represent a risk to the surface water, groundwater, atmosphere and soil components (Sabahi et al. 2009a; Scheutz et al. 2004; Lou et al. 2009).

MSW landfills may constitute a source of four major types of hazards to the environment (Ozkaya et al. 2005; Slack et al. 2005):

- a. Emissions of volatile organic compounds
- b. Landscape alterations
- c. Airborne particulate matter
- d. Liquid effluents (leachate)

Of the sources mentioned above, leachate is discussed in the next section.

2.2.4 Landfill Leachate

Solid waste composition varies substantially with socio-economic conditions, location, season, waste collection and disposal methods, sampling and sorting procedures and many other factors (Slacka et al. 2005). These solid wastes placed in landfills are gradually decomposed, and liquids such as water, which infiltrates and percolates through the waste layer in a landfill, can remove soluble compounds encountered in the refuse or compounds formed by chemical and biological processes (Jeong-Hoon et al. 2001; Tatsi et al. 2002). Leachate formation results from the removal

of these soluble compounds by the percolation of liquids through the refuse mass (El-Fadel et al. 1997).

2.2.4.1 Factors Affecting Leachate Composition

Landfill leachate typically contains water, but may have a high amount of organic and inorganic compounds including heavy metals due to disposal of metal-containing wastes into landfills (Cecen and Gursoy 2000). Leachate composition varies significantly among landfills and many factors contribute to the production and composition of leachate. One major factor is the climate but other factors, such as: location, design and operation, age of landfill, type, management and composition of waste, also contribute to the composition of landfill leachate (Baun et al. 2004; Ozkaya et al. 2005; Pinel-Raffaitin et al. 2006; Jeong-Hoon et al. 2001; Słomczyńska et al. 2004).

2.2.4.2 Pollutants in Leachate

Municipal landfill leachate is considered one of the types of wastewater with great potential to impact the environment, if migration is allowed, due to the presence of diverse pollutants (Tengrui et al. 2007). The most critical pollutants present in MSW landfill leachate can be divided into four groups (Baun et al. 2004): Leachate may contain organic and inorganic compounds, xenobiotic organic compounds (XOCs) and/or heavy metals, and are generally classified according to the hazardous substances present (Slacka et al. 2005; Christensen et al. 2001).

1. Dissolved organic matter is quantified as Chemical Oxygen Demand (COD), or Total Organic Carbon (TOC) and volatile fatty acids.
2. Inorganic macrocomponents include: Ca, Mg, Na, K, NH₄, Fe, Mn, Cl, SO₄ and HCO₃.
3. Xenobiotic organic compounds (XOCs) are organic compounds which originate from household or industrial chemicals and are usually present in relatively low concentrations.
4. Heavy metals include: Cd, Cr, Cu, Pb, Ni, Hg and Zn.

These pollutants can harm the health and the environment, for example hazardous XOCs and heavy metals, besides being bioaccumulative and/or persistent, can be toxic, corrosive, flammable, reactive, carcinogenic, teratogenic, mutagenic and ecotoxic (Slacka et al. 2005; Christensen et al. 2001).

2.2.4.3 Environmental Impact of Leachate

The major environmental problems experienced at landfills have resulted from the loss of leachate from the site and although environmental regulations require that the level of leachate generated in landfills be controlled, in many cases the proper treatment (biological and physical /chemical treatment) and disposal of leachate does not occur (Robinson et al. 2005; Panthee 2008). The conventional leachate treatment methods include a combination of physical, chemical and biological methods for example a combined sequencing batch reactor and Electro-Fenton oxidation, ultrasound methods (Neczaj et al. 2005). Therefore leachate emerging from landfill areas with highly undesirable contaminants present may be a threat for the environment (Lin et al. 2000; Ozkaya et al. 2005; Baun et al. 2004). The major potential environmental impacts related to landfill leachate are the pollution of groundwater and surface waters, with associated deleterious impacts on aquatic ecosystems, as well as soil impact (Lema et al. 1988; Baun et al. 2004; Mor et al. 2006; Ozkaya et al. 2005; Pinel-Raffaitin et al. 2006; Plotkin et al. 1984; Calleja et al. 2006).

2.2.4.4 Groundwater Impact

The risk of groundwater pollution is probably the most severe environmental impact from landfills (Fatta et al. 1999; Mor et al. 2006). Historically, most landfills were built without engineered liners and leachate collection systems and, although regulations to ensure landfill compliance with liners, leachate collection systems and plans for leachate treatment have been implemented, today in many countries most landfills do not have these controls (Baun et al. 2004). These areas near unlined landfills with

leakage of leachate problem have a greater possibility of groundwater contamination (Sabahi et al. 2009a).

The USEPA has estimated that 75% of the 55,000 landfills in the USA have contaminated aquifers due to the possibility of migration of leachate from these unlined landfills (Buket et al. 2005; Lee et al. 1993). Outward or lateral flow of leachate can result in discharge at the surface, or leachate springs; whereas downward flow through the underlying soil can reach the unsaturated zone and continue to migrate until it eventually reaches the groundwater or aquifer (Robison 2005). Generalized movement of the leachate plume away from the landfill is shown in Figure 2.02.

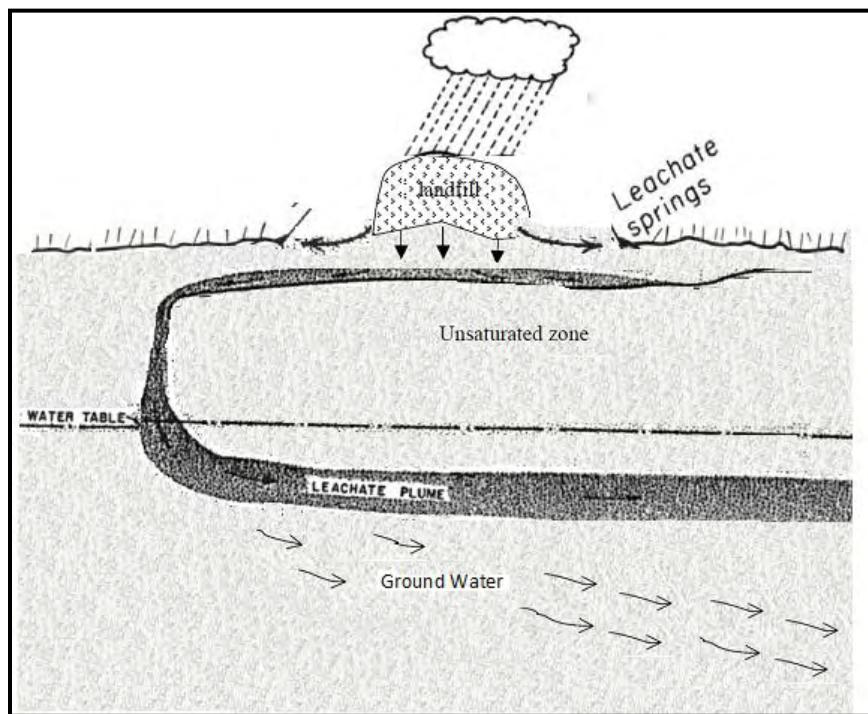


Figure 2.02. Generalized movements of leachate plume.

(Modified from Robison 2005).

The water present in groundwater deposits, also known as aquifers, can be extracted through wells (Sabahi et al. 2009b). The soil distribution of water is illustrated in figure 2.03. In the unsaturated zone, water (and leachate, if present) moves downward

due to gravity, so when rainwater or leachate falls on the ground much of the water is pulled through the soil until it reaches the zone of saturation. However, once it reaches the saturated zone leachate will generally follow the same flow lines as groundwater. The direction of water movement in the zone of saturation is determined by the relative height of water at different locations (Michel et al. 2008).

2.2.4.4.1 Research on Groundwater Impact by Landfills the Adverse Impact of Landfill Leachates on Groundwater

The adverse impacts of landfill leachates on groundwater resources have motivated a great number of research projects worldwide because of its devastating environmental significance (Fatta et al. 1999; Assmuth and Strandbergl 1993; Cecen and Gursoy 2000; Mort et al. 2006; Singh et al. 2007). Many empirical and experimental approaches have been used to assess the contamination of groundwater (Singh et al. 2007; Fatta et al. 1999; Mor et al. 2006). In India, Singh et al. (2007) estimated the quality of leachate with respect to heavy metals and its impact on groundwater quality, using statistical and empirical relationships. They found an empirical relation between leachate and groundwater quality and the results indicate that the pollution sources dominate over natural process in the vicinity of this landfill. Fatta et al. 1999 using an experimental approach studied constituents of leachate and their effect on groundwater quality and they found that groundwater near the landfill site was characterized as not potable, since most of the physical and chemical parameters examined exceeded the permissible limits given by USEPA (Fatta et al. 1999; Mor et al. 2006).

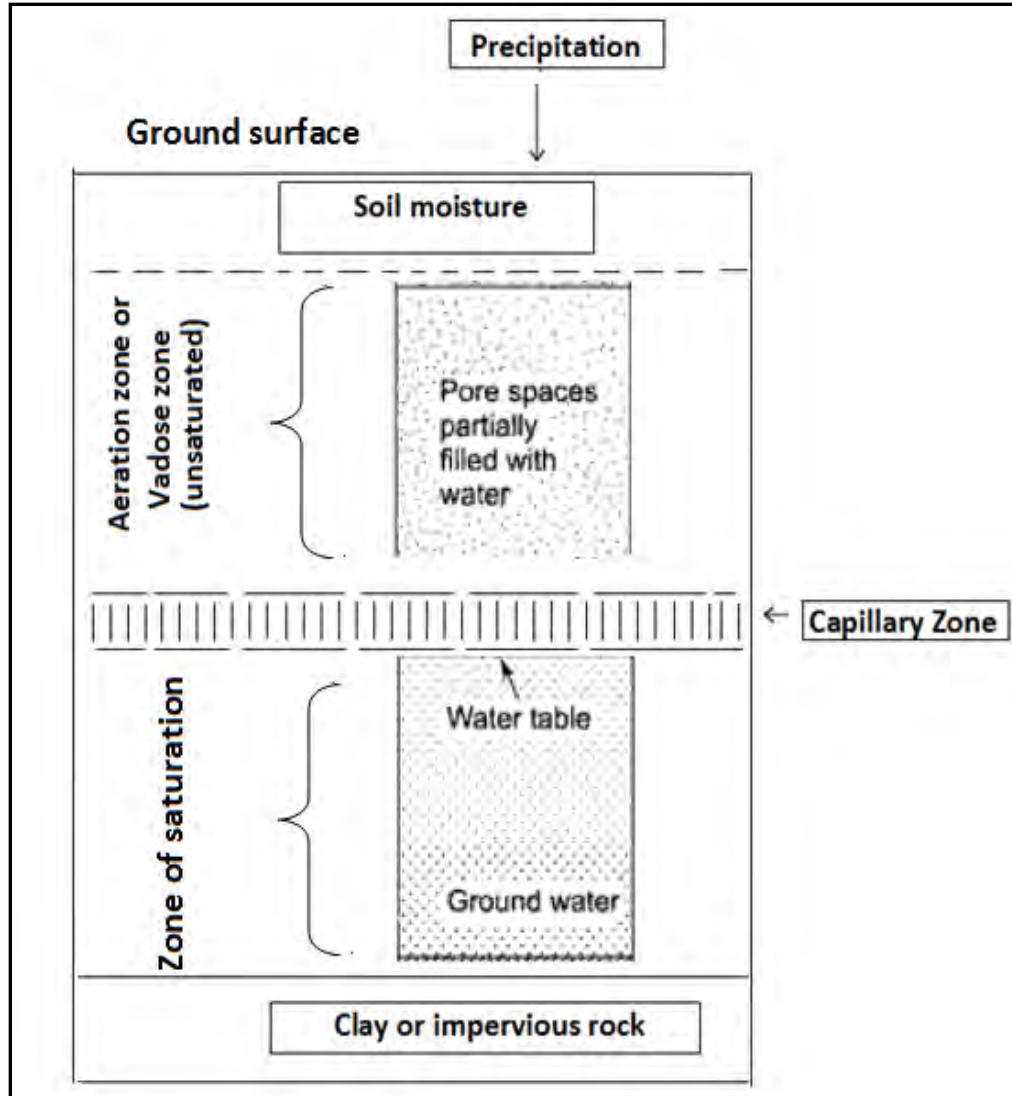


Figure 2.03. Schematic illustration of soil moisture and groundwater

(Modified from Michel et al. 2008).

The groundwater and leachate parameters analyzed in this case included heavy metals concentration (Cd, Cr, Cu, Fe, Ni, Pb and Zn) and total coliforms. The authors found a moderately high concentration of some of these parameters in groundwater near the landfill. These parameters with positive values contribute to deteriorate water quality for drinking and other domestic purposes (Mor et al. 2006).

2.2.4.4.2 Role of Soil and Groundwater Protection

The migration of leachate through soil and groundwater is complex due to the fact that its components may be subject to physical, biological and chemical processes. This may cause, in some cases, natural attenuation, that is, the natural way in which contaminants decay, and decrease in concentration. According to Bjerg et al. (2005) and Christensen et al. (2001) heavy metals from landfill do not constitute a groundwater pollution problem due to the strong attenuation (resulting from dilution, dispersion, biodegradation, irreversible sorption and radioactive decay) of these metals in the landfill itself or due to the type of surrounding soil. Other studies have reported the impact of leachate on groundwater, probably due to the fact that the attenuation process was not as effective. Longe, et al. (2007) found in groundwater near a municipal landfill in Nigeria, high concentrations of heavy metals such as Cr, Cd and Cu. in another study conducted in India Mor et al. 2006), different physical and chemical parameters were measured and moderately high concentrations of certain metals such as iron and zinc were found; and other studies found that the concentrations of Zn and Cu were high when compared to the standards (Sabahi et al. 2009b; Longe et al. 2007).

2.3.0 Leachate Characterization

Measures of concentration of the pollutants in leachate and other chemical and physical parameters such as pH and conductivity are commonly used to characterize the leachate. Leachate characterization should be conducted prior to assessing its impact. This information is also essential to design a new generation of landfills as well as effective systems for treating leachate before it is discharged into the environment. The most typical physical, chemical and biological parameters that are used to characterize leachate are summarized in the Table 2.03.

Table 2.03. Leachate sampling parameters (Barnar et al. 2006).

Physical	Appearance, pH, oxidation-reduction potential and conductivity.
Organic constituents	Organic chemicals, phenols, chemical oxygen demand (COD), total organic carbon (TOC), volatile acids, tannins and lignins, organic-N, ether soluble (oil and grease), methylene blue active substances (MBAS), organic functional groups and chlorinated hydrocarbons .
Inorganic constituents	Suspended solids, total dissolved solids, volatile suspended solids, volatile dissolved solids, chloride, sulfate, phosphate, alkalinity, acidity, nitrate-N, ammonia-N, sodium, potassium, calcium, magnesium, hardness, heavy metals (Pb, Cu, Ni, Cr, Zn, Cd, Fe, Mn, Hg, Ba, Ag) arsenic, cyanide, selenium and fluoride.
Biological	Biochemical oxygen demand (BOD), coliform bacteria (total, fecal, fecal streptococci) and standard plate count.

Different studies on this topic have been published (Baun et al. 2004; Cecen and Gursoy. 2000; Banar et al. 2006). In Turkey, characterized the leachate from a landfill during a period of 8 months, parameters such as BOD₅ and COD for organics, alkalinity, hardness and heavy metals were studied. The heavy metals analyzed were Cu, Pb, Fe, Mn, Zn, Ni, Cr, Cd (Cecen and Gursoy 2000).

Méndez et al. characterized landfill leachate of MSW in Merida City, Mexico and found values of pH in the range of 8.34 to 8.50, and average metal concentrations for Fe, Zn, Cd, Cr and Cu of 102.9 mg/L, 5.02 mg/L, 0.0107 mg/L, 6.98 mg/L, and 0.320 mg/L, respectively. These parameters were measured in order to evaluate the efficiency of the liner used (Méndez et al. 2002). Although typical ranges of values for the components of leachate may be found in the literature, these values should be

considered only as a reference point, because as discussed above, the composition of leachate may vary from region to region. Table 2.04 describes the ranges of landfill leachate composition in terms of different parameters (Kjeksen et al. 2002).

Although the compounds listed in Table 2.04 are used to characterize the leachate, some of them are known to be essential nutrients for plants. Most of them are supplied by the soil. Nutrients, which are required in large concentrations, are macronutrients such as nitrogen, phosphorus, potassium, calcium, magnesium and sulphur. Iron, manganese, zinc, copper, cobalt, and nickel are micronutrients because plants require them in low concentrations

In the landfills, many of these essential nutrients and other common components of leachate are mainly from anthropogenic, rather than natural, sources. In the case of some parameter such as iron and heavy metals its contained in landfill are mainly due to the disposal of metals and metal-containing inorganic compounds (household, commercial and industrial waste as well as treatment sludges) that are used in many industrial and manufacturing processes and that are commonly found on landfill solid waste. More information on iron as a macro-component, and other heavy metals commonly found in leachate such as chromium, cooper, lead, cobalt, nickel and zinc, is included below (Suess 1982; Adriano 2001; Yu et al. 2001).

Table 2.04. Composition of landfill leachate (Kjeldsen et al. 2002).

Parameter	Range (mg/L)
pH	4.5-9.0
Spec. Cond. ($\mu\text{S}/\text{cm}^1$)	2500-35 000
Total Solids	2000-60 000
Organic Matter	
Total Organic Carbon (TOC)	30-29 000
Biological Oxygen Demand (BOD_5)	20-57 000
Chemical Oxygen Demand (COD)	140-152 000
BOD_5/COD (ratio)	0.02-0.80
Organic nitrogen	14-2500
Inorganic Macrocomponents	
Total phosphorous	0.1-23
Chloride	150-4500
Sulphate	8-7750
Hydrogenbicarbonate	610-7320
Sodium	70-7700
Potassium	50-3700
Ammonium-N	50-2200
Calcium	10-7200
Magnesium	30-15 000
Iron	3-5500
Manganese	0.03-1400
Silica	4-70

Table 2.04., continued.

Heavy Metals

Arsenic	0.01-1
Cadmium	0.0001-0.4
Chromium	0.02-1.5
Cobalt	0.005-1.5
Copper	0.005-10
Lead	0.001-5
Mercury	0.00005-0.16
Nickel	0.015-3
Zinc	0.03-1000

2.3.1 Inorganic Macro-Components

Presence of Na, Mg, Ca, K, Fe, among others, is often used to assess the impact of leachate on groundwater because ionic concentrations that exceed the allowed limits may be used to determine poor water quality. Major cations such as Fe, Na, K, Ca and Mg have been used among the parameters measured for Sabahi et al. (2009b), to establish possible impact of leachate on several boreholes located close to a landfill.

The results indicated that the concentration of Fe, Mg, Ca and other parameters of interest were above the standard acceptable levels. Therefore, the authors concluded that some of the boreholes were affected by the migration of leachate to the groundwater. Iron is studied more extensively below.

2.3.1.1 Iron**2.3.1.1.1 General Information and Uses**

Iron is an abundant chemical element in the Earth's crust and the most abundant element in its core. Iron is the most useful of all metals but many applications do not use

it in its pure form. In the United States iron is used mainly for making steel. Steel is an alloy of iron and carbon with small amount of other elements such as manganese, silicon, phosphorous, sulphur and oxygen. This iron alloy is used in the manufacture of automobiles, the hulls of large ships, and structural components for buildings (Adriano 2001).

2.3.1.1.2 Sources, Chemical and Distribution of Iron in the Environment

Iron is found in various iron oxides, such as the minerals hematite (Fe_2O_3 ; 70% iron), magnetite (Fe_3O_4 ; 72% iron), and taconite, which contains up to 30% magnetite and hematite. In the environment, Fe occurs as either ferrous Fe (Fe^{+2} reduced) or as ferric Fe (Fe^{+3} ; oxidized). In a reducing environment, ferrous (+2) iron is relatively soluble (Adriano 2001).

The pH and the oxidation-reduction potential of natural waters are factors determining the solubility and form of iron so, under normal pH conditions Fe occurs in one of two oxidation states, Fe^{+2} (soluble) and Fe^{+3} (insoluble), but only at $\text{pH} < 3$ is Fe^{+3} found in solution (Allen et al. 1993). In aquatic medium, iron can undergo various chemical reactions including speciation, oxidation-reduction; precipitation, microbial interactions, photochemical reactions, and sorptive interactions. For example Fe^{+2} ions may be converted into Fe^{+3} ions, when an increase in the oxidation-reduction potential of the water occurs and allows ferric iron to hydrolyze and precipitate as hydrated ferric oxide, which is highly insoluble (Allen et al. 1995).

Both natural and anthropogenic sources are responsible for the presence of iron in the atmosphere. Natural sources may include continental dust, wind erosion, volcanic and forest fires; while anthropogenic sources include industrial emissions and burning of fossil fuels. Although Fe (II) may be predominant in oxygen-deficient soil, the iron in Fe (III) state is mainly found in soil (Jasen 2002). The chemical and microbiological

reactions in soil and its capacity to sorb iron-organic complexes govern the fate of iron compounds in soil (Suess 1982).

2.3.2 Heavy Metals

Heavy metals are one of the typical components and of the essential parameters for the characterization of leachate. They may constitute an environmental problem if the leachate migrates into surface water or groundwater (Gupta 2009). Thus, during recent decades, monitoring of heavy metals in landfill leachate has commonly been prescribed by the authorities and routinely performed by landfill operators (Kjeldsen et al. 2002). This arises from the fact that metals are dissolved during landfill stabilization (Pinel-Raffaitin et al. 2006; Cecen and Gursoy 2000). Although the concentration of heavy metals changes from one landfill to another, in most landfill leachates the main heavy metals reported in the literature are Cd, Pb, Zn, Ni, Cr, and Cu (Cecen and Gursoy. 2000).

2.3.2.1 Chromium (Cr)

2.3.2.1.1 General Information and Uses

Chromium is one of the most abundant elements on Earth (Yu et al. 2001). Chromium is one of the most versatile metals and is widely used in alloys (Pires et al. 2007). Cr and its compounds have diverse industrial uses and are extensively employed in leather processing and finishing, in electroplating, in catalytic manufacturing and in the production of chromic acid and specialty chemicals (Bielicka et al. 2004; Yu et al. 2001).

2.3.2.1.2 Chemical, Sources, and Distribution of Chromium in the Environment

Chromium is an element naturally found in rocks, animals, plants, soil, in volcanic dust and gases but in its natural state is highly uncommon. Chromium occurs primarily in chromite (FeCr_2O_4) and krokoite (PbCrO_4) (Bielicka et al. 2004) It may be found in oxidation states from II to VI, but the trivalent Cr(III) and the hexavalent Cr(VI) species

are the most stable forms of Cr (Shanker et al. 2005). In aqueous solutions it exists in the Cr(III) and the hexavalent Cr(VI) species,. Cr (III) is an essential nutrient while the hexavalent form is the most toxic of all the oxidation states of the Cr and is generally produced by industrial processes (Pires et al. 2007; Abreu and Toffoli 2009; Mazloum et al. 2008). Cr(VI) is usually associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) oxyanions (Saygi et al. 2008).

Chromium can be found in all phases and varying concentration in the environment, including air, water and soil, after being *released* during the manufacture and industrial process (Shanker et al. 2005). In aqueous solutions chromium occurs mainly as Cr(III) and Cr(VI). Under neutral pH conditions the trivalent chromium cations present in water tend to form hydroxide colloids (Bielicka et al. 2004).

The hexavalent form is almost exclusively present as oxo-anions which can persist only in the absence of substances that are oxidizable by them at a given pH. The chromium in soil is present mainly as an insoluble oxide (Cr_2O_3) (Mazloum et al. 2008).

2.3.2.2 Copper

2.3.2.2.1 General Information and Uses

Copper is one of the most commercially important metals. Copper is used mainly in the production of wire and in alloys, which are among the most versatile engineering materials available. The use of copper has contributed enormously to the development of industries such as, transportation, telecommunications, and all kinds of electrical and electronic appliances (Yu et al. 2001).

2.3.2.2.2 Sources, Chemical and Distribution of Cooper in the Environment

Copper and its compounds are common in the environment but copper is found in moderate abundance. The most common minerals containing copper are chalcopyrite (CuFeS_2), chalcocite (Cu_2S), covellite (CuS), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), and Azurite (carbonate compounds). This metal occurs in nature in the 1+ and 2+ valence states. Cu

in the divalent oxidation state (II) is generally encountered in water and, when introduced in the environment, it can bind to inorganic and organic materials contained not only in water but also in soil, groundwater and sediment (Callender 2004). The stability of the complexes formed depends on various factors such as pH, temperature, hardness, alkalinity and ligand concentration.

2.3.2.3 Cobalt

2.3.2.3.1 General Information and Uses

Cobalt is often associated with Ag, Ni, Pb, Cu, Fe ores from which it is commonly obtained as a by-product. Cobalt is a metal with many uses, but it is mainly used in the manufacturing of alloys such as magnetic alloys, high-grade steels and superalloys. (Adriano 2001).

2.3.2.3.2 Sources, Chemical and Distribution of Cobalt in the Environment

Sources of environmental cobalt are both natural and anthropogenic. Natural sources include rocks, soils, water and vegetation. It is usually found in association with copper or nickel. Cobalt occurs in two oxidation states (Co^{2+} and Co^{3+}). In rocks and soils it is usually found as Co^{2+} , and although in aqueous medium Co^{2+} is the predominant species, Co^{3+} can also be found if it is stabilized by complexation with chelating organic molecules (Adriano 2001). Cobalt is often found in solid solution and may substitute for other trace metals (e.g., Cu, Pb and Zn) in a wide variety of minerals due to its similarity in ionic radii, so that formation of mixed Co-metal solids (e.g., sulfates, carbonates, hydroxides), may limit dissolved Co concentrations (Tengrui et al. 2007).

2.3.2.4 Nickel

2.3.2.4.1 General Information and Uses

Nickel is usually found in nature as a component of silicate, sulfide, or arsenide ores. Underground nickel is mostly found in the form of sulfide minerals and on the surface it is found in the form of silicate minerals (Suess 1982, USEPA 1986).

Nickel is used in coins, but the most important industrial use is as a component of several alloys, such as stainless steels, low-alloy steels and some specialty steels. Other uses for nickel are in coatings, battery electrodes and filters. Its widespread use for alloys is due in large part to its desirable properties such as corrosion resistance, heat resistance, hardness, and strength. Nickel is also an important component of rechargeable batteries (Landner and Reuther 2004).

2.3.2.4.2 Sources, Chemical and Distribution of Nickel in the Environment

Although Nickel can occur in the 0, I, II, and III oxidation states, the most important and common oxidation state of nickel is +2. Because nickel is a natural element of the Earth's crust, it can be found in food, water, soil, and air (CEPA 1994). In the atmosphere, nickel is present as constituent of particulate matter and both natural sources and anthropogenic activity contribute to the presence of nickel. Once in the atmosphere, nickel can be removed by precipitation processes and reach the soil and water, where it can undergo various chemical and physical interactions, which determine its fate and behavior (Adriano 2001; USEPA 1986).

Nickel is a natural component of the soil. In soils, it may exist in several forms such as inorganic crystalline mineral or precipitates, as free ion or chelated metal complex. The pH, and presence of organic and inorganic ligands can affect the form of nickel, for example, nickel forms stable complexes with organic ligands and, under anaerobic conditions, sulfite may control the solubility of Ni. In aquatic systems nickel mainly occurs as Ni^{2+} (CEPA 1994; Allen et al. 1983).

2.3.2.5 Zinc

2.3.2.5.1 General Information and Uses

Zinc is found in several ores such as smithsonite (ZnCO_3), heminorphite [$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$] and sphalerite (ZnS) (Adriano 2001).

Zinc has diverse uses such as manufacturing of batteries, rubber goods, paints, cosmetics, chemicals, and pharmaceuticals, but its primary use is in protective coating for iron and steel, although it also plays an important role in alloys such as brass and bronze. It is also used as a micronutrient in agricultural fertilizers, in household items and for drying textiles.

2.3.2.5.2 Sources, Chemical and Distribution of Zinc in the Environment

Zinc metal is not found freely in nature, but instead is found as a salt or oxide. Zinc is divalent in all its compounds. Anthropogenic sources contribute to the presence of zinc in the atmosphere, as do industrial and domestic emissions. Zinc is virtually insoluble in water, and high levels of zinc in surface water represent industrial and urban pollution (USEPA 1987).

Zinc reacts with both acids and alkalis, it can be found in several chemical forms in natural water, such as hydrated ions, metal-inorganic complexes, or metal-organic complexes. Soils with $\text{pH} = 5$ or greater strongly absorb zinc ions, reducing their mobility (USEPA 2005).

2.3.2.6 Lead

2.3.2.6.1 General Information and Uses

Lead occurs in nature in the form of ores. The most important lead ore is galena (PbS) other less common forms of the mineral are cerussite (PbCO_3), anglesite (PbSO_4), and crocoite (PbCrO_4). Lead (Pb) is one of the most ubiquitous and useful metals known to humans. In the United States the main uses of lead are in storage batteries (72%),

gasoline additives and other chemicals (13%), ammunition (4%), solder (2%), and other uses (9%) (Yu et al. 2001).

2.3.2.6.2 Sources, Chemical and Distribution of Lead in the Environment

Lead is a naturally occurring element and is the most abundant in the Earth's crust. Lead occurs in rocks as a discrete mineral. It exists in four valence states: elemental (Pb^0), monovalent (Pb^+), divalent (Pb^{2+}), and tetravalent (Pb^{4+}). Pb (II) is only oxidized to Pb^{4+} under strong oxidizing conditions, but few compounds of Pb^{4+} are stable.

The production, consumption and release of lead have occurred for thousands of years and it has contributed to the presence of Pb in the atmosphere, soil and natural water (Reuer and Weiss 2002). Lead, once released into the environment can persist, and will accumulate. In the atmosphere, several factors such as particle size, chemical form and distribution and height of the release can influence the transport of lead (USEPA 1982).

Lead enters drinking water systems through the corrosion of brass and chrome-plated brass faucets. Lead salts may be slightly soluble in water (chloride and bromide) or almost insoluble (carbonate and hydroxide) (Allen 1988). In groundwater, the form and amount of lead can be affected by pH, minerals and concentration of dissolved salts. Lead can appear as a precipitate ($PbCO_3$, Pb_2O , $Pb(OH)_2$, $PbSO_4$). In soils lead is one of the most common anthropogenic contaminants and the form of Pb in soil is controlled by the soil's mechanical composition, mineralogy, pH and organic content. In soil lead may be strongly complexed to organic materials or adsorbed to inorganic solids (Yaron et al. 1996; Reuer et al. 2002).

2.3.3 Methods of Analysis Used for Leachate Characterization

Several studies present diverse methods used for the characterization of leachates. The most used are flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP-AES) (Esakku et al.

2003; Pinel-Raffaitin et al. 2006; Fatta et al. 1998). In the last decades, the method of ICP-AES has become very popular due to the advantages of being sensitive and is an overall multielement atomic spectroscopy technique.

2.3.3.1 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES),

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is a technique used to measure the concentration of an element in a solution. Components of the ICP-AES instrument include the peristaltic pump, the nebulizer, the spray chamber, a radiofrequency (rf) generator, a torch where the plasma is formed, a spectrometer that isolates the wavelength(s) required for the analysis, a detector, and a read-out device (see Figure 2.04) (Mannig and Grow 1997; Hill 2007).

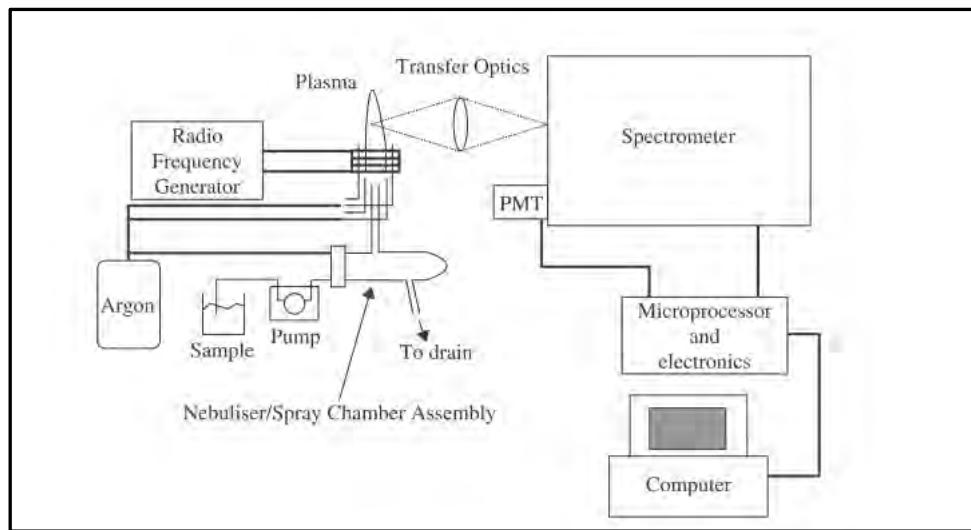


Figure 2.04. Schematic diagram of an ICP-AES instrument (Hill 2007).

The nebulizer transforms a stream of liquid sample into a nebula, a fine spray or mist of droplets. The nebulized sample then passes through the spray chamber, which removes any droplets with diameters $>8 \mu\text{m}$ in diameter. The remaining droplets are injected to the center of the plasma at very high temperature. This not only dissociates the droplets into atoms, but also causes different atoms in the sample to become excited

(Figure 2.05). The excited atoms return to the ground state by emitting light of a unique frequency (characteristic of each element) which is detected by the instrument. In the case of lead (Pb), for example, the emission wavelength is 220.351 nm (see Figure 2.06) (Mannig and Grow 1997; Clesceri et al.1989).

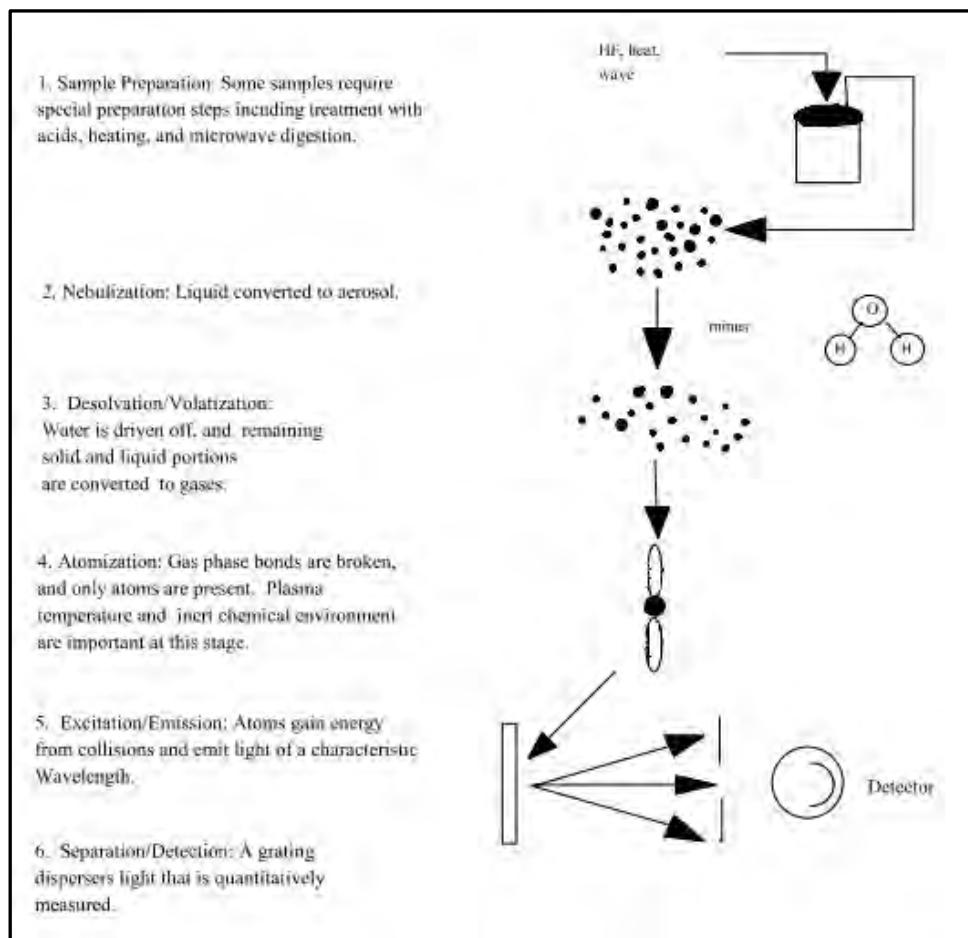


Figure 2.05. Steps involved in the analysis of aqueous samples by ICP-AES (Mannig and Grow 1997).

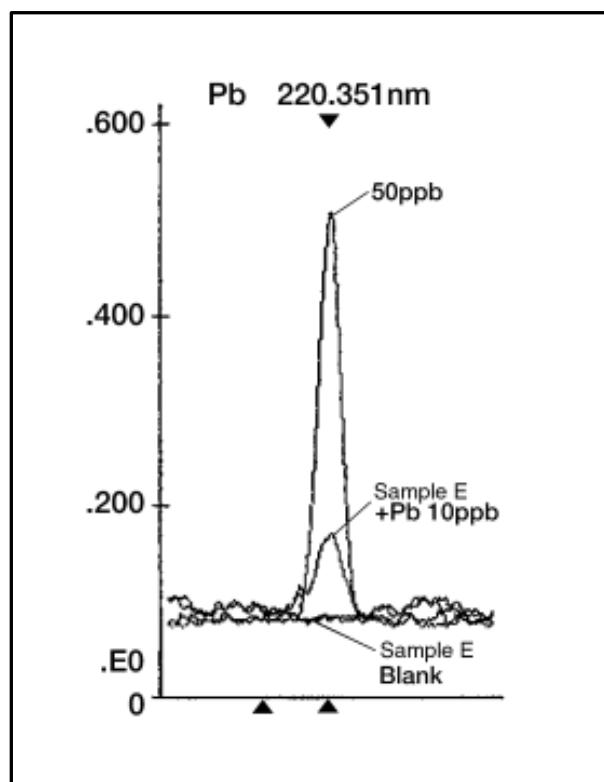


Figure 2.06. ICP-AES peak profile of lead
(Mannig and Grow 1997).

Analytical advantages of the ICP-AES over other techniques, such as flame atomic absorption spectrometry (FAAS), include the multielement analysis capability of ICP-AES, coupled with its high sensitivity; the large dynamic linear range of detection; the reduction of matrix interferences and enhanced productivity (Hill 2007).

2.4.0 Fate and Transport of Heavy Metals in Groundwater and Soil

The behavior and distribution of a contaminant in the environment is generally referred to as “fate and transport” (Gupta 2009). Several mechanisms influence the presence of heavy metal in groundwater and soil (USEPA 1988). The movement of a particular metal in soil and groundwater is determined by factors such as its amount, the reactions suffered by the metal and the chemical and physical properties of the soil's to

which the metal is associated (USEPA 1988; Gupta 2009; Karaca 2004). Some of these mechanisms can retard the movement of metal and provide a long term source of metal contamination (Bjerg et al. 2005).

Groundwater typically contains a few mg/L dissolved organic matter, but near a landfill this content can increase to a few hundred mg/L of this parameter. Most approaches to study the transport and fate mechanisms of metals consider groundwater as a two-phase system (aqueous and solid), although the movement of contaminants in groundwater is primarily a liquid phase process (Huling 1989). In this two-phase system the movement of contaminants is affected by chemical reactions that could partition the contaminant mass between the mobile aqueous and the immobile solid phases, or convert the dissolved species from one form to another (Boulding et al. 1996; Sen et al. 2004, 2006).

Metals are associated with the aqueous phase of soils and may be transported through the vadose zone and reach the groundwater. Therefore, in addition to the chemical reactions that occur in the two-phase system, heavy metal retention in soil is another important process that can govern the transport and chemical fate of heavy metals in groundwater (USEPA .1988; USEPA 2002).

2.4.1 Factors That Affect Heavy Metals Mobility in Groundwater and Soil

The chemical composition of both soil and groundwater can be affected by complex sets of reactions that occur when water moves through the soil (Karaca 2004.) Metals present in the soil/groundwater system will undergo diverse processes and reactions that can affect their mobility and presence in the environment (Huling 1989; Delleur 1991). The soil/groundwater system is closely related, and many of the contaminants in the soil can migrate and reach the groundwater. Thus, the chemical form and reactions of metals that occur in the soil/groundwater system are keys to understanding the transport and fate of heavy metals in the environment. For example,

Huang et al. (1977) reported heavy metals in solution as free or complex ions; and in particulate form adsorbed onto other particles or incorporated into biomass and inorganic precipitates such as hydroxides, carbonates, sulfides and sulfates.

The main factors that can affect mobility and presence of heavy metals in the environment are pH, complexation, precipitation/dissolution, and redox reactions (Huang et al. 1977; John and Levanthal 1995). Figures 2.07 summarize the principal processes in soil-groundwater system.

2.4.1.1 Hydrogen Ion Activity (pH)

The pH exerts direct influence on heavy metal behavior in environmental systems. In the case of heavy metal such as Pb, Cu, Zn, Cr and Ni, solubility increases with a decrease in soil pH (John and Levanthal 1995). In general terms, the soil's ability to immobilize heavy metals increases with rising pH, and peaks under mildly alkaline conditions (Elzahabi et al. 2001). At an acidic pH range between 4.2 and 6.6, Ni and Zn are highly mobile, Cr is moderately mobile, and Cu and Pb practically immobile, and in neutral to alkaline conditions (pH 6.7 - 7.0) Cr is highly mobile, Zn are moderately mobile and Ni is immobile (Aydinalp et al. 2003). In other processes such as sorption capacity and reduction-oxidation (redox) reactions, pH also plays a key role with the sorption of heavy metals increasing with increasing pH, and for redox reactions the pH indirectly influences its intensity (Aydinalp et al. 2003).

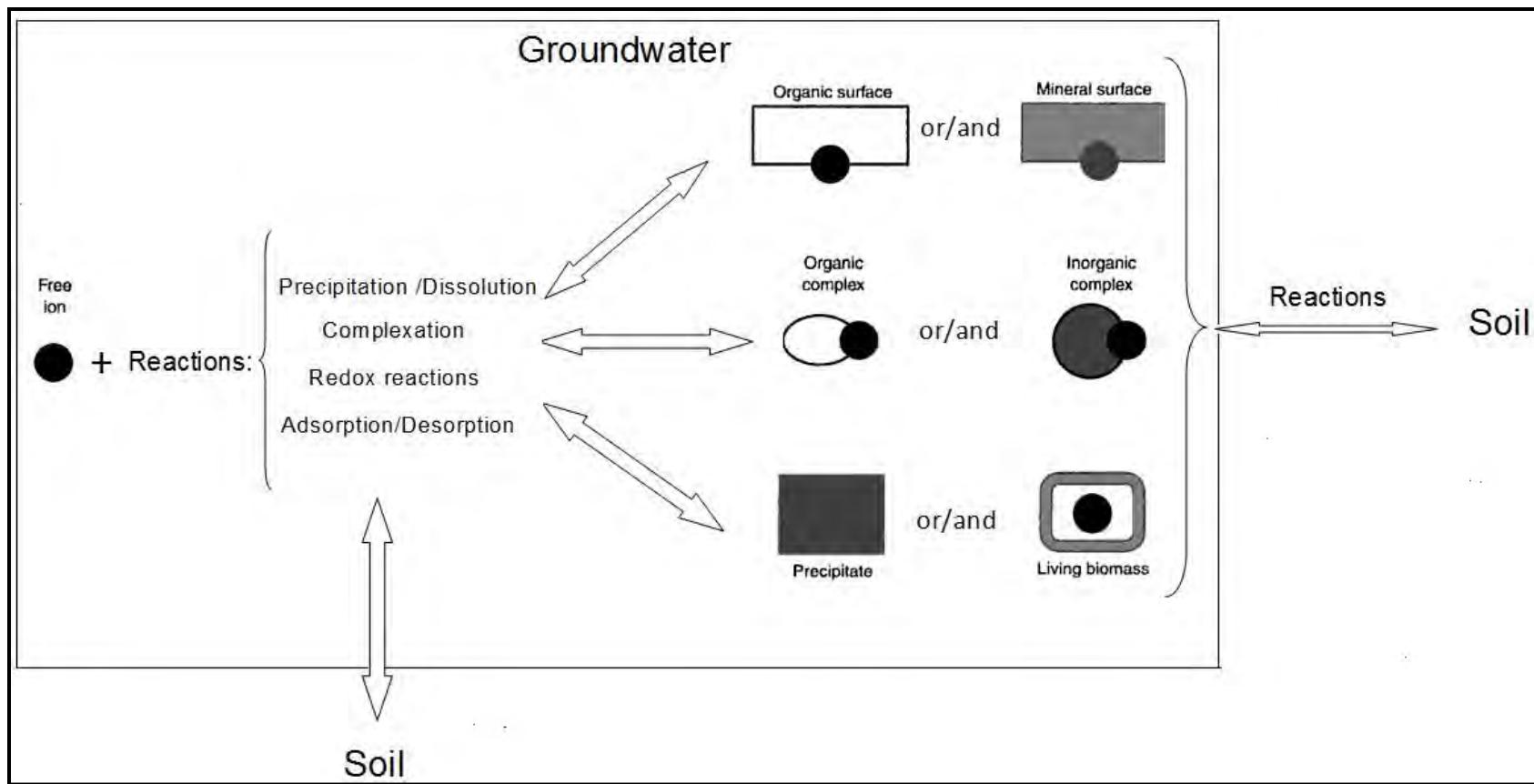


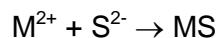
Figure 2.07 .Heavy metal interactions (Modified from Huang et al. 1977).

2.4.1.2 Complexation

Heavy metals in solution may exist as free ions, or complexed with other dissolved inorganic or organic compounds. Heavy metals tend to form complexes with organic matter in the soil (humic and fulvic acids) and with inorganic ligands. A metal complex is a dissolved species that exists because of the association of a metal cation with an anion or neutral molecule (Boulding et al. 2004). The metal cation is called the central atom, and the anions, often called ligands, include many of the common inorganic species found in groundwater, such as S^{2-} , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , NO_3^- , Cl^- . Complexation facilitates the transport of metals such as, Cr, Ni, and Pb. For example the mobility of Ni in soil can increase when they form soluble complexes with inorganic and organic ligands (Boulding 1996). In water solutions free of other ligands, Cu (II) is present mainly as a complex $[Cu(H_2O)_6]^{2+}$. Trivalent chromium forms hydroxy complexes in natural water, including $Cr(OH)^{+2}$, $Cr(OH)_2^+$, $Cr(OH)_3$, and $Cr(OH)_4^-$ (Rowe et al. 2001).

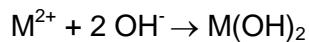
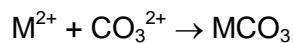
2.4.1.3 Precipitation/Dissolution:

Precipitation reduces mobility and dissolution increases mobility of contaminants. The precipitation/dissolution of heavy metals is strongly dependent of Eh (redox potential) and pH of the soil/groundwater system and also depends on the presence of competing anions and cations (Boulding et al. 1996). In general, heavy metals in groundwater are most soluble at low pH, and ignoring the effect of sorption, this solubility declines once the pH increases (Boulding et al. 2004; Delleur 1991.). Metal precipitates may be pure solids, such as PbS , ZnS , $Cr(OH)_3$ or mixed solids, such as $(Fe_x, Cr_{1-x})(OH)_3$, $Ba(CrO_4, SO_4)$ (Suthersan 1986). In groundwater, for example, metal sulfides (MS) can be produced when sulfide ions (S^{2-}) precipitate with metal ions (M^{2+}) (Suthersan 1986):



Although precipitation as sulfides is considered the main process that limits the solubility of many heavy metals, an exception is chromium which does not precipitate as the sulfide, but as the hydroxide (Allen et al. 1993).

Precipitation is not a major mechanism of retention for Ni and Zn due to the fact that Ni does not form insoluble precipitates and Zn compounds have a relatively high solubility in soil (McLean et al. 1992; Boulding et al. 1996). Many heavy metals can precipitate out of solution as insoluble carbonates or hydroxides:



For other metals such as Co and Zn in soil/groundwater systems, precipitation is an important mechanism of retention (Boulding et al. 1996; McLean et al. 1992). Cr (VI) is substantially more soluble in water and much more mobile than Cr (III), which will readily precipitate as the mineral Cr_2O_3 and is thus rather immobile (Balla et al. 2004).

2.4.1.4 Sorption/Desorption

Dissolved metals can be transferred from the aqueous phase to the solid phase (phase distribution) through the process of sorption, process that is usually fully or partially reversible (desorption.) (Bradl 2004; Boulding et al. 2004). This process plays a key role in the mobility of some heavy metals, for example the mobility of nickel can be controlled by the capability of various sorbents such as clays, iron oxides, manganese oxides, and organic matter to adsorb nickel from the solution, despite the fact that nickel is one of the most mobile metals in the aquatic environment (USEPA 1995).

With the exception of lead, which is too strongly adsorbed on clay surfaces at pH values above 6 units.; and although hexavalent Cr is relatively mobile in soils, trivalent Cr, on the other hand, is relatively immobile in soil because it is adsorbed by soils at pH=5 (Mclean et al. 1992).

Adsorption of Zn in soils depends on pH, adsorption of Zn increases with increasing pH (values greater than 7.7) due to the fact that it hydrolyzes under these conditions and these hydrolyzed species are strongly adsorbed to soils surfaces (John and Levanthal 1995; Boulding 1996).

2.4.1.5 Oxidation-Reduction Reactions

Other mechanisms that control the mobility of metal ions are oxidation-reduction reactions. In groundwater or soil systems, redox potential (Eh) is a measure of the oxidizing capacity or availability of electrons in these systems. Oxidation frequently involves a gain in oxygen atoms or a loss of hydrogen atoms, whereas reduction involves the reverse process (Deutsch 1997).

In groundwater the redox potential is low when oxygen is absent, but high if it is present. Native groundwater environments are generally reducing, but oxidizing conditions can be created by pollution (McCreadie et al. 1993). In reducing conditions, heavy metals are generally more mobile than in oxidizing conditions. For example, the oxidized Cr species is relatively soluble, but the reduced chromium species is characterized by low aqueous solubility, which decreases its overall rate of migration (Guha et al. 2001).

Deutsch (1997) presents a classification of metals for purposes of contaminant analysis, according to their ability to cause changes in redox conditions. He classified as simple metals those metals that are not redox sensitive such as Pb, Ni and Zn, although other components of minerals containing these metals may be affected by the redox potential. For example, under oxidizing conditions, Pb, Ni and Zn can form carbonate (NiCO_3 , PbCO_3), and can also form oxide/hydroxide Pb(OH)_2 , NiFe_2O_4 , Ni(OH)_2 , ZnFe_2O_4 . Ni and Pb can also form sulfide minerals.

Fe, Mn, Cr, and Cu are classified as redox sensitive metals. They may occur in more than one valence state and at pH values greater than 5.5. Under oxidizing

conditions, they may form relatively insoluble minerals. For example Cr forms an hydroxide mineral (Cr(OH)_3), Cu can form a cupric ferrite mineral (CuFe_2O_4) and Fe can form ferrihydrite (Fe(OH)_3). Fe and Co can also form other compounds under reducing condition if sulfide is present. Cu may form the cuprous ferrite mineral ($\text{Cu}_2\text{Fe}_2\text{S}_4$) and Fe can form insoluble sulfide minerals (Elzahabi et al. 2001).

2.5.0 Situation of MSW Landfills in Puerto Rico

When the Environmental Protection Agency (USEPA) published in 1991 the document Final Criteria (CRF40, Part 248, Criteria for Non-Hazardous Solid Waste Landfill Systems) it granted a period of 24 months so that all of the states, including PR, could adopt and implement measures and programs to insure that the existing MSW landfills comply with what the law established (ADS 2004). In Puerto Rico, the PREQB was in charge of adopting and implementing these programs. Due to this, regulation number 4972 known as Regulations for Management of Non-Hazardous Solid Wastes was developed. This document incorporates the federal requirements necessary to insure that the management of solid wastes causes minimal impact on the environment. This Regulation was effective on Oct 7, 1993. With this new regulation, most MSW landfills on the island did not fulfill the requirements, and in 1994, out of 61 existing landfills on the island, 32 were closed (ADS 2004).

The diagnosis in 1994 was that most MSW landfills did not comply with the stipulations of the Regulation. They showed failures such as: deficient operation, lack of covering material, limited collecting capacity, absence of systems for: gas control, groundwater monitoring, leachate collection and treatment, and runoff deviation, among others (ADS 2004). Though time has passed, and the laws and rulings have suffered many amendments to correct the failures present in the MSW landfills, the truth is that today the MSW landfills of the island continue to be in use even though most of them do not comply with the legal requirements to minimize environmental impact. The project

Operation Compliance in PR is the most recent strategy to confront the crisis of the MSW landfills put forth by the PREQB and the ADS in conjunction with the private and municipal operators of the MSW landfills.

2.5.1 The State of the Landfill System in Puerto Rico

PREQB (2004) reported that twenty eight (28) out of the thirty two (32) existing MSW landfills were documented. The conditions of the MSW landfills were classified in the following categories: Satisfactory, Average, and Poor. The criteria for each category were the following: A landfill is classified as Satisfactory if it meets, as a minimum, all of the following requirements:

1. Covering the wastes daily.
2. Having the trained personnel and the necessary equipment.
3. A runoff control system
4. A leachate control system.
5. Installation of wells to monitor groundwater.
6. Compliance with the requirements of access, entrance log, and inspection of the received wastes.

It is classified as Average if it complies only with requirements 1, 2, and 6 of the satisfactory category; and as Poor if the MSW landfill does not comply with the minimum requirements for the Average. The results of the report, as can be seen in Figure 2.05, were as follows: 32% of the MSW landfills were classified as in Satisfactory condition, 36% was classified as Average and 32% were classified in the Poor category. The general condition of MSW landfills in PR is summarized in Table 2.08. PREQB generated the data in 2004 and also included the data for the estimated useful life of landfill that was determined in 2003 (PREQB 2004).

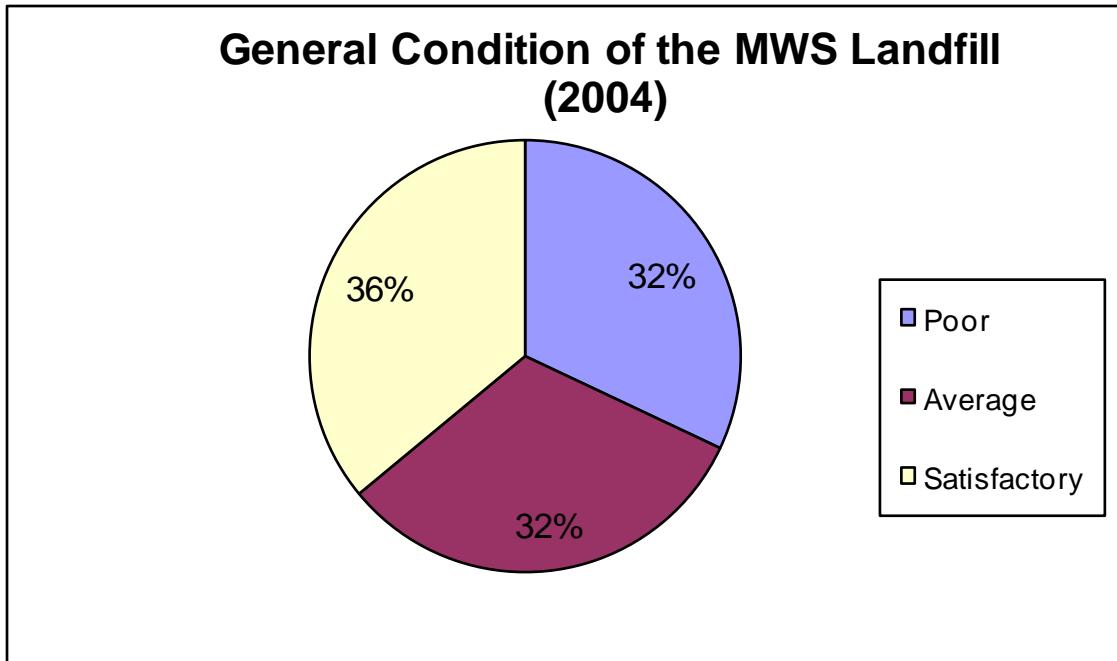


Figure 2.08. General condition of MWS landfills in PR (PREBQ 2004).

Table 2.05. General information of MSW landfill of PR (Modified from PREBQ 2004).

MSW Number	Locality	Useful life estimated in 2003 (year)	Quality Condition		
			S-Satisfactory	Daily amount of solid waste	
			R- Average	P- Poor	
1	Aguadilla	Temporally closed	R	382 m ³	
2	Añasco	6-10	P	107 m ³	
3	Arecibo	6-7	S	621-680 t	
4	Arroyo	1-5	P	306 m ³	
5	Barranquitas	1-3	R	191 m ³	
6	Cabo Rojo	11 or more	S	688 m ³	
7	Carolina	1-3	S	544 t	
8	Cayey	1-4	P	229 m ³	
9	Culebra	1-2	P	Not Record	
10	Fajardo	6-7	R	1911m ³	
11	Florida	15-20	R	268 m ³	
12	Guayama	1-7	R	153 m ³	
13	Guaynabo	< 1	S	363 t	
14	Hormigueros	3-4	S	130 m ³	
15	Humacao	11 or more	R	2994 t	

Table 2.05., continued.

16	Isabela	1-5	P	459 m ³
17	Jayuya	1-2	No inspection	No inspection
18	Juana Diaz	1-3	R	713 m ³
19	Juncos	1-2	P	1564 m ³
20	Lajas	1-6	S	245 m ³
21	Mayaguez	6-10	S	408 t
22	Moca	3-5	P	459 m ³
23	Peñuelas	No inspection	No inspection	No inspection
24	Ponce	6-10	S	3021 m ³
25	Salinas	6-10	S	1529 m ³
26	Santa Isabel	11 or more	R	199 m ³
27	Toa Alta	1-2	R	1911m ³
28	Toa Baja	1-2	P	1602 t
29	Vega Baja	1-2	R	210 m ³
30	Vieques	15 or more	No inspection	No inspection
31	Yabucoa	1-2	P	459 m ³
32	Yauco	11 or more	No inspection	No inspection

2.5.2 Common Failures Found in the MSW Landfills in Puerto Rico

In its 2004 report, the PREQB informed the main failures shown by the MSW landfills existing in the Island. As mentioned above, they took into consideration characteristics such as: the presence or absence of leachate, the existence or absence of a system to control runoff, the presence or absence of wells to monitor groundwater, and the availability and use of a system to weigh or measure the daily wastes received at the landfill. Also, they evaluated, individually as Satisfactory, Average, and Poor, the daily practice of covering the wastes, the availability of heavy equipment, and the safety controls. The main failures in 28 of the 32 MSW landfills in PR that were included by PREQB in its 2004 report (see Table 2.06).

Table 2.06. Operational Activities of the MSW Landfill 2004 (PREBQ 2004).

Number of the MSW Landfill	Locality	Leachate	Daily Covering	System control of run-offs	Exposed wastes	Availability of Equipment	Monitoring	System for measurement	Safety Controls
1	Aguadilla	X	S	X	X	S		E	S
2	Añasco		P			S		E	S
3	Arecibo	X	S	*declivity		S	X	PJ	S
4	Arroyo	X	P		X	P		E	S
5	Barranquitas	X	R		X	R		E	S
6	Cabo Rojo		S	X		S	X	E	S
7	Carolina		S	X		S	X	PJ	S
8	Cayey	X	P		X	P		E	S
9	Culebra		P		X	P	X	E	P
10	Fajardo	X	S	X	X	S		E	R
11	Florida	X	S	*declivity	X	S	X	E	R
12	Guayama		R		X	S	X	E	S
13	Guaynabo	X	S	X	X	S	X	E	S
14	Hormigueros		R			P	X	E	S

Table 2.06., continued.

15	Humacao	X	S	X		S	X	PJ	S
16	Isabela		P			S	E		S
17	Jayuya	NI	NI	NI		NI	NI	NI	NI
18	Juana Diaz	X	R			X	R	E	R
19	Juncos	X	P	**		X	R	E	P
20	Mayaguez		S	X		S	X	PJ	R
21	Moca		P			X	P	E	S
22	Peñuelas	NI	NI	NI		NI	NI	NI	NI
23	Ponce	X	S	X		S	X	E,PJ	S
24	Salinas	X	S	X		S	X	E,PJ	S
25	Santa Isabel		R			X	P	E	R
26	Toa Alta	X	P	X		X	X	PJ	PJ
27	Toa Baja	X	R	X		X	S	X	PJ
28	Vega Baja	X	S	*declivity		S	X	E	R
29	Vieques	NI	NI	NI		NI	NI	NI	NI
30	Yabucoa	X	R			X	R	E	R
31	Yauco	NI	NI	NI		NI	NI	NI	NI

X: Existing/ observed; P: weighing; E: writing; NI: not inspected. *Control of groundwater of run-off with declivity

2.8.3 Lack of a Leachate Control System

Most MWDLs in PR do not have a leachate control system. Thus, the presence of leachate has become one of the main problems faced by MWDLs in PR. MWDLs should have, in their lower level, diverse impermeable layers to avoid leachate leakage or runoff filtration into the landfill, so that the volume of leachate does not increase. It is also recommended to have a system to capture and treat the leachate that accumulates at the bottom.

Fifty three percent (53%) of the MWDLs have problems with the presence of leachate, which may potentially cause surface and groundwater contamination (Figure 2.09).

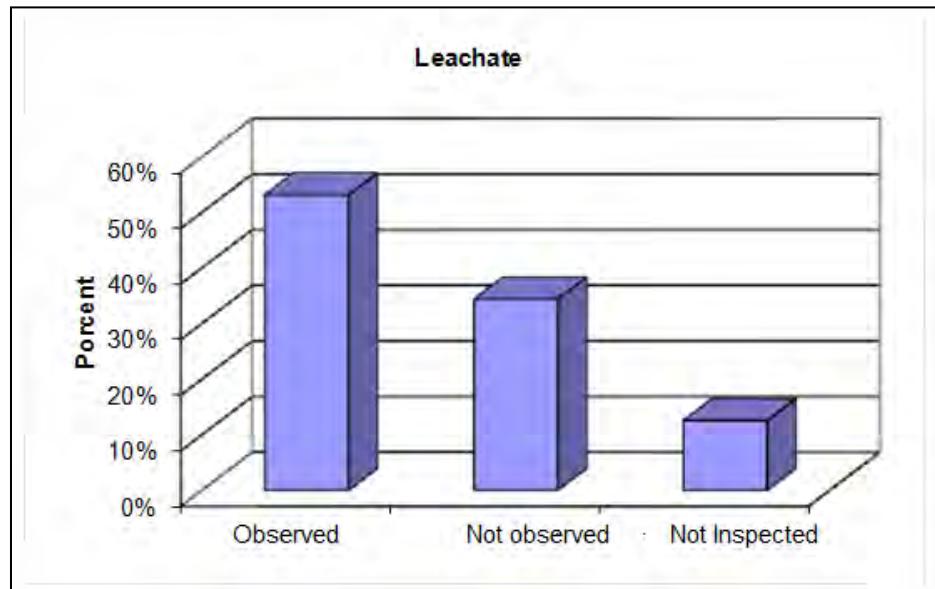


Figure 2.09. Percent of Lehate in MWDL in PR (PREQB 2004).

Chapter Three

General Materials and Methods

This chapter is divided in 7 sections. The first one presents the materials, methods and procedures used to analyze the samples from the landfill, groundwater and soil. The subsequent sections present the general characteristics of the study area, and the sites used for sampling. The procedures used to collect and analyze samples are described and explained for each sampling area.

3.1.0 Materials and Instrumentation

In this section the instrumentation and materials needed to perform this study will be introduced.

3.1.1 Gases: Argon and nitrogen.

3.1.2 Solvents and Analytical Standards: Deionized water, concentrated hydrochloric acid and nitric acid, trace metal grade (Fisher Chemical), hydrogen peroxide 30% (Fisher certified ACS), Cr, Pb, Cu, Zn, Ni, Co, Fe, Reference Standard Solutions (1000ppm +/-1% High purity certified, Fisher Chemical) and Leco Corp for ICP analysis and montana soil NIST 2711.

3.1.3 Cleaning materials: Alconox detergent and 10 to 15 percent nitric acid solution

3.1.4 Safety: First-aid kit, waders, latex gloves and mask.

3.1.5 Laboratory Instrumentation: Analytical balance (accuracy 0.001 g), Model Preiser Scientific, Analytical balance metler Toledo Mode AX 205 (accuracy 0.0001 g), KTS oven (Precision), air drying oven (Preiser Scientific), laboratory Mill, desiccators, digestion vessels (50ml).

3.1.6 Sampling Materials and Field analysis instrumentation: Coolers with ice for samples, thermometers, nalgene rectangular 500 ml Sterile High Density Polyethylene (HDPE) bottle with screw caps (labeled with the appropriate analyses IDs), zip-loc bag

(for packing plastic bottles), cloth bag, trowel or scoop, spade or shovel, decontamination supplies/equipment, litmus paper for pH checks , pH meter, buffer solutions (pH 4, 7; 9 and 10), conductivity meter, Global Positioning System (GPS) unit.

3.1.7 Specific Field Sheets for Documentation of Sample information: Description of the area sheets, weather from site sample sheets, topographic maps, report and chain of custody forms (equipment calibration), field notebook and sample labels.

3.1.8 Analytical Instrumentation: ICP-Spectro Ciros CCD from Spectro Co , MDS-2000 Microwave Laboratory Digestion System (CEM Corp., USA), Cpi Mod Block digestor.

3.1.9 Data Analysis: Computer software ICP WIN LAB and Minitab program to perform statistics analysis of data.

3.2.0 Program Field and Laboratory Quality Assurance and Quality Control (QA/QC)

Appropriate QA/QC procedures were incorporated to the study in order to enhance sample integrity, increase the confidence of analytical data and to identify and minimize the sources of error or contamination that may be introduced from the time of sample-container preparation through sample analysis. Cleaning, collection of field samples, field documentation procedures and laboratory quality assurance methods were applied,

3.2.1 General Cleaning

The general cleaning procedure for all glassware, instrumentation and sampling devices was performed. This procedure was conducted in order to maintain sample integrity and minimize interferences and cross-contamination at each sample location.

3.2.2 Standard Operation Procedures (SOPs)

All samples were collected following appropriate SOPs: The faithful implementation of SOPs insures common sample collection methods, helps assure the quality and consistency in sampling procedures throughout the study, and ensures that the chemical integrity of samples is maintained from the time of collection until chemical analysis.

3.2.3 QA/QC Samples

The QA/QC sampling for groundwater and leachate included trip and temperature blanks for each day of sampling, a field blank for every sampling point, and replicate samples at each sampling point. For soil samples, QA/QC sampling included a background soil sample and a field blank. The expected “non-detected” (ND) result for all different QA/QC samples affords confidence that samples were not contaminated during container preparation, field sampling and handling, transportation, storage and analysis.

3.2.4 Sample Handling

Groundwater and leachate samples were preserved immediately ($\text{pH} < 2$ and 4°C), after collection. Unambiguous labels were used to identify all sample containers before they were properly stored. To decrease the possibility of cross-contamination new pair of disposable gloves for each sample point were used and all sample of landfill were placed in cool container and the all groundwater samples in other cool container

3.2.5. Field Documentation Sheet

Specific field sheets for sample documentation including equipment calibration, weather conditions, description of sampling area, sampling procedure and chain of custody forms were filled out in each sampling campaign.

3.2.6. Laboratory Quality Assurance Methods

To ensure the validity of the data, all analyses were performed within the appropriate holding time. The ICP analyses were conducted accordance with SOPs from USDA Forest Service Institute of Tropical Forestry Laboratory. Blank samples, calibration curve for external standards and spiked samples were performed as part of the internal laboratory QA/QC procedure.

3.3.0 Research Design and Methodology

The research process began with a literature search in order to assess the current state of research regarding heavy metal concentration in landfill leachate, as well as to identify USEPA approved procedures for sampling and analysis of heavy metals in water and soil. These procedures approved by USEPA were used to elaborate Standard Operation Procedures (SOPs) which were then submitted to PREQB for review (see appendix A). The SOPs developed as part of this project were used during the sampling campaigns.

The methodology designed for this study consisted of sampling the leachates as well as the groundwater from neighboring wells; recording physical field and chemical parameters; and analyzing the samples in the laboratory for inorganic macrocomponents and heavy metal content. Soil samples were also collected and analyzed to determine the inorganic macrocomponents and heavy metal concentrations at one of the landfills and at a facility where one of the groundwater wells is located.

3.3.1 General Description of the Study Area

3.3.1.1 Selection Criterion of an Area of Puerto Rico for Research

The area of Puerto Rico where the research was carried out was selected based on input from the PREQB as well as on the results of a literature review. The study area included five experimental sites, all located in the northern coast of Puerto Rico. This

area was chosen because it presented both aquifers and landfills with apparent leachate problems.

3.3.1.2 Geographical Setting of the Study Area

Puerto Rico is the smallest and easternmost island of the Greater Antilles. It is located at an approximate lat 18° 15'N and a long 66° 30' W. Puerto Rico is divided into three geographical areas: the Central Interior Mountain Range, the Coastal Plains and the Northern Karst (Veve et al. 1996).

The presence of calcium carbonate (limestone) of sedimentary origin is typical and extensive in the Northern karst region. This area shows very specific characteristics, both above ground and in its underground extension. Its surface shows the presence of dolines, some of which are surrounded by hills known as mogotes (Monroe 1996) (see Figure 3.01). The underground karst component is characterized by a main aquifer system, the North Coast Limestone Aquifer System, whose overall structure consists of two limestone aquifers, (one above the other) (Rosado 2008). These are known as the Upper or Shallow Aquifer (Acuífero Llano) and the Lower or Artesian Aquifer (Acuífero Artesiano) (Rosado 2008). This aquifer system supplies water to many regions of the island (Monroe 1996) (Rosado 2008) (see Figure 3.02).

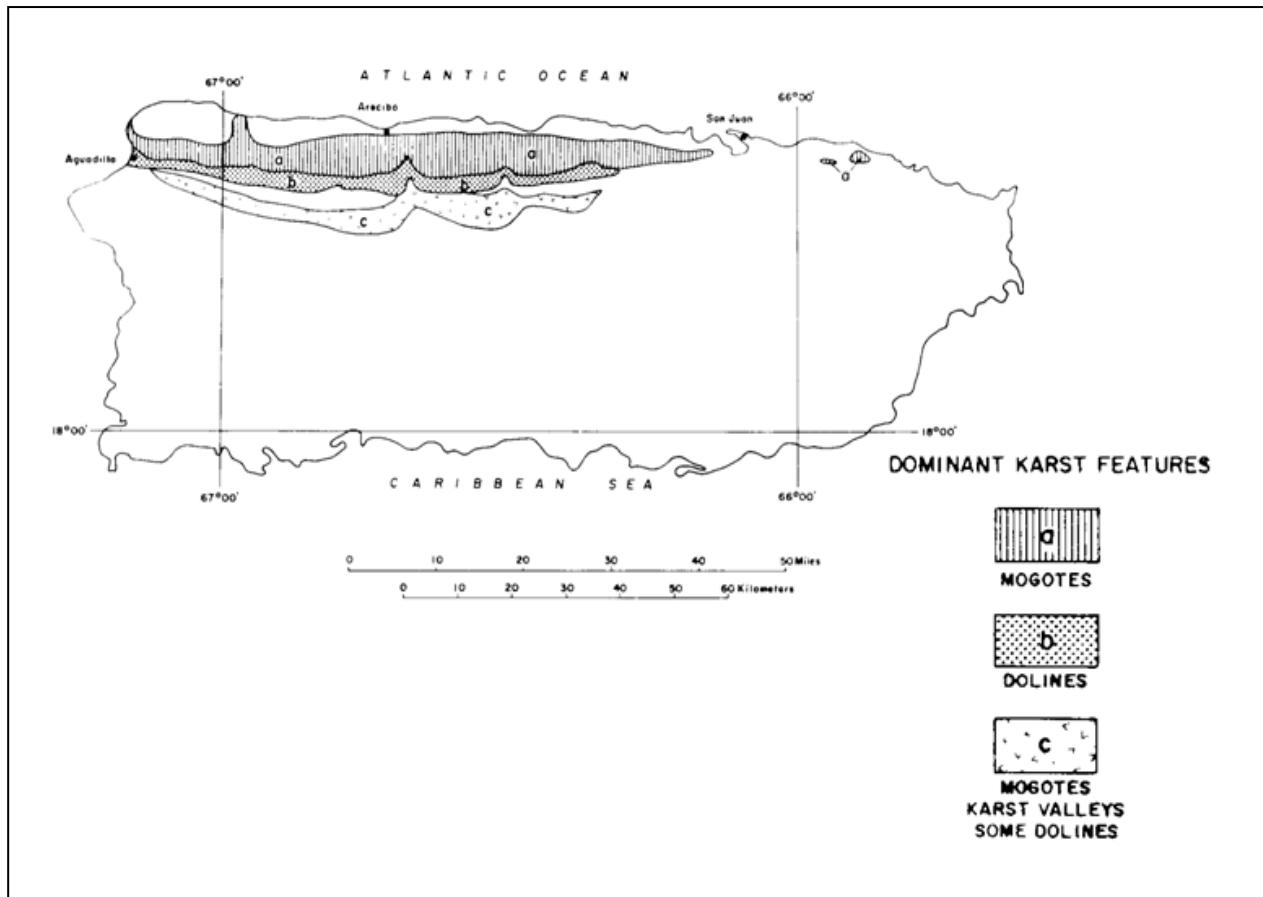


Figure 3.01. Map of Puerto Rico's northern karst region (Monroe 1996).

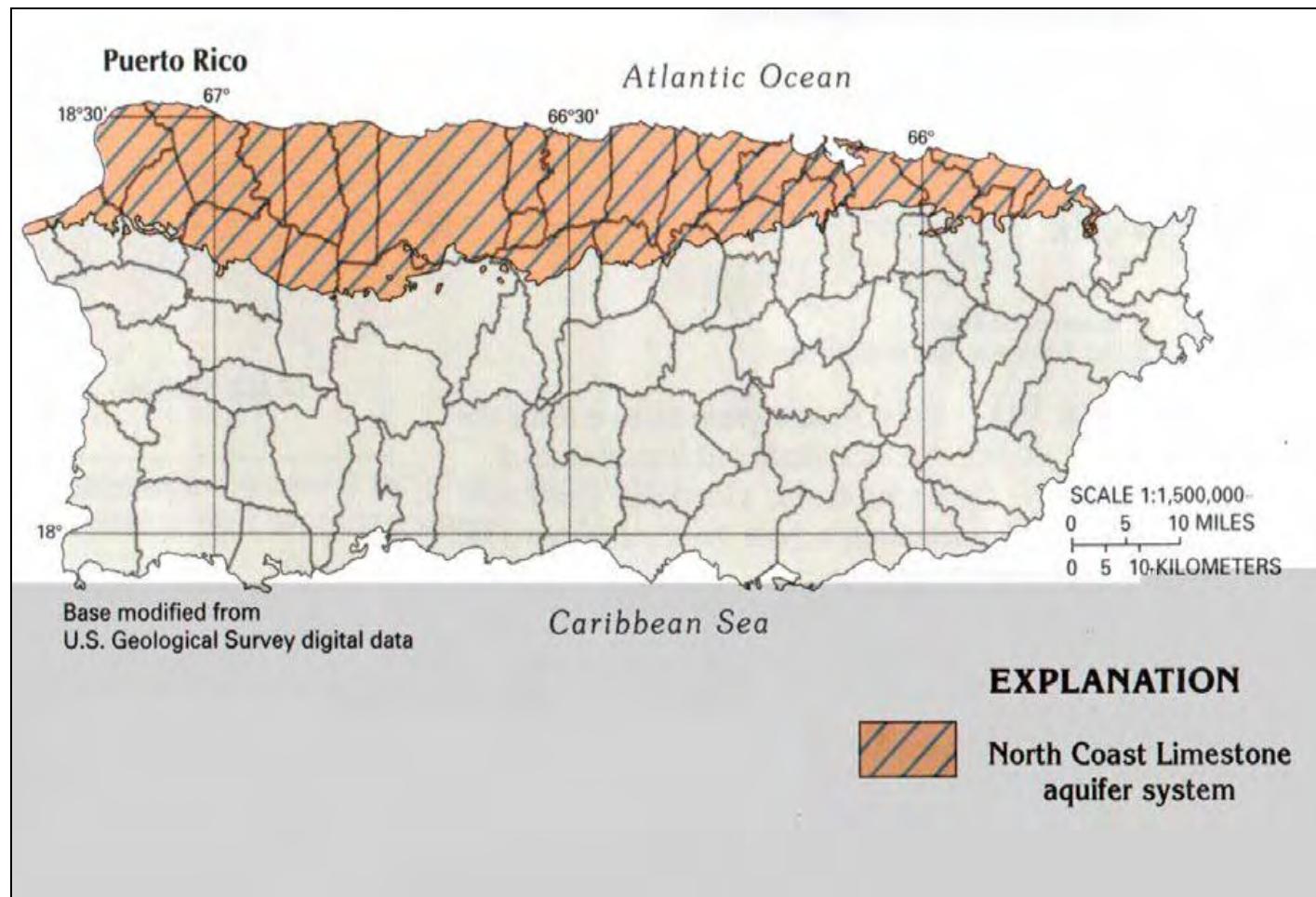


Figure 3.02. Map of north coast limestone aquifer system.

3.3.2 Landfills and Wells Study Locations

3.3.2.1 Selection Criterion

Input from PREQB and PRASA was considered for the selection of landfill sites and groundwater wells to be studied. The selection was based in the following criteria: existence of leachate, accessibility of leachate sampling source, and geographic location of the site. The geographic and geological situation is very important to identify areas susceptible to impact. Wells that are located down gradient from the landfill can have the potential to be impacted. A total of 5 locations were chosen for the study, all of them located in the north central region of Puerto Rico: two municipal landfills, the Toa Alta and Toa Baja landfills, and three groundwater wells (Campanilla 7, Levittown 6, and Caribbean Primate Research Center (CPRC)). Leachate and groundwater samples for this study originate from a total of 6 sampling points of the five locations listed above, a point in each of the localities (Campanilla, Levittown, Centro de Primate and the Toa Alta and Toa Baja Landfills), and an additional point in the Toa Baja landfill, for a total of six points.

For the purpose of characterization, the Toa Alta and Toa Baja landfills locations were selected; and for assessing the potential impact on the environment, the Campanilla, Levittown and CPRC wells and the Toa Baja Landfill were selected. To assess potential impact on groundwater, as well possible impact on the soil around the landfill, the Caribbean Primate Research Center and the Toa Baja Landfill were selected. The sampling locations and points were identified in consultation with PREQB, municipal authorities and CPRC personnel.

3.3.2.2 Landfills Sampling Locations

The Toa Alta and Toa Baja landfills were chosen for the characterization of leachate because their size and the type and amount of waste collected differ significantly among both landfills, but both have landfill leachate problems according to a PREQB report issued in 2004. Figures 3.03 and 3.04, shown Toa Alta and Toa Baja leachate landfill problems, respectively.



Figure 3.03. Pond formed of leachate from the Toa Alta landfill.



A.



B.

Figure 3.04. Ponds formed of leachate from the Toa Baja landfill (A and B).

3.3.2.3 The Toa Alta Landfill Characteristics

3.3.2.3.1 Location and Background of the Toa Alta Landfill

The Toa Alta landfill has been in operation for approximately 44 years. It is located in Km 8.2 of PR-165 road, and occupies approximately 12.6 ha. This landfill is a municipally-owned management facility and is privately operated by Landfill Technologies. the Toa Alta landfill accepts wastes from the municipalities of Corozal, Toa Alta, Bayamón, Comerío and Naranjito (ADS 2003b). Figure 3.05 shows the location site of the Toa Alta landfill. The Toa Alta landfill is located in a karst limestone region that dominates the north-central region of Puerto Rico. The landfill property is surrounded by undeveloped forest areas and scattered residential properties (see Figure 3.06).

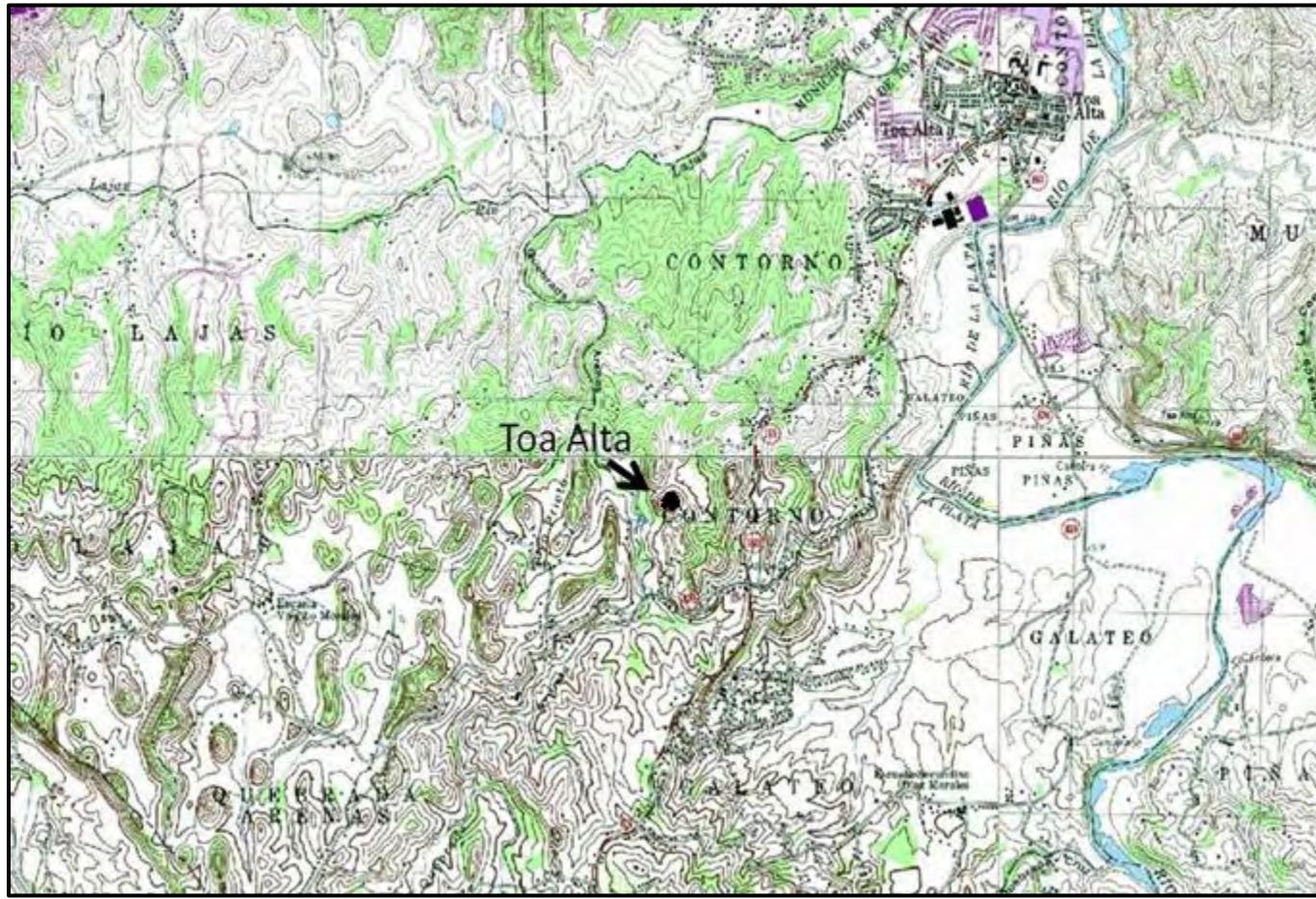


Figure 3.05. Topographic map depicting the location of the Toa Alta landfill.



Figure 3.06. Aerial photo of Toa Alta landfill and surrounding area.

3.3.2.3.2 Waste Composition at Toa Alta Landfill:

Waste composition is an important consideration to evaluate leachate components. The Toa Alta landfill currently serves as a municipal sanitary landfill and accepts solid non-hazardous waste. It receives around 1783 t of waste per week and the most common waste material types accepted at the landfill include municipal solid waste, construction debris and yard wastes (see Table 3.01) (ADS 2003b).

Table 3.01. Waste composition data of Toa Alta landfill (ADS 2003b).

Component	Fraction of Waste Stream (Percent)
Municipal Solid Waste	79
Construction Debris	20
Yard Wastes	1

3.3.2.4 The Toa Baja Landfill Characteristics

3.3.2.4.1 Location and Background of the Toa Baja Landfill

The Toa Baja landfill site, which comprises approximately 42 ha is an active landfill that has been in operation since 1970. It is located Km 4.2 of PR-865, Barrio Candelaria in Toa Baja, Puerto Rico (see Figure 3.07). This landfill is a municipally-owned management facility and is privately operated by Landfill Technologies.

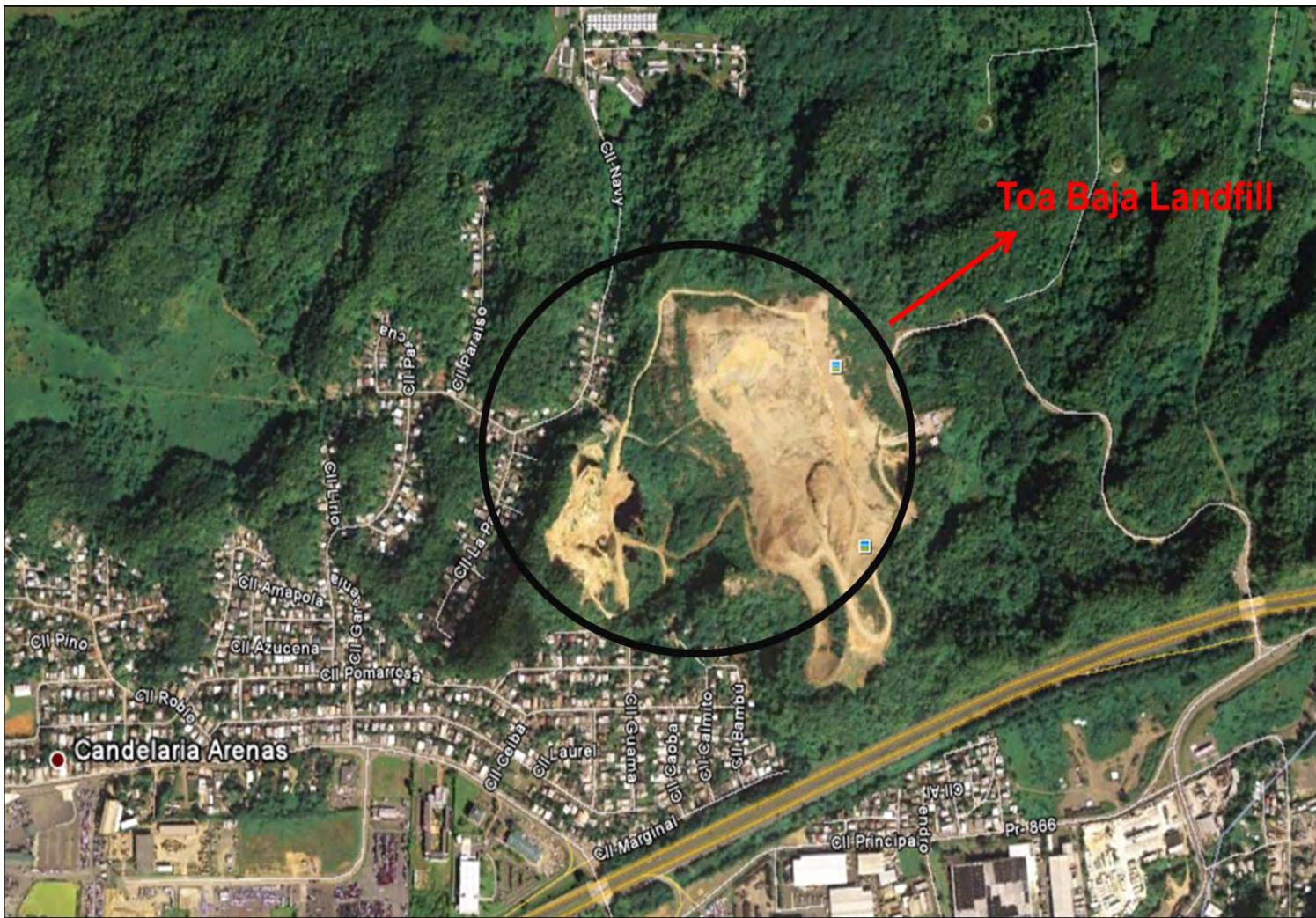


Figure 3.07. Aerial photo of Toa Alta landfill and surrounding area.

The landfill is located in the karst limestone province that dominates the north-central region of Puerto Rico. It sits above the coastal aquifer system, which has a general groundwater flow direction to the north. Several municipal, agricultural and industrial supply wells are located near the landfill, outside the landfill property. The Toa Baja Landfill accepts wastes from the municipalities of Carolina, Cataño, Guaynabo, San Juan, Toa Baja, and Morovis (ADS 2003b).

The Toa Baja landfill is adjacent to the US Navy Base property. Besides the active landfill, the landfill site also contains undeveloped areas. Within the active landfill there are two sections: one where municipal solid wastes are deposited and another one where scrap metal and construction demolition debris are dumped.

3.3.2.2.2 Waste Composition at Toa Baja Landfill

Waste composition is an important consideration to evaluate leachate components. The Toa Baja Landfill serves as a municipal sanitary landfill and accepts solid non-hazardous waste. It receives around 8615 t of waste per week and the most common waste material types accepted at the landfill including municipal solid waste, construction debris, yard wastes and, to a lesser extent, auto wastes and other special wastes (see Table 3.02) (ADS 2003b).

Table 3.02. Waste composition data of Toa Baja landfill (ADS 2003b).

Component	Fraction of Waste Flow (Percent)
Municipal Solid Waste	77.8
Construction Debris	16.6
Yard Wastes	5.0
Minor Composition of Auto Wastes	0.5
Special Wastes	0.1

3.3.2.2.3 Landfill Sampling Points

The landfills sampling points were identified upon consultation with the personnel responsible for operation and management of the sites, as well as on the basis of waste type and landfill size difference.

3.3.2.2.3.1 The Toa Alta Landfill Leachate Sampling Point

The sampling point at the Toa Alta landfill is located within the northern portion of the landfill (see Figure 3.08). This point was selected because there is a large-sized pond of leachate formed by the deposition of landfill leachate runoff. Leachate samples were taken directly from the leachate runoff stream before it reached the pond (see Figure 3.09).

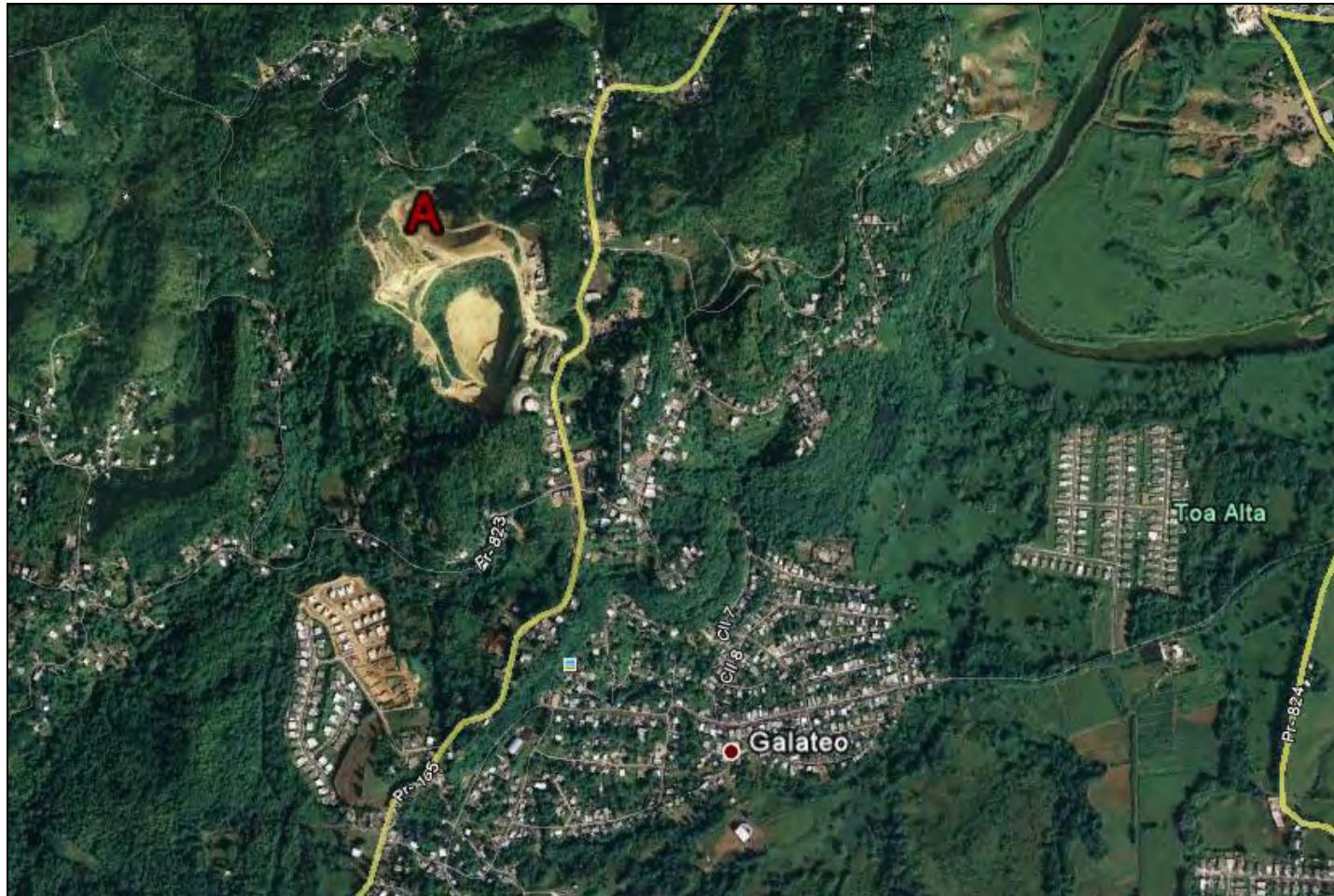


Figure 3.08. (A) Location of sampling point in Toa Alta.

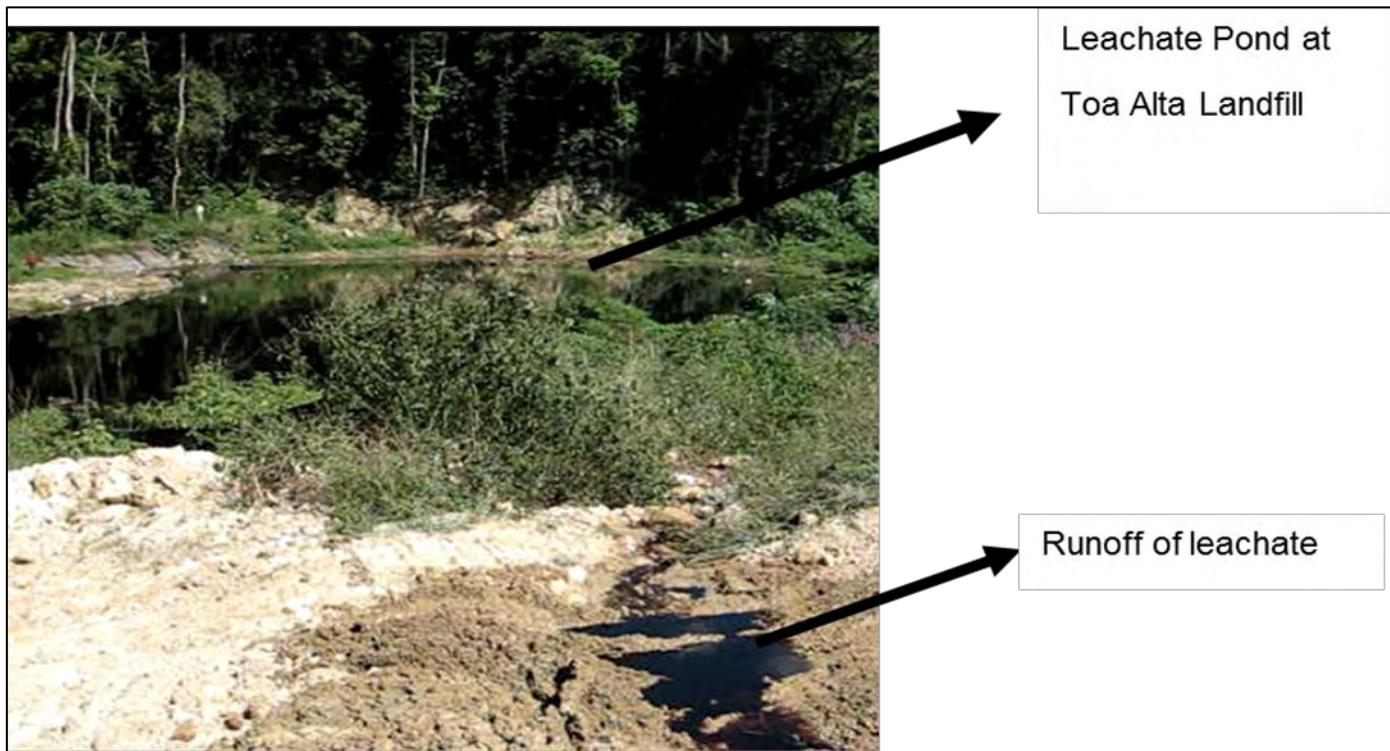


Figure 3.09. View of Toa Alta landfill sampling point.

3.3.2.2.3.2 Toa Baja Landfill Leachate Sampling Points

Because leachate composition may vary not only from landfill to landfill, but also between different sections of the same landfill, two sampling points were selected: Toa Baja A and Toa Baja B in order to study the heavy metal content of leachate resulting from different types of wastes (see Figure 3.10). Metal scrap is not currently deposited in the landfill, but if it was previously deposited years ago in a section of the landfill. The Toa Baja A sampling point is close to the deposit of scrap in a part of the landfill known as "Minga's Hole". In "Minga's Hole" there are two leachate ponds which could percolate the ground and reach the groundwater below it. A leachate sample was collected from the leachate runoff stream before it reached the leachate pond (see Figure 3.11). The Toa Baja B sampling point is located away from the scrap deposit in another section of the landfill (see Figure 3.12).

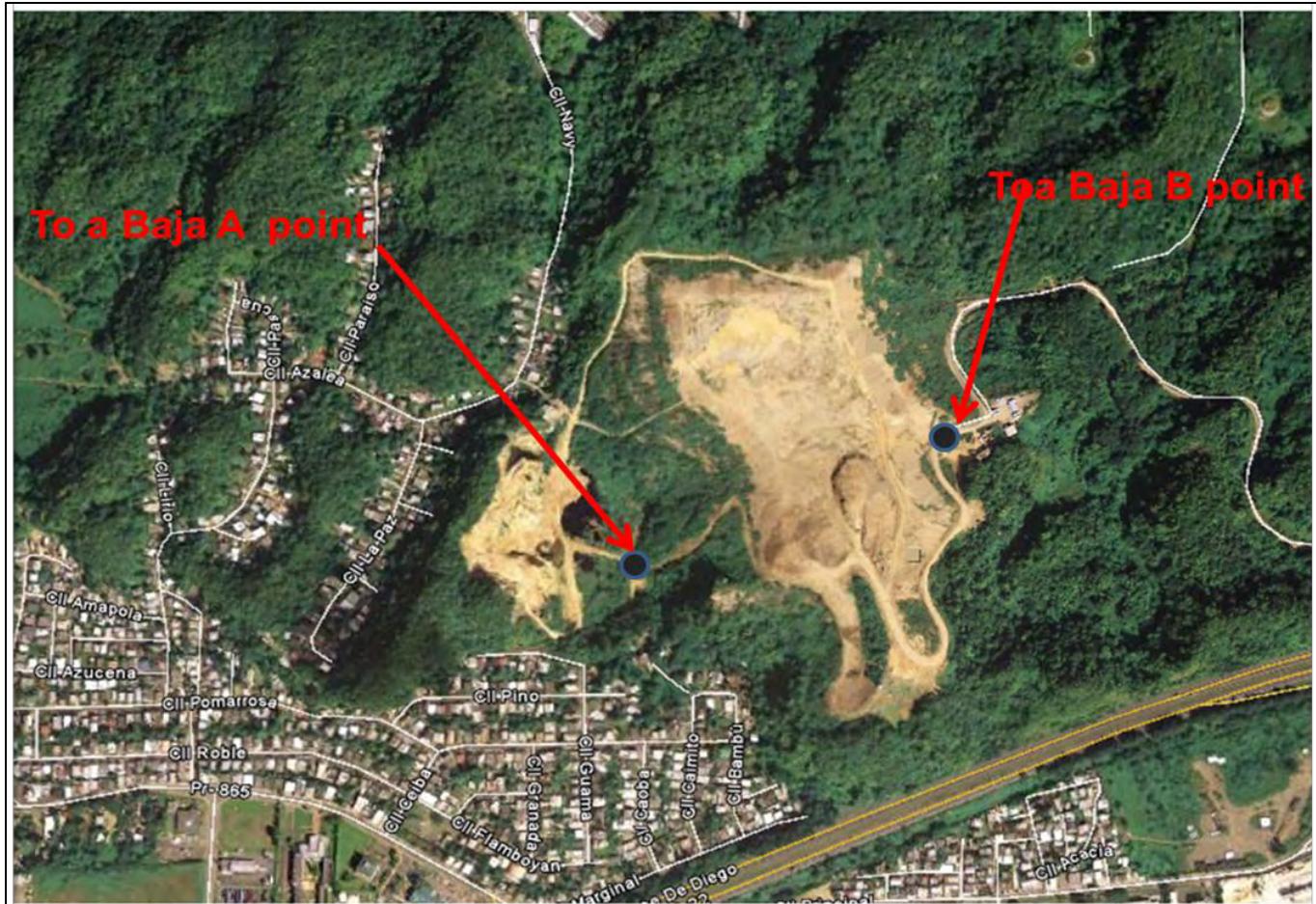


Figure 3.10. Location of leachate sampling points at the Toa Baja landfill.

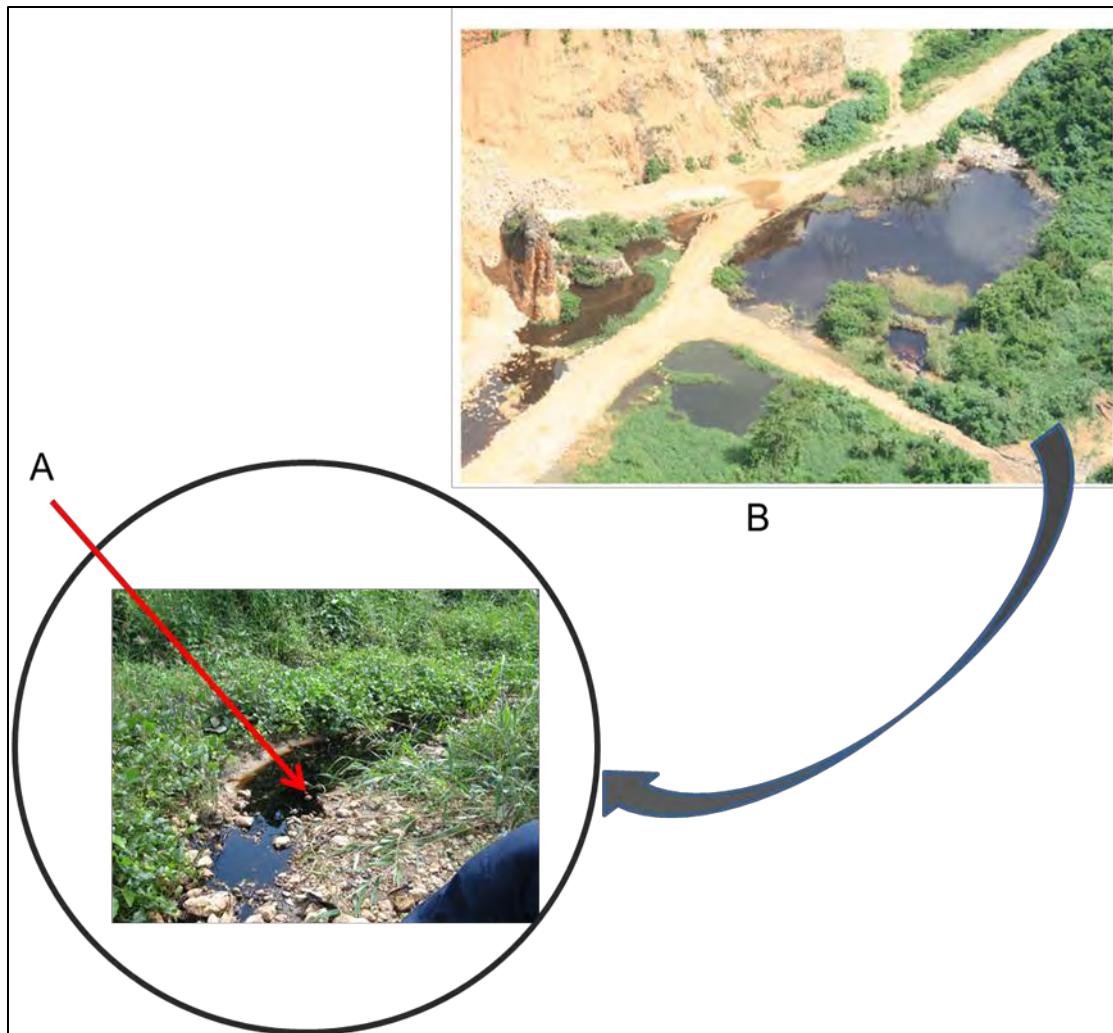


Figure 3.11. Toa Baja sampling point A. Photo A shows the leachate runoff stream that flows towards the pond. Photo B is an aerial photo of the leachate ponds formed by runoff (Source Google Earth).



Figure 3.12. Photograph showing of Toa Baja sampling point B.

3.3.2.3 Groundwater Sampling Locations

To evaluate a possible potential impact to groundwater by leachate from the Toa Baja landfill, a total of 4 sampling locations (Toa Baja landfill and three wells) were selected. Figure 3.13 shows a topographic map depicting the Toa Baja landfill and the groundwater sampling locations. Figure 3.14 shows photography of all the wells chosen. Two of these wells, the Campanilla 7 and Levittown 6 are owned by the Puerto Rico Aqueducts and Sewers Authority (PRASA); the other well is owned by the Caribbean Primate Research Center (CPRC).

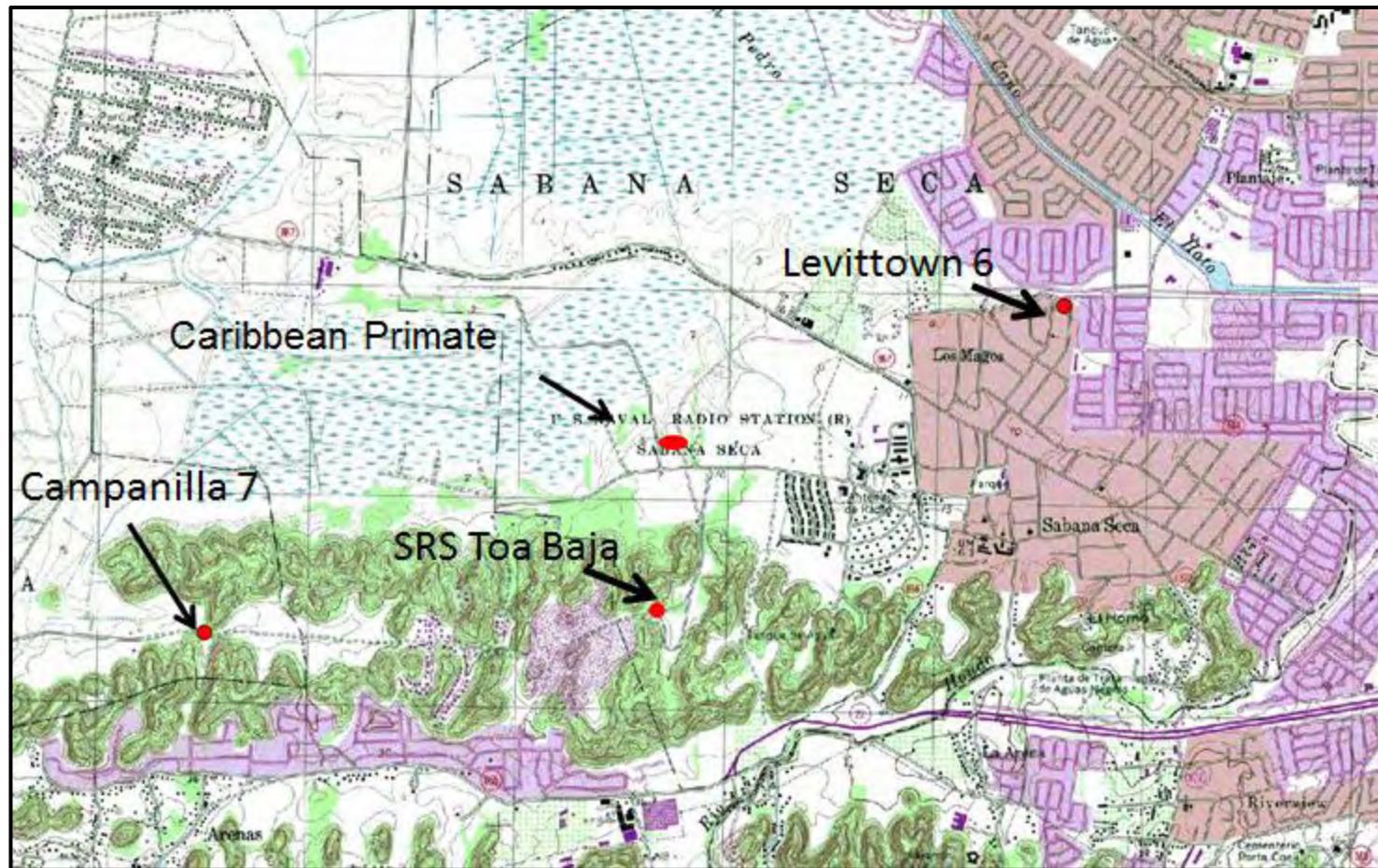


Figure 3.13. Topographic map depicting the Toa Baja landfill and the groundwater sampling locations.



Figure 3.14 .Photos showing (A) Levittown 6 well; (B) Campanilla 7 well; and (C) Caribbean Primate well.

3.3.2.3.1 Groundwater Sampling Points Associated to the Toa Baja Landfill

The Figure 3.15 presents sampling points of groundwater wells and Toa Baja Landfill. The wells to be sampled were chosen after considering, among other factors, their distance from the Toa Baja landfill, their ease of access and the groundwater flow direction, which in the north region of Puerto Rico is generally towards the coast (see Figure 3.15). Both, the Caribbean Primate and Levittown 6 wells are upstream but at different distances from the Toa Baja landfill. Campanilla 7 well comparison at Levittown 6 well, there are mostly near but adjacent to the Toa Baja landfill site (see Figure 3.16). For purposes of this study the adjacent point (Campanilla 7 well), serves as reference site and the points located downstream are impact sites of different degrees, depending on the distance of the discharge point in the Toa Baja landfill.



Figure 3.15. Location of sampling points of groundwater wells and Toa Baja landfill.

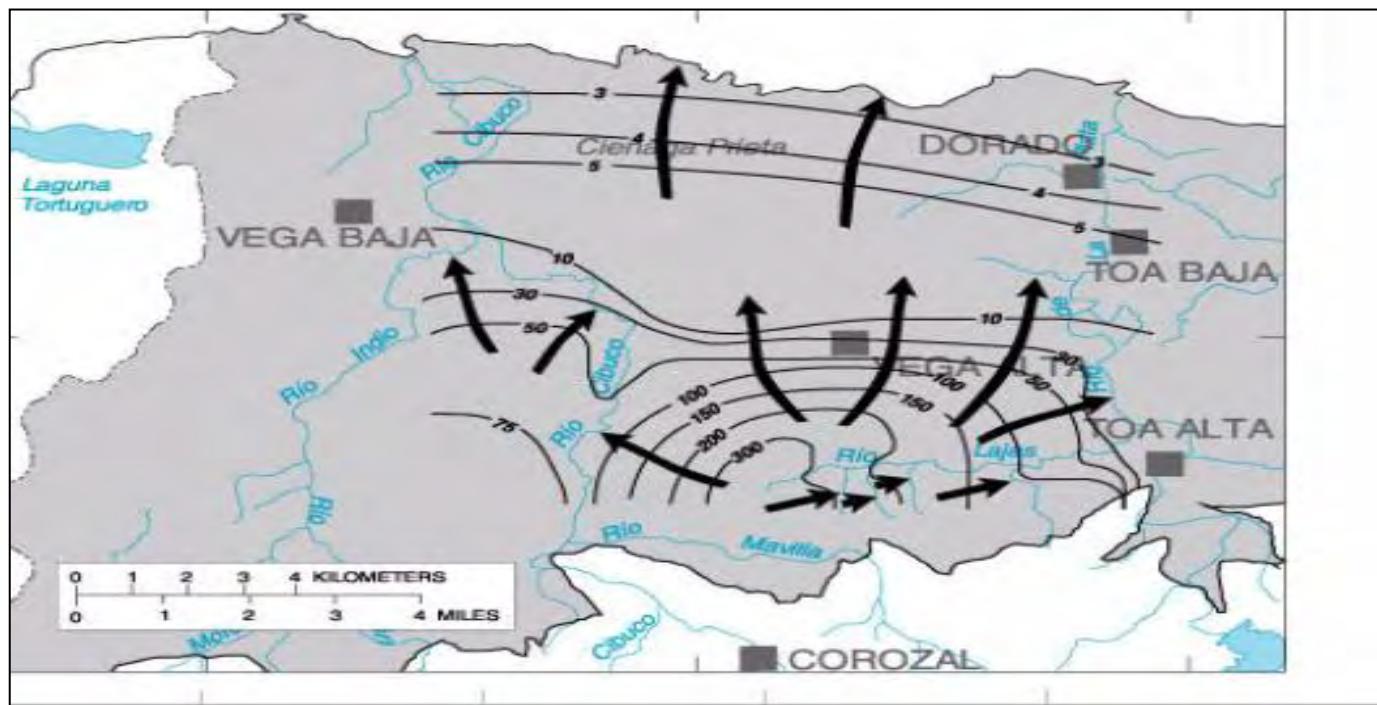


Figure 3.16. Direction of groundwater flow (Veve et al. (1996).

3.3.2.3.2.2 General Summary of Leachate Landfill and Leachate/Groundwater Sampling Points

The following Table 3.03 describes the type and role of each sampling site within the design of the research methodology.

Table 3.03. Description of the sampling sites within the design of the research methodology.

Sampling sites	Type	Description
Toa Baja landfill	Source (Point A)	Municipal waste disposal landfills, located in the Toa Baja municipality. (Near a deposit of scrap metal)
Toa Baja landfill	Source (Point B)	Municipal waste disposal landfills, located in the Toa Baja municipality. (Away from area of scrap metal deposit)
P1 = Well		Site located adjacent from Toa Baja Landfill, with the same geochemical regional background. This well is located outside the Toa Baja landfill area of influence (2.29 km away).
Groundwater, Campanilla 7	Reference site	
P2 = Well		Site located downgradient from the Toa Baja municipal landfill, vulnerable to possible contamination (3.06 km away)
Groundwater, Levittown 6	Possible impact site	
P3 = Well		Site located downgradient from the Toa Baja municipal landfill, vulnerable to possible contamination (0.48 km away)
Groundwater, Caribbean Primate Center	Possible impact site	
Toa Alta and Toa Baja Landfills	Leachate characterization	Municipal waste disposal landfill, located in the Toa Alta and Toa Baja municipality

3.3.2.4 Soil Sampling Locations

To evaluate a possible potential impact by the Toa Baja landfill on surrounding soils, sampling points were selected within and around the Toa Baja landfill facilities. Two locations were chosen, the Toa Baja landfill, and the Caribbean Primate Center. Only the latter is described here, since the Toa Baja landfill was previously described.

3.3.2.4.1 Soil Points Selection Criterion

Input from the personnel of the Primate Center was considered for the selection of point soil sampling to be studied. For several years, the Primate Center present problems of formation of pools of leachate, which may have impacted the soil in the center. The presence or absence of a leachate pond was considered for the selection of the sampling areas inside the Primate Center. A total of three points were chosen, point 1 represents an area of potential impact, to be located in the area of formation of leachate pond, another point was chosen because it is farther from the formation of the pond, but even with the possibility of impact, but on a smaller scale, and the last of the points was chosen to be at a greater distance to the landfill. The difference in distance between these points determine the variation of impact in relation to distance from potential source of contamination.

3.3.4.2 The Caribbean Primate Research Center Location

The Caribbean Primate Research Center (CPRC) is a world renowned center for the study of non-human Primate. Established in 1938, it has four facilities in Puerto Rico, one in Cayo Santiago, two laboratories located in the Medical Sciences Campus and another facility in Sabana Seca (Toa Baja).

The Caribbean Primate Research Center is located behind the US. Navy facilities and adjacent to the Toa Baja landfill. It is comprised of 102 ha of land, of which only 6.9 ha used for their operations because the remaining area serves as a conservation and ecological buffer zone of limestone hills, subtropical forests and

wetlands. For several years the Primate Center has been affected by fire, runoff and leachate resulting from Toa Baja landfill operations (see Figure 3.17).



Figure 3.17. Runoff leachate coming from Toa Baja landfill.

3.3.4.2.1 Soil Sampling Points

A total of four sampling points were selected to determine the potential soil impact in the Primate Center (see Figure 3.18). These sites were chosen according to their distance to the landfill. One point is within the Toa Baja landfill, and the other three are within the Primate Center (point 1, 2 and control site). The sampling point located in the Toa Baja landfill is in an area close to the Primate Center. The sampling points 1, 2 and the control site are located within the Primate Center facilities, close to the leachate runoff streams. The sampling point 1, described as a “Possible soil contamination on Primate Center”, was chosen, because the soil in this area has been impacted during a long time by both, leachate runoff and a pond from the Toa Baja landfill.

The sampling point 2, described as “Soil Primate”, was used as a reference value for soils impacted by contamination from the Primate Center. The reason for this choice is because of its proximity to the primate's cages, which are directly subjected to contaminants from the Primate Center. Both point 1 and 2 are downgradient. Point 2 is more distant from the landfill, but closer to the contamination of the Primate Center. An increase in the concentration in point 2 (Soil Primate), compared to point 1 (Possible soil contamination on Primate Center), could be linked to the contamination from the Primate Center, but not from the Toa Baja landfill and an increase in the concentration in point “possible soil contamination on Primate Center”, compared to point “Soil Primate” could be linked to the contamination from the Toa Baja Landfill. Finally, the sampling point described as “Control Site” was used as a reference value for soils of this type in the area, not only because it is far from the landfill, but because it is far away from the typical contamination from the Primate Center.



Figure 3.18. Map location of all points where soil samples were collected.

Table 3.04. Description of the sampling soil points within the design of research methodology.

Sampling sites	Type	Description
Toa Baja landfill	Source	Municipal waste disposal landfills, located in the Toa Baja municipality. (Near a Primate Center).
P1 = Soil at Caribbean Primate Center	Possible impact soil	Site located downgradient and 0.48 Km away from the Toa Baja municipal landfill, vulnerable to possible contamination.
P2 = Soil at Caribbean Primate Center	Soil Primate	Site located downgradient and 3.06 Km away, from the Toa Baja municipal landfill, less vulnerable to possible contamination.
P3 = Soil at Caribbean Primate Center	Control site	Reference site with the same geochemical regional background. This well is located 0.74 km away the Toa Baja landfill area of influence.

3.4.0 Climate

3.4.1 Field Climate and Season Data

Northern Puerto Rico has a humid subtropical climate and, although Puerto Rico does not have the four seasons), but two predominant climatic seasons may be distinguished: a dry season (between January and April) and a wet or rainy season (between May and December) (Picó 1969) (see Table 3.05). Since leachate composition is influenced by climatic conditions, these two climatic seasons were considered in this study.

Table 3.05. Periods of interest.

Season	Months of The Year	Remarks
Dry	January	
	February	Driest
	March	
	April	
Wet	May	1st Maxima
	June	
	July	Minima
	August	
	September	
	October	
	November	2nd Maxima
	December	

The drier and more rainy (wet) seasons are expected to influence the volume of leachate by respectively decreasing or increasing leachate production at the landfill site. Thus, four sampling campaigns were conducted, two during the wet season and another two during the dry season. The sampling campaigns were planned on the basis of the two periods established (Picó 1969).

The climatic and analytical data included in this report belong to the period between March 2009 and March 2010. Although this study began in 2007, samples taken from 2007 to November 2008 could not be included, since the laboratory personnel at the PREQB were not able to analyze the samples within the holding time. All samples collected on and after January 2009, however, were analyzed within the holding time in collaboration with the US Forest Service. Due to the aforementioned situation, only the results for samples collected between March 2009 and March 2010 are included.

Because no site-specific climatic data are available for the study site, data for the Toa Baja-Levittown station are reported because this is the National Weather Service station closest to the study site. Table 3.06 shows information of average monthly and annual maximum and minimum temperatures, as well as average monthly rainfall from March 2009 to March 2010 for the study area.

According to rainfall data analysis for the period between March 2009 and March 2010 in the study area, the months of March, April, July and December 2009 and February and March 2010 are part of the dry season with lower recorded total monthly rainfall with average values ranging between 2.87 and 4.47 mm.

Table 3.06. Mean monthly and annual rainfall and minimum and maximum temperature of the area study.

Month	Mar (2009)	Apr (2009)	May (2009)	Jun (2009)	Jul (2009)	Aug (2009)	Sep (2009)	Oct (2009)	Nov (2009)	Dec (2009)	Jan (2010)	Feb (2010)	Mar (2010)
Average													
Minimum Temperature	20.8	21.7	23.1	24.1	24.4	24.7	24.4	23.7	22.7	22.4	21.6	22.2	22.9
	(°C)												
Average													
Maximum Temperature	28.5	29.9	29.7	32.1	32.2	32.3	32.5	31.8	30.6	30.0	28.7	30.3	31.2
	(°C)												
Max 24 hr. rainfall (mm)													
	3.49	3.24	8.71	9.74	4.3	9.57	9.84	9.12	11.22	2.67	11.12	2.87	4.47

On the other hand, the months of May, June, August, September, November 2009 and January 2010, which belong to the rainy season, reported average annual rainfall values ranging from 8.71 to 11.22 mm In terms of temperature, the average temperature recorded in the study area between March 2009 and March 2010 ranged from 20.7 °C to 32.5 °C

3.5.0 Sampling Methodology

3.5.1 Sampling Campaign

A total of four campaigns were carried out to collect leachate and groundwater samples, and one additional campaign was conducted to collect soil samples in the study area. According to climatic data, the first and fourth campaigns (April 2009 and March 2010) were collected in the dry season, with rainfall of 3.24 and 4.47 mm, respectively; while the second and third campaigns (June 2009 and October 2009) were collected during the wet season, with average rainfall of 9.74 y 9.84 mm, respectively (see Table 3.07).

3.5.2 Sampling Procedure

3.5.2.1 Leachate and Groundwater Sampling

The main objective for collecting the leachate and groundwater samples was to obtain a representative sample from a given source. All leachate and groundwater samples were collected and handled according to approved SOPs. All reagents employed were analytical grade, and water used was ultrapure water.

A total of four sampling campaigns were conducted between April 2009 and March 2010. During each sampling date and campaign conducted during this period, 26 samples were collected.

Table 3.07. Sampling dates for sampling campaigns.

Sampling Campaign	Date	Matrix
First Campaign	9-Apr-09	36 Leachate and groundwater samples/ 32 soil samples
Second Campaign	18-Jun-09	36 Leachate and groundwater samples
Third Campaign	9-Oct-09	36 Leachate and groundwater samples
Four Campaign	5-Mar-10	36 Leachate and groundwater samples

That means that a total of 104 samples were collected in the four sampling campaigns included in this study. For the reasons already explained before and despite the fact that 208 samples were taken from November 2007 to March 2010, only the 104 samples taken from April 2009 to March 2010 could be used for this study.

The 26 samples collected at each sampling campaign include: 2 trip blanks for each day of sampling, 6 field blanks for every sampling point, and 18 samples at each sampling point (three per sampling point). Leachate and groundwater samples were collected in 500 mL polyethylene containers, which were rinsed three times with deionized water, rinsed with nitric acid 10%, and rinsed with the source (leachate or groundwater) to be sampled before performing the actual sample collection. Both leachate as well as groundwater samples were directly taken from the source.

3.5.2.1.1 Leachate Sampling

Leachate samples were collected following the SOPs developed specifically for this study (see Appendices A-1). For collection of leachate samples, sample containers were slowly submerged (to prevent disturbances) in the leachate stream until the volume of leachate filled the sample container 500 mL.

3.5.2.1.2 Groundwater Sampling

Groundwater samples were collected following the SOPs already developed by the PREQB. Before the groundwater samples were obtained, the boreholes were purged to remove stagnant water, so that the groundwater sample was representative of the in situ groundwater. Stagnant borehole water is known to be affected by several processes which make it different from that present in the aquifer. While stagnant borehole water was being purged, the pH and electrical conductivity were monitored. Water was purged until both the pH and the conductivity exhibited constant values. Once stabilized, the groundwater sample was taken directly from the well's water jet. (Figure 3.19 shows the leachate and groundwater collection process).

3.5.2.1.3 Soil Sampling

Soil sampling was performed according to the FDEP standard operating procedures (FDEP 1992). Gloves and a stainless steel spoon were employed in the sampling process at each sampling point. Prior to sample collection, the soil at each sampling point was homogenized by kneading. All soil samples were collected on 5 March 2010 at three different sampling points from two distinct locations (the Toa Baja landfill and the Caribbean Primate Research Center).



A



B

Figure 3.19. The sample collection process at (A) the Toa Alta landfill and (B) the Levittown 6 wells.

To obtain each sample, a shovel was forced into the soil to a final depth of 30 cm. Four holes, following the runoff contour and at a one-meter distance from each other, were bored at each sampling point. Samples were taken at two different depths, the top layer sample included soil material taken at depths between 0 cm and 15 cm; and the bottom layer sample included material collected at depths between 15 cm and 30 cm. A total of 32 holes were drilled. All soil samples (200 g approximately), were placed in appropriate sample bags by means of a spoon. Figure 3.20 shows a schematic diagram of the four-hole sampling procedure used to sample soil in the Toa Baja landfill.

Soil samples were labeled according to ID number, sampling point and sample depth. The name before of comma represents the nomenclature given to the sampling point and the number after the comma represents the depth at which samples were taken. For instance, "Toa Baja 1, 0-15 cm" represents a sample taken on the sampling point of Toa Baja near Minga's Hole at a depth of 0-15 cm.

3.5.3 Handling and Storage Procedure

3.5.3.1 Groundwater and Leachate Samples

To ensure proper identification of samples, all containers were labeled according to the previously established nomenclature. To assure the representativeness of the collected sample with respect to the conditions at the time of sampling, all groundwater and leachate samples was preserved immediately after collection. To reduce cross-contamination, sample containers and soil bags were placed in individual zip-loc bags. To satisfy the low temperature requirement, all samples were placed in an ice cooler immediately after collection.

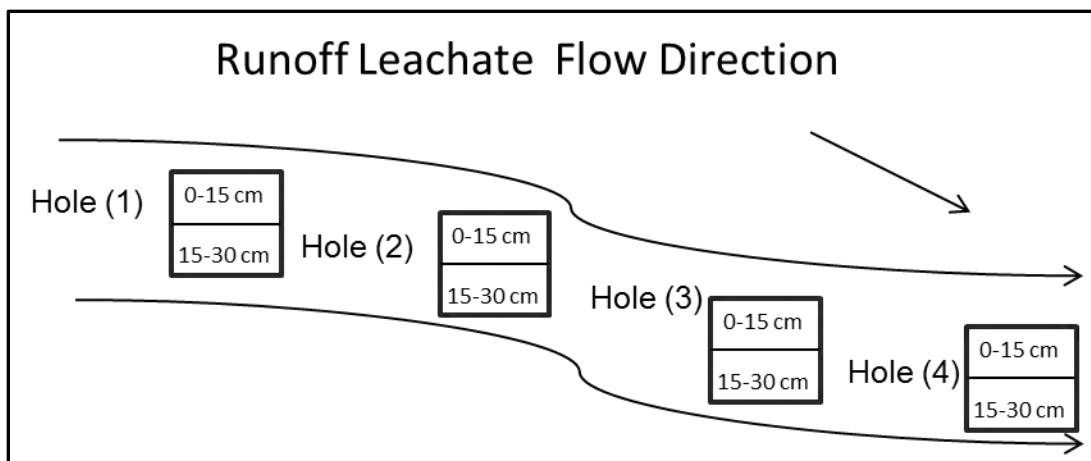


Figure 3.20. Schematic diagram depicting sampling procedure at the Toa Baja landfill. Each hole was sampled at two different depths.

3.5.3.2 Groundwater and Leachate Samples Preservation

The samples must be preserved in order to maintain and ensure the sample have approximately the actual quality as in site for a period of time. Immediately after collection, leachate and groundwater samples were preserved at 4 °C and pH < 2 by addition of concentrated HNO₃ to each sample container until the pH reading was less than 2. In general terms, groundwater samples reached the desired pH of less than 2 to by adding one mL of the acid to the sample container. Leachate samples, however, required the addition of 8 to 10 mL of concentrated HNO₃. After adding the acid, the sample containers were mixed thoroughly and their pH determined with litmus paper.

Each sample container was immediately labeled using a unique identification code to exclude the possibility of interchanging the samples or confusing their identity during the sampling campaign. The affixed sample labels were filled out with the following information written in waterproof ink: date and time of collection, initials of person(s) that collected the sample, preservative used, parameter to be analyzed, location where sample was taken, and sample name and ID.

To prevent contamination, all sample containers were handled with gloves at all times, sealed and bagged in double plastic bags immediately after they were collected. The samples were transported inside coolers filled with ice in order to maintain a temperature below 4 °C (Figure 3.21), and brought to the laboratory for analysis. All sample containers and coolers were inspected before each use. Collected samples of landfill leachate and groundwater were stored in separate ice coolers during the sampling trip.



Figure 3.21. Leachate samples in an ice cooler.

3.5.3.3 Soil Samples

In the case of soil samples, between sampling locations the shovel was thoroughly rinsed with distilled water in order to remove any soil from the previous sampling point, and used gloves were removed and replaced with new gloves prior to collecting each sample at every location. As a sampling strategy and in an effort to help prevent contamination of the background and field samples from any material that might

have remained on the shovel, soil samples at the point where contamination was presumed to be less were collected first.

All soil samples were collected in individual bags and then placed in zip-loc bags. Uniform slices of the same approximate volume of soil were obtained at each sampling point. To minimize the effects of microbial activity, sample bags were placed in a cooler partially filled with ice for transportation back to the laboratory. All soil samples were dried at 40 °C in an air drying oven (Figure 3.22) for at least 24 hours. Once dried, the samples were cleaned of any stones and plant residues. Before digestion, the soil samples were ground in a laboratory mill and passed through a 20 mm mesh sieve (see Figure 3.23). The sieved soil was collected and stored in plastic bottles for the required digestion process.



Figure 3.22. Oven used to dry soil samples.



Figure 3.23. Laboratory Mill.

3.6.0 Quality Assure and Quality Control (QA/QC) Procedures

3.6.1 General Cleaning Procedure

All glassware, instrumentation and sampling devices were cleaned before each sampling campaign to minimize interferences. The following procedure was performed: the device was rinsed with hot tap water, soaked in a solution of alconox detergent (in some cases, a non-metal brush or scrub pad was used to remove any particulate matter or surface film), rinsed with tap water while shaking vigorously for 30 seconds. After discarding the rinse water, the device was rinsed thoroughly with deionized water and finally rinsed with a 10% or 15% nitric acid solution (one volume concentrated nitric acid to five volumes deionized water). After decontamination, all sampling devices were wrapped in aluminum foil and stored.

3.6.2 Standard Operating Procedures (SOPs) and Documentation Procedure

Before embarking on each groundwater, leachate and/or soil sampling campaign, some additional preparations were required. These included use of the SOPs during all sampling process, calibration of the field pH and conductivity meters, preparation of field blanks, and filling out some portions of the field documentation sheets. Upon arrival at the sampling site, the field data record, GPS tracking and field inspection sheets were filled out. After sampling is performed, chains of custody sheets are also filled. All of these forms must be filled out in its entirety and signed by the person collecting the sample.

The field inspection sheet is used to report general information, weather conditions and possible sources of sample contamination near the sampling site. It is also used to report data regarding measured field parameters at the sampling point. A chain of custody form accompanies each sample from the moment of collection until its final disposition. The chain of custody process is designed to protect the integrity of the collected samples until they are analyzed. It includes information such as sample ID and

description, exact location and description of the site where sample was taken, volume and quantity of sample, type and size of container, dates and times of collection, type of sample (grab, composite, etc.), preservatives used (if any), the parameter and analysis to be performed, and the names and signatures of every person in custody of the sample from the moment of collection to the moment of disposal. For this study, field sheets containing GPS coordinates of each sampling point were also used. All documentation was signed or initialized with waterproof ink by the person responsible.

3.6.3 QA/QC Sample Procedure

At the same time that leachate and groundwater samples were collected, appropriate QA/QC samples were also gathered. The purpose of these samples is to determine any possible contamination introduced by the containers, the applicable preservatives, or the process of transportation and storage. QA/QC samples underwent the same process as the samples, with the only exception that they contained neither leachate nor groundwater.

3.6.3.1 Groundwater and Leachate QA/QC Samples

3.6.3.1.1 Trip Blanks

One trip blank was included in each cooler with ice that contained leachate or groundwater sample containers to verify and evaluate the potential cross-contamination that may occur during transport and storage. Trip blanks were prepared, prior to going into field, by filling sample containers with 500 mL of deionized water and treating with preservatives in the same manner as samples. Trip blanks are not opened in the field, nor are removed from the ice during the time of sample collection, but are submitted for analysis along with the samples.

3.6.3.1.2 Field Blank

A field blank is a sample container with 500 mL of deionized water that is prepared with the other bottles, and transported to the sample site to check for possible on-site contamination from the surroundings, and to verify if sample contamination occurred as result of adding a preservative (nitric acid in this case) to the sample. Contamination from the surroundings may result, for example, from exposure to polluted air at the sampling site. The field blank container cap was removed at the sampling point to expose the blank to ambient air while samples were collected (Figure 3.24). Once samples were taken, acid was added to the field blank container and then it was sealed again and placed in the cooler with the other samples until arrival at the laboratory. One field blank container was used for each sampling site.

Trip blanks and field blanks are treated exactly as samples. They were labeled, preserved, cooled, transported, stored, handled and documented as if they were samples.

3.6.3.1.3 Temperature Blank

A temperature blank was also used during all sampling campaigns. This blank consisted of a container filled with 500 mL deionized water that was placed in the ice cooler before embarking in the sampling process. It was used to measure the water temperature in order to insure that proper sample temperature (4 °C) was maintained during sample collection and until the samples were delivered to the laboratory. One temperature blank per cooler was used. The temperature blank allows the temperature of samples to be checked without disturbing or contaminating any of the field samples.

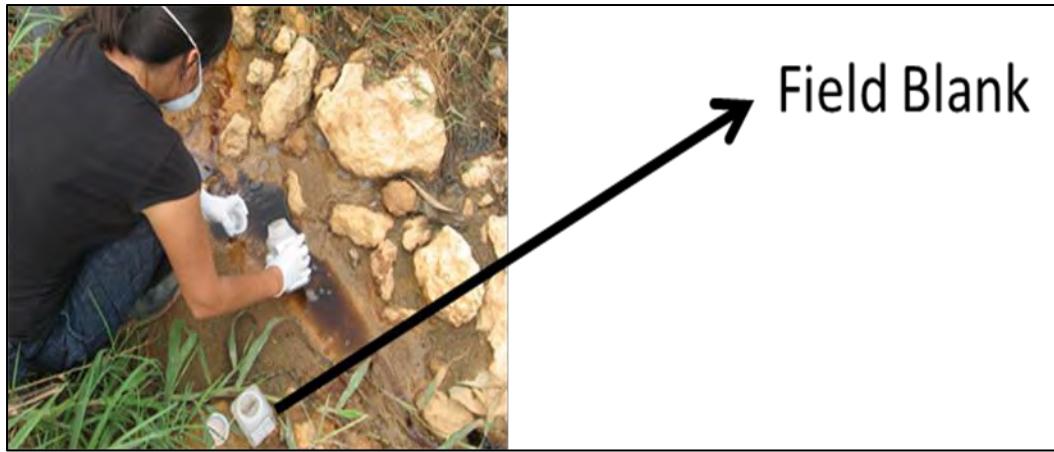


Figure 3.24. Uncapped field blank during the sample collection procedure.

3.6.4 QA/QC in Analysis

3.6.4.1 Field Triplicates Leachate and Groundwater Sample

For this study, field samples at each sampling point were collected in triplicate.

Field triplicates are three samples collected in series at the same sampling point and using the same sampling methodology. Field triplicates were used to evaluate the precision of the overall sample collection, site heterogeneity, and variability in the analytical process.

3.6.4.2 Field Quadruplicates Soil Sample

In the case of soil samples, field quadruplicates were collected at each sampling point. Field quadruplicates are four samples collected in series at the same sampling point and using the same sampling methodology. Field quadruplicates were used to assess change in heavy metal concentration in the soil, with increasing distance from the source of leachate, and also to evaluate the precision of the overall sample collection, site heterogeneity, and variability in the analytical process.

3.6.4.3 Spiked Samples:

Spiked samples were used to evaluate the recovery efficiency of the digestion process. An aliquot of 0.010 (± 0.005) mL of ICP-AES spike sample standard solutions of copper, lead, cobalt, nickel, zinc, chromium and iron, respectively, was added to 50.00 (± 0.02) mL of real sample. This yielded spiked samples with a total volume of 50.07 (± 0.05) mL and a spike analyte concentration of 0.200 ppm. Spiked samples were subjected to the same digestion and analytical procedure as all other field samples.

3.7.0 Sample Analysis

3.7.1 Field Measurements Procedure

Field measurement of temperature, conductivity and pH was performed in situ. The first two of the aforementioned parameters were determined using a HACH Model Sension 5 multiparameter meter; and the sample pH was measured using a HACH Model Sension 1 pH field meter (Figure 3.25). Conductivity is used as an indicator of dissolved inorganic species or total concentration of ions.

3.7.1.1 Leachate and Groundwater Procedure

In the case of groundwater samples, field measurements were taken prior to sample collection. After purging the stagnant water in the borehole, 50 mL of groundwater is poured into a 100 mL beaker and the probe of the conductivity meter is lowered into the sample. The meter's AUTOREAD function key is pressed. Once the reading is stabilized and an indicator STAB is displayed, the measured values for temperature and conductivity of the groundwater sample may be recorded on the field data sheet.



Figure 3.25. Conductivity and pH meters used to measure field parameters.

To measure the pH of a groundwater sample, the pH meter electrode is inserted into the sample beaker and the key AUTOREAD is pressed. Once the reading is stabilized, the measured value of pH for the groundwater sample may be recorded on the field data sheet.

For leachate samples, all three field measurements were performed after sample collection using the same procedure described above, with the only difference that the probe or electrode was immersed directly in the leachate stream.

All measured values were recorded on field data sheets. To check the accuracy and proper functioning of the meters throughout the sampling campaign, the field parameters were measured every ten samples in duplicate to insure that measured values were reproducible.

3.7.1.2 Soil Procedure

In the case of soil samples, field measurements were performed after sample collection. A total amount of 20.0 g of soil was placed in a 50 mL beaker and 20 mL of deionized water was added. The suspension was continuously stirred for 5 min. The soil suspension was left standing for about 1 hr to allow most of the suspended clay to settle out of suspension. After an hour had elapsed, pH and conductivity measurements were made following the same procedure described above for groundwater and leachate samples.

3.7.2 Laboratory Analyses

3.7.2.1 Sample Preparation

The samples were subjected to acid digestion prior to analysis in order to reduce interference by organic matter and to insure that all metals associated to the soil particulate are in a form than can be determined by inductively-coupled plasma (ICP) spectroscopy (usually as free metal ions).

3.7.2.1.1 Sample Digestion of Groundwater and Leachate

All leachate and groundwater samples were digested at the Research Center of the Pontifical Catholic University (PUCPR) in Ponce. This procedure was performed using a Microwave Digestion System MDS 2000 with temperature and pressure control (CEM Corp, USA) (see Figure 3.26). This instrument has an operator selectable power output with a range of 0 to 630 W \pm 50 W, and a direct drive alternating turntable. The digestion procedure used at the PUCPR laboratory is specifically designed for use with USEPA-approved methods for the analysis of sample; so, in order to insure compliance, the same procedure was used for this study. The Table 3.08 summary of conditions of equipment.

Table 3.08. Microwave conditions for the digestion of leachate and groundwater samples.

Temperature (°C)	85
Power % (12 vessels)	100
Pressure (psi)	32
Time at Pressure (min)	8
Time (min)	20
Fan Speed	100



Figure 3.26. MDS-2000 microwave system.

Prior to performing the digestion, the microwave vessels and all materials used were soaked in alconox, rinsed with deionized water and rinsed with nitric acid solution. The nitric acid (HNO_3) as well as the hydrochloric acid (HCl) used for sample digestion were Fisher trace-metal grade acids. A volume of 3.0 mL concentrated HNO_3 and 2.0 ml

of concentrated HCl were added to 50 mL of sample in a microwave transparent vessel.

Figure 3.27 shows the main components of the digestion vessels. These were put together following the instructions provide by the manufacturer. These involve, among other things, connecting a chemically resistant inner line, using a cover to contain and isolate the sample while under high pressure, and placing a hollow plastic screw. The correct order to assemble all pieces is shown in Figure 3.28. The vessels were capped, placed in a carrousel and then positioned in the turntable. The carrousel has capacity for one control digestion vessel (which only contains deionized water and both acids) and 11 sample vessels. Each position in the carrousel was marked with a number to identify the samples. Whenever less than 12 containers were placed in the carrousel, the containers were distributed to achieve weight balance in the carrousel. Figure 3.29 shows a carrousel with a control digestion vessel and 7 sample vessels.

The carrousel with the control and sample vessels was then placed inside the microwave digester and heated under pressure at the conditions shown in Table 3.08. All containers were labeled and recorded in the log book to prevent problems with sample identification. Once the digestion process was completed, the clear, colorless samples were allowed to cool, and quantitatively transferred to acid-clean centrifuge vessels for ICP analysis (see Figure 3.30).

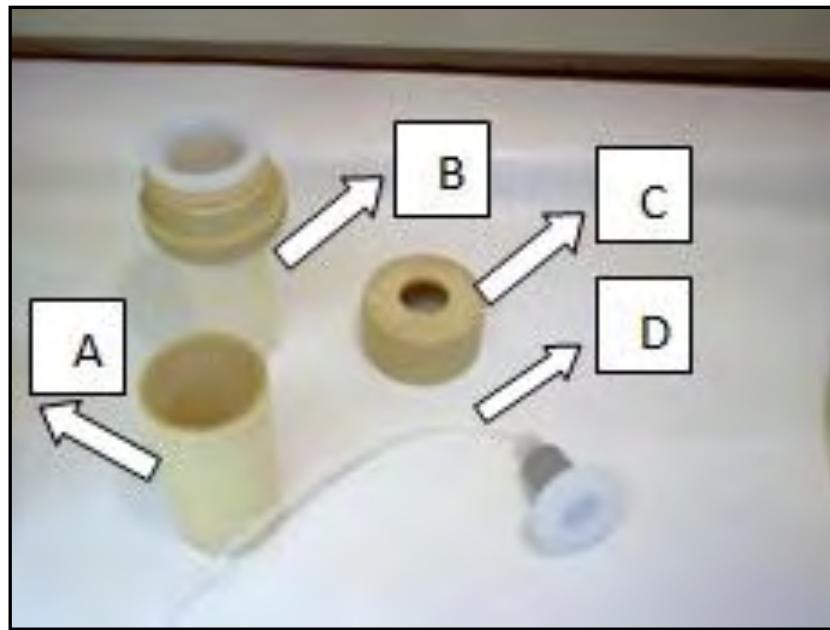


Figure 3.27. The main components of the digestion vessel:

(A) Special cover; (B) Sample vessel; (C) Hollow plastic screw;
and (D) High-Pressure resistant threaded closure.

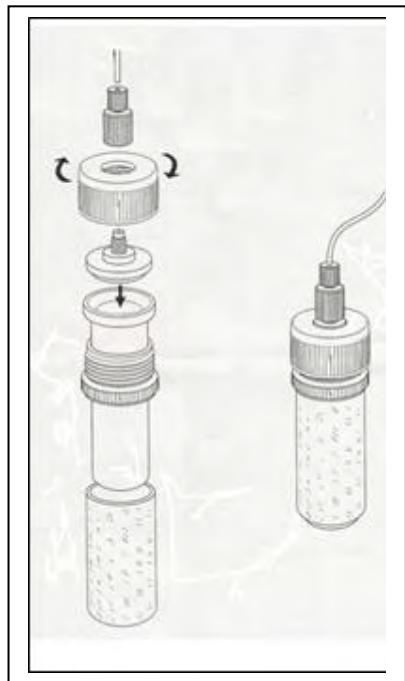


Figure 3.28 Digestion vessel assembly

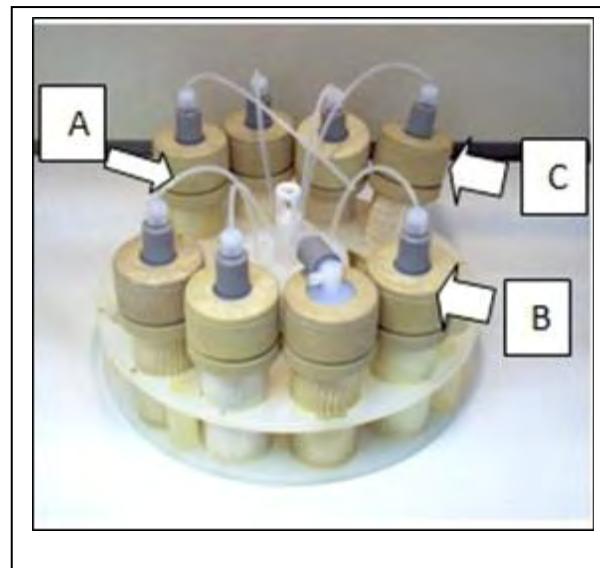


Figure 3.29. View of microwave carrousel with seven digestion vessels (A), one control vessel (B) and (C), for example.



A



B

Centrifuge Vessel

Figure 3.30. A: The carrousel inside the microwave oven after digestion. Photo B: samples that have been transferred to centrifuge vessels for ICP analysis.

3.7.2.1.2 Soil Sample Digestion

All soil samples were digested at the USDA Forest Service Institute of Tropical Forestry Laboratory, following SOPs based on USEPA method 3050 B. (USEPA SW-846 update 2008). The digestion procedure used was specifically designed for use with EPA methods for the analysis of sample. Soil samples were digested in an open vessel system, using 50 mL HD polyethylene vials and an aluminum-heating block with remote temperature control (Figure 3.31).

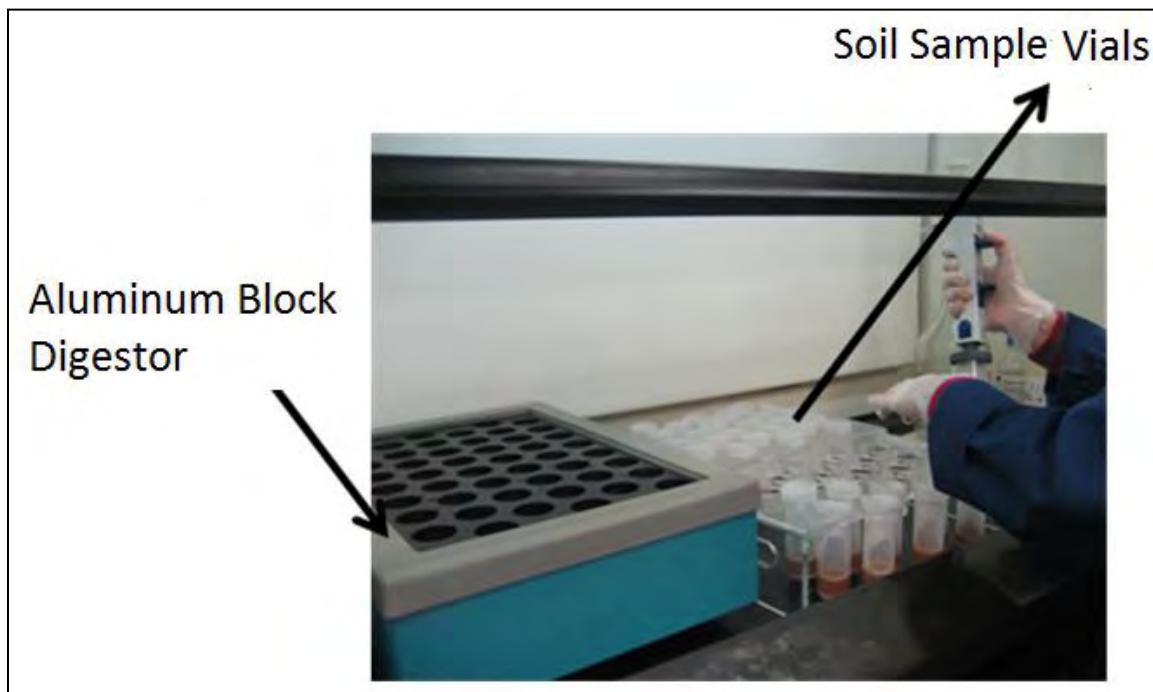


Figure 3.31. Aluminum Block Digestor and soil sample vials.

A volume of 5 mL of concentrated HNO_3 was added to each sample (which contained approximately 0.5000 g of dry soil) and the treated sample was left to stand overnight at room temperature. The following day, each sample was heated to 100 °C for 15 min in the digestor. After a cooling period, a 10 mL mixture of 1:1 HNO_3 and deionized water was added, and each sample was heated to 95 °C for 2 h. After cooling,

4 mL of 30% H₂O₂ was added. The samples were once again heated to 95 °C for 10 min and then cooled. This was followed by the addition of 2 mL concentrated HCl, after which the samples were again heating to 95 °C for 30 min.

During the digestion, all vials were covered with watch glasses. The samples were then cooled and the volume was adjusted to 50.0 mL by adding deionized water. To determine the accuracy and precision of the analysis, soil standard samples were digested along with the field samples. Finally, all samples were filtered and collected in HDPE bottles. To avoid any possible metal and/or boron contamination during the digestion process, the body of all digestion vessels was made of Teflon PFA and the watch glasses were made of polypropylene. Figure 3.32 shows the soil samples in the digestor and the final filtration of soil samples. All samples were analyzed for Ca, Mg, P, K, AL, Fe, Mn, Cr, Co, Zn, Ni and Pb, by means of an Inductively Coupled Plasma (ICP) Emission Spectrometer (Spectro Ciros CCD).

3.7.2.2 Analytical Procedure for Leachate, Groundwater and Soil Samples

The groundwater, leachate and soil samples were analyzed for 7 inorganic macro components and to six heavy metals. All samples were characterized using Inductively Coupled Plasma Optical Emission Spectroscopy following of USEPA methodology (USEPA SW 846 2008) and US Forest Service procedures.

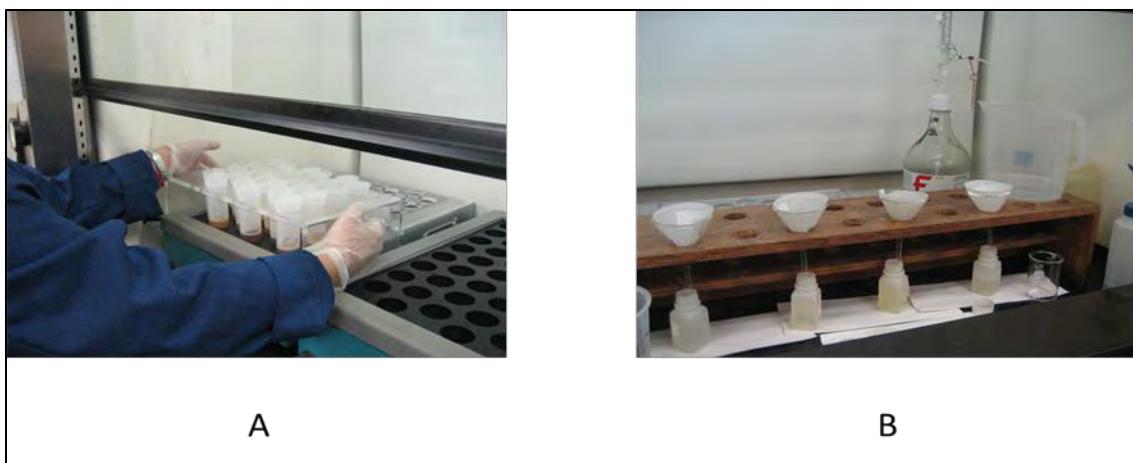


Figure 3.32. The soil samples in the digestor and the final filtration of these samples.

3.7.2.2.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP optical emission spectroscopy measurements to determine the concentration of aluminum, calcium, iron, potassium, magnesium, manganese, sodium, copper, cobalt, chromium, lead, zinc, and nickel were performed by the USDA Forest Service Institute of Tropical Forestry Laboratory using a Spectro Ciros CCD ICP optical emission spectrometer (Spectro Analytical Instruments, Kleve, Germany) with axial plasma viewing and auto sampler.

Prior to measurement, the following procedure was performed. The instrumental parameters were adjusted and the ICP system was cleaned and conditioned according to the manufacturer's specifications. Helium supply and gas lines were verified for leaks, and system performance was checked by running a system blank. Five data point calibration curves in the 0.00100 to 100 ppm range were developed using multi-element standard solutions. The control samples used: Montana (NBS-2511), Peach Leaves (NIST-1547) and Pine Needles (NIST-1575) were obtained from the National Institute of Standards and Technology (NIST, USA). All groundwater and leachate samples were analyzed in triplicate and the soil samples were analyzed in quadruplicate. All data were

recorded in Excel software and expressed as ppm. Table 3.09 shows the ICP-OES operational parameters; and Table 3.10 shows the instrumental conditions for analysis of each metal ion.

Table 3.09. ICP-OES operational parameters.

Operating power	1400 w
Plasma gas flow rate	12L/min
Auxiliary gas flow rate	1L/min
Sample pump flow	2L/min
Nebulizer gas flow rate	1L/min
Spray chamber	cyclonic
Background correction	0
Plasma viewing	Axial
Processing mode	Area

Table 3.10. Estimated detection limits, wavelength and excitation energy for heavy metal.

Metal	Wavelength (nm)	Estimated IDL (mg/L)	Excitation energy (ev)
Cr	267.716	0.0027	3.57-11.14
Cu	324.754	0.0067	3.82-15.96
Fe	259.94	0.0004	15.01-2.64
Pb	220.353	0.0015	13.05
Ni	231.604 X2	0.0008	13.22
Zn	213.856 X2	0.0044	5.8- 7.78

3.7.3. Holding Time and Summary of the Requirements Used for Sampling and Analysis

All procedures and requirements, including the waiting time for the measurements or analysis in this study were based on USEPA-approved methods which are widely reported in the literature (Pinel-Raffaitin et al. 2006). Table 3.11 summarizes these requirements.

3.7.4 Data Analysis

Sampling results for leachate, groundwater and soil parameters from all sampling sites and points were tabulated. The full data set for leachate and groundwater samples are included in appendix B and C and those for soil are included in appendix D. All data were entered in Microsoft Excel and exported to Minitab 16 for statistical analyses

Table 3.11. Collection, preservation and holding time requirements.

Parameters	Volume ml	Container	Preservation	Holding time
pH	100	Polyethylene	None required	Analyze immediately
Temperature	100	Polyethylene	None required	Analyze immediately
Total Metal	500	Polyethylene	HNO ₃ to pH <2, cool 4°C	6 months

Note: Immediately is defined as “within 15 min of sample collection”.

Descriptive statistics such as mean, range, minimum, maximum and standard deviation were generated for all parameters measured. For statistical purposes, a value of zero was entered in Excel for any analyte not detected in a given sample. However, if an analyte was not detected in all samples taken at a given point, a value of ND (not

detected) was entered in the data tables. Mean comparison statistics was performed for all field parameters, inorganic macrocomponents and heavy metals. Variations in leachate quality parameters in relation to the seasons (dry and wet) and to the type of waste deposited were also studied. Other studies conducted include the statistical analysis of (1) leachate analyte concentrations between two points of the same landfill, (2) leachate analyte concentrations between landfills, and (3) groundwater and soil analyte concentrations as a function of distance to the Toa Baja landfill. To test the hypothesis of equal variance between the populations, a t-student test and Anova were performed. Statistical difference between the sites or point sampling for each parameter analyzed would be determined with the results of the test statistic (unpaired and paired t-test).

Chapter Four

Results

This chapter begins with a presentation of the SOPs developed for this research and a presentation of QA/QC results. It also provides an extensive explanation, by section, of the results obtained for the different sample matrices (leachate and groundwater). Sampling and analysis was performed for leachate, groundwater and soil. Each of these matrices was characterized in terms of field parameters, inorganic macrocomponents and heavy metals. The results obtained for each matrix are presented separately. Whenever sufficient data were available, graphs were prepared to show trends or comparisons between the parameter observed for each site or sampling point. The means and standard deviations obtained for each parameter are also listed.

4.1.0 Standard Operating Procedures and Control QA/QC

4.1.1 Elaboration and Implementation of Standard Operating Procedures (SOPs)

Before engaging in any sample collection, a literature search was conducted to determine if SOPs for leachate sampling were available. After some searching it became clear that SOPs for these procedures did not exist. SOPs based on USEPA approved procedures, standard methods and literature search were elaborated and implemented (USEPA SW 846 update 2008; Clesceri et al. 1989; Csurus. 1994; Cecen et al. 2000; Pinel-Raffitin et al. 2006). SOPs were designed, prepared and implemented in order to ensure good data quality throughout all sampling campaigns. Appendix A presents the SOPs elaborated. For groundwater well sampling, SOPs 023 prepared by the PREQB was used. Soil sampling was performed using FDEP standard operating procedures (IITFL 2007).

4.1.2 Field and laboratory QA/QC Results

4.1.2.1 Field Parameters QA/QC

In each of the campaigns and after meter calibration, duplicate pH and conductivity (EC) measurements were made in order to determine accuracy and consistency of results. The measured values were similar to one another, with a standard deviation of 0.014 for the March, July and October campaigns, and 0.007 for the April campaign, at a 95% uncertainty interval.

4.1.2.2 Laboratory Analysis QA/QC Results

Results of QA/QC analyses (field and trip blanks and spike, duplicate and quadruplicate samples), were used to evaluate the quality of the data for leachate and groundwater samples. Assessment of the blank and trip results show that these values, with the exception of Cr (0.033 mg/L), were negligible with respect to those obtained for the samples. The sample concentrations of Cr were thus corrected by subtracting the Cr concentration in the blank. As a result of this correction, three samples had to be censored for having the same Cr concentration (0.033 mg/L) as the blank. According to Georgian (2000) and Zaugg et al. (2002), the acceptable range for set spike recoveries is 70-130% (R) and is defined by the following equation

$$R = 100 (C_f - C_l) / C_s$$

Where C_f is the measured amount of analyte for the unspiked sample, C_l is the measured amount of analyte for the spiked sample and C_s is the amount of analyte that is spiked. For this study, percent recovery of samples taken during the March 2010 campaign fall in the range of 83% - 105% R (Cr = 97%; Cu = 90%, Zn = 105%, Co = 102% and Pb = 83%). In general terms, for the vast majority of parameters measured, the concentrations reported accurately represent the actual concentration in samples taken from each site and point.

4.2.0 Leachate Samples

This section details the results obtained from the analysis of leachate from the Toa Alta and Toa Baja landfills and the Toa Baja Landfill's "Camino" and 'Minga' Points. Leachate samples were characterized for field parameters, inorganic macrocomponents and heavy metals. Two of the goals were to determine the influence of waste composition and seasonal variation on leachate quality.

4.2.1 Toa Alta and Toa Baja Leachate Characterization

The leachate characterization or quality parameters for the Toa Alta and Toa Baja landfill are listed in Tables 4.1 to 4.6. All leachate samples were characterized in terms of field parameters, inorganic macrocomponents and heavy metals. All data obtained are included in Appendix C.

4.2.1.1 Field Parameter Results

Leachate temperature, pH and conductivity (EC), which are measured directly in the field, are classified as field parameters. Values obtained for these field parameters are listed in Table 4.01. Leachate temperature from the Toa Alta landfill, taken during the April 2009 at March 2010 campaigns, was found to be in the range of 26.0 °C to 30.0 °C; whereas leachate from the Toa Baja landfill, taken during the April 2009 at March 2010 campaigns, ranged from 34.4 °C to 36.9 °C.

Table 4.01. Field parameters for leachate at the Toa Baja and Toa Alta landfills.

Variables	Mean ± SD		Minimum		Maximum	
Parameter	Toa Alta Landfill	Toa Baja Landfill	Toa Alta Landfill	Toa Baja Landfill	Toa Alta Landfill	Toa Baja Landfill
Temperature (°C)	28.5±1.7	35.7± 0.9	26.0	34.4	30.0	36.9
pH	8.20 ± 0.14	8.20 ± 0.21	8.05	7.93	8.38	8.56
EC (µS/cm)	10 115 ± 7297	18 485±3782	4300	13 975	19 700	22 825

The pH values ranged from 8.05 to 8.38, and from 8.56 to 7.93, at the Toa Alta and Toa Baja landfills, respectively. The highest (8.56) and lowest (7.93) leachate pH values were measured in the Toa Baja Landfill. However, no statistical difference in pH was observed among leachate from the two landfills (*p*-value = 0.938).

Large variations in leachate EC were observed, with mean values of $10,115 \pm 7,297$ and $18,485 \pm 3782 \mu\text{S}/\text{cm}$ for the Toa Alta and Toa Baja landfills, respectively. The EC measurements for collected samples were found to be in the range of 4300 to 19,700 $\mu\text{S}/\text{cm}$ at the Toa Alta landfill, and 13,975 to 22,825 $\mu\text{S}/\text{cm}$ at the Toa Baja landfill. During all sampling campaigns, the conductivity of the Toa Baja landfill leachate was consistently higher than that for the Toa Alta landfill. The relatively high values of electrical conductivity (EC) indicate the presence of inorganic ions in the samples.

4.2.1.2 Inorganic Macrocomponent Results:

Results for the inorganic macrocomponents analyzed are shown on Table 4.02. Mean values for Al, Ca, Mg, Mn, Fe, K and Na in Toa Baja landfill, are $1.580 \pm 1.065 \text{ mg/L}$; $58.109 \pm 43.770 \text{ mg/L}$; $31.033 \pm 19.525 \text{ mg/L}$; $0.277 \pm 0.324 \text{ mg/L}$; $15.446 \pm 17.029 \text{ mg/L}$; and $723.421 \pm 251.328 \text{ mg/L}$, respectively. These mean values are higher than those found in the Toa Alta landfill. The maximum concentrations of these macrocomponents were also found in Toa Baja (Al: 3.671 mg/L; Ca: 163.833 mg/L; Mg: 74.267 mg/L, Mn: 1.050 mg/L; Fe: 14.063 mg/L; K: 989.333 mg/L; Na: 2025.333 mg/L). These concentrations are higher than those measured in Toa Alta (Al: 0.531 mg/L; Ca: 81.533 mg/L; Mg: 42.837 mg/L, Mn: 0.203 mg/L; Fe: 6.447 mg/L; K: 494.267 mg/L; Na: 624.733 mg/L).

Table 4.02. Statistical summary for inorganic macrocomponents of leachate at Toa Baja and Toa Alta landfills.

Parameter (mg/L)	Mean ± SD		Minimum		Maximum	
	Toa Alta Landfill	Toa Baja Landfill	Toa Alta Landfill	Toa Baja Landfill	Toa Alta Landfill	Toa Baja Landfill
Aluminum	0.440±0.074	1.580±1.065	0.353	0.441	0.531	3.671
Calcium	66.183±13.445	58.109±43.770	53.233	28.457	81.533	163.833
Magnesium	24.068±12.807	31.033±19.525	14.477	14.467	42.837	74.267
Manganese	0.146±0.061	0.277±0.324	0.085	0.024	0.203	1.051
Iron	2.705±2.501	15.446±17.029	1.216	1.041	6.447	14.053
Potassium	267.958±154.614	723.421±251.328	155.433	156.367	494.267	989.333
Sodium	501.842±100.070	1503.390±475.499	388.902	398.933	624.733	2025.333

Na presented the highest relatively concentration of all inorganic macrocomponents detected in leachate samples in both Toa Alta and Toa Baja landfills, followed by K and Ca. The parameter of lowest concentration among those measured in both landfills was Mn, with values of 0.203 mg/L and 1.050 mg/L, respectively, for the Toa Alta and Toa Baja landfills. For all inorganic macrocomponents, with the exception of calcium, the Toa Baja landfill showed higher concentrations than Toa Alta landfill (see Figure 4.01).

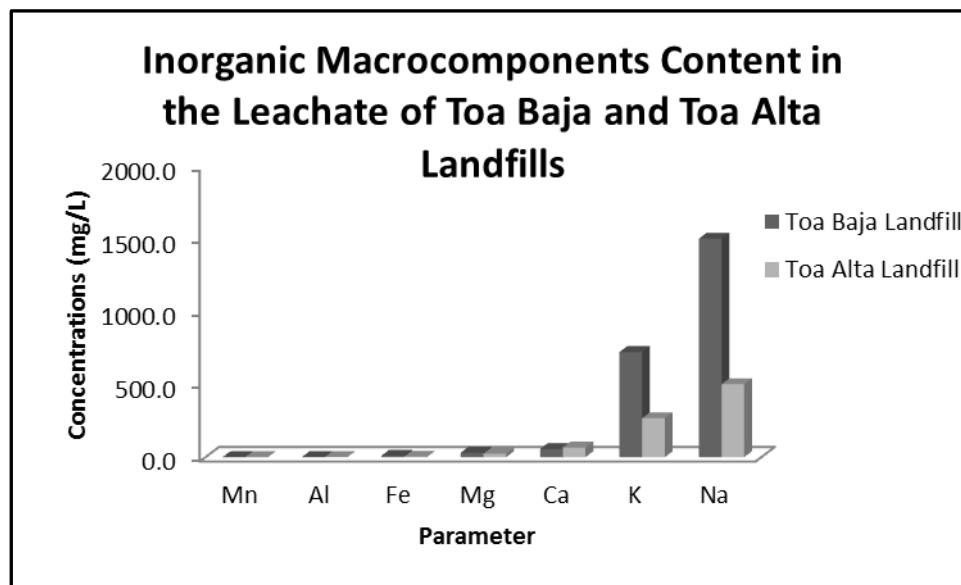


Figure 4.01. Inorganic macrocomponent concentrations at Toa Alta and Toa Baja landfills.

4.2.1.3 Heavy Metal Results

Leachate samples were analyzed for six heavy metals: Cr, Co, Cu, Ni, Pb and Zn. Values for heavy metals in Toa Alta and Toa Baja landfills leachate, including Co, Cr, Cu, Ni Pb, and Zn, are shown in Table 4.03. The mean values with standard deviations (in mg/L) for Toa Alta are: Cr: 0.068 ± 0.051 ; Ni: 0.088 ± 0.044 ; Zn: 0.134 ± 0.232 ; Co: 0.023 ± 0.020 ; and Pb: 0.001 ± 0.000 . For Toa Baja, the means are: Cr: 0.280 ± 0.132 ; Cu: 0.072 ± 0.101 ; Ni: 0.164 ± 0.143 ; Zn: 0.580 ± 0.492 ; Co: 0.115 ± 0.112 ; and

Pb: 0.039 ± 0.034 . Of all the heavy metal concentrations studied, the highest in both landfill leachates (Toa Alta and Toa Baja) is Zn, with concentrations of 0.482 mg/L and 1.278 mg/L , respectively.

Table 4.03. Heavy metal of leachate at Toa Baja and Toa Alta landfills.

Parameter (mg/L)	Mean \pm SD		Minimum		Maximum	
			Toa		Toa	
	Toa Alta Landfill	Toa Baja Landfill	Toa Alta Landfill	Baja Landfill	Toa Alta Landfill	Baja Landfill
Chromium (Cr)	0.068 ± 0.051	0.280 ± 0.132	0.036	0.022	0.137	0.412
Cobalt (Co)	0.023 ± 0.020	0.115 ± 0.112	0.000	0.007	0.050	0.377
Copper (Cu)	0.000 ± 0.000	0.072 ± 0.101	0.000	0.000	0.000	0.264
Lead (Pb)	0.001 ± 0.000	0.039 ± 0.034	0.000	0.000	0.004	0.078
Nickel (Ni)	0.088 ± 0.044	0.164 ± 0.143	0.047	0.000	0.127	0.346
Zinc (Zn)	0.134 ± 0.232	0.580 ± 0.492	0.000	0.014	0.482	1.278

The lowest concentrations of heavy metals recorded in Toa Alta and Toa Baja landfill leachate were for Cr and Co. In general terms, among all heavy metals studied in Toa Alta and Toa Baja landfill leachates, the highest concentrations were recorded at the Toa Baja landfill (see Figure 4.02).

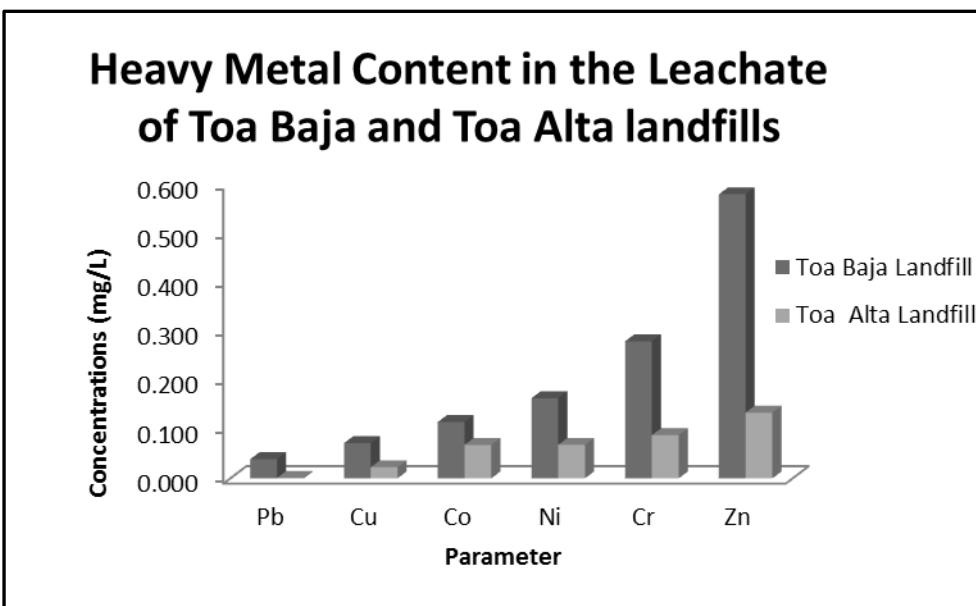


Figure 4.02. Heavy metal concentrations of Toa Baja and Toa Alta landfills.

4.2.2 Toa Alta and Toa Baja Leachate Characterization in Dry and Wet Seasons

In order to analyze the seasonal variability of leachate quality for the Toa Alta and Toa Baja landfills, samples collected during the dry and wet seasons were compared. Table 4.04 present of values of parameter in dry and wet season for Toa Alta and Toa Baja Landfills.

4.2.2.1 Field Parameters Results

The pH values for leachate samples collected at Toa Alta landfill were found to be slightly more alkaline during the dry season; but in general terms, the leachate pH value for both landfills remained relatively constant during both seasons. Leachate samples from Toa Alta landfill had mean pH values that ranged from 8.28 ± 0.14 during the dry season to 8.12 ± 0.10 during the wet season. Leachate from Toa Baja landfill exhibited pH values in the 8.19 ± 0.18 to 8.19 ± 0.26 range during the dry and wet seasons, respectively. As to electrical conductivity, however, leachate samples from the Toa Alta and Toa Baja landfills exhibit higher EC values during the wet season.

4.2.2.2 Inorganic Macrocomponents Results

The concentration of inorganic macrocomponents in leachate collected at the Toa Alta and Toa Baja landfills was higher during the dry period than in the wet period (see Figure 4.03). These results are consistent with the fact that in the wet season, rain percolating through the landfill wastes results in a larger volume of dilute leachate, thus lowering the measurable concentration of soluble ions (Tatsi et al. 2002).

Table 4.04. Physicochemical characteristics of Toa Alta and Toa Baja leachate samples during the dry and wet seasons.

Parameter	Toa Alta Landfill		Toa Baja Landfill	
	Dry Season	Wet season	Dry Season	Wet season
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Field Parameter				
pH	8.28±0.14	8.12±0.10	8.19±0.18	8.19±0.26
EC µs/cm	8100± 5374	12 130±10 706	15 590±3218	21 380±2246
Inorganic Components (mg/L)				
Aluminum (Al)	0.442±0.126	0.439±0.022	1.907±1.220	1.253±0.930
Calcium (Ca)	67.383±20.011	64.983±11.667	73.141±61.131	43.077±11.433
Iron (Fe)	3.950±3.531	1.462±0.348	9.530±3.621	7.866±4.610
Potassium (K)	339.600±218.732	196.317±57.818	778.667±147.189	668.175±342.908
Magnesium (Mg)	30.313±17.711	17.823±4.733	35.338±26.731	26.728±11.202

Table 4.04., continued.

Manganese (Mn)	0.139±0.076	0.152±0.072	0.402±0.440	0.153±0.101
Sodium (Na)	544.467±113.514	459.217±99.443	1674.500±248.105	1333.400±623.25
Heavy Metal (mg/L)				
Chromium (Cr)	0.098±0.056	0.039±0.004	0.332±0.068	0.228±0.169
Copper (Cu)	ND	ND	0.332±0.068	0.228±0.169
Nickel (Ni)	0.124±0.004	0.052±0.008	0.160±0.186	0.167±0.096
Zinc (Zn)	0.267±0.305	0.002±0.003	0.610±0.423	0.550±0.617
Cobalt (Co)	0.041±0.000	0.005±0.007	0.105±0.023	0.125±0.171
Lead (Pb)	ND	0.002±0.003	0.046±0.031	0.033±0.039

ND: Not detected

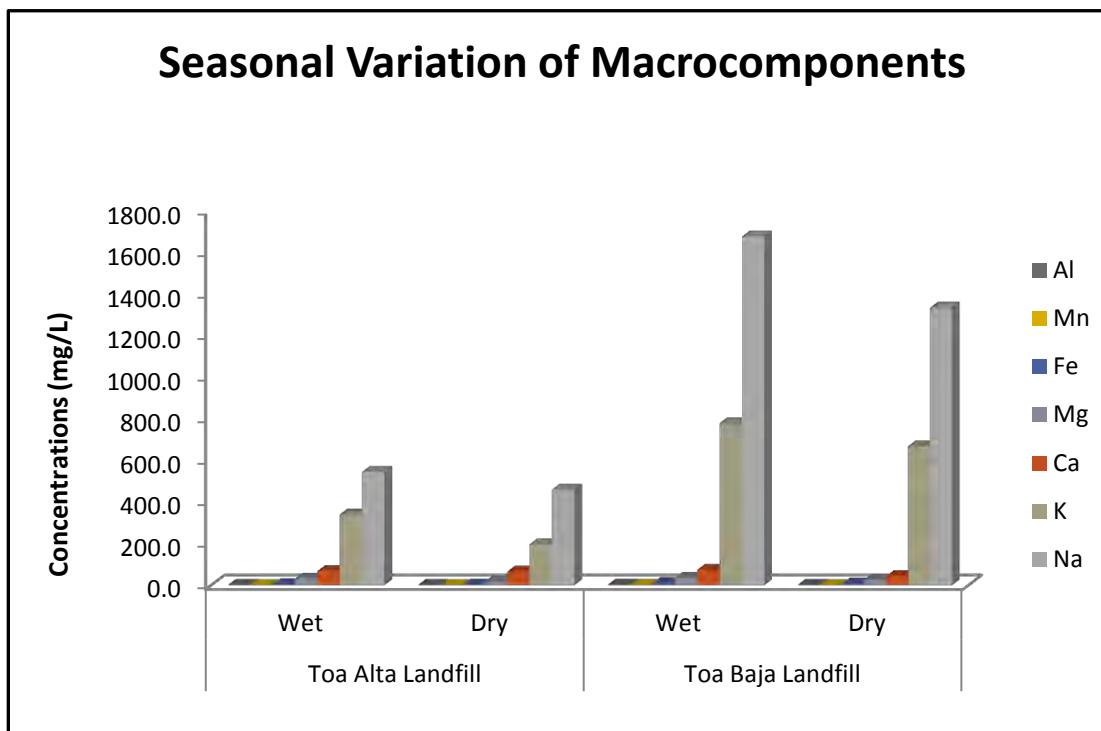


Figure 4.03: Seasonal variation of inorganic macrocomponent concentration in the Toa Alta and Toa Baja landfills.

4.2.2.3 Heavy Metal Results

In the case of heavy metals the same pattern is observed for the Toa Alta landfill, as all mean values of heavy metals in leachate were highest during the dry period (see Figure 4.04). With the exception of Co and Ni, this observation is also true for leachate collected at the Toa Baja landfill (see Figure 4.05).

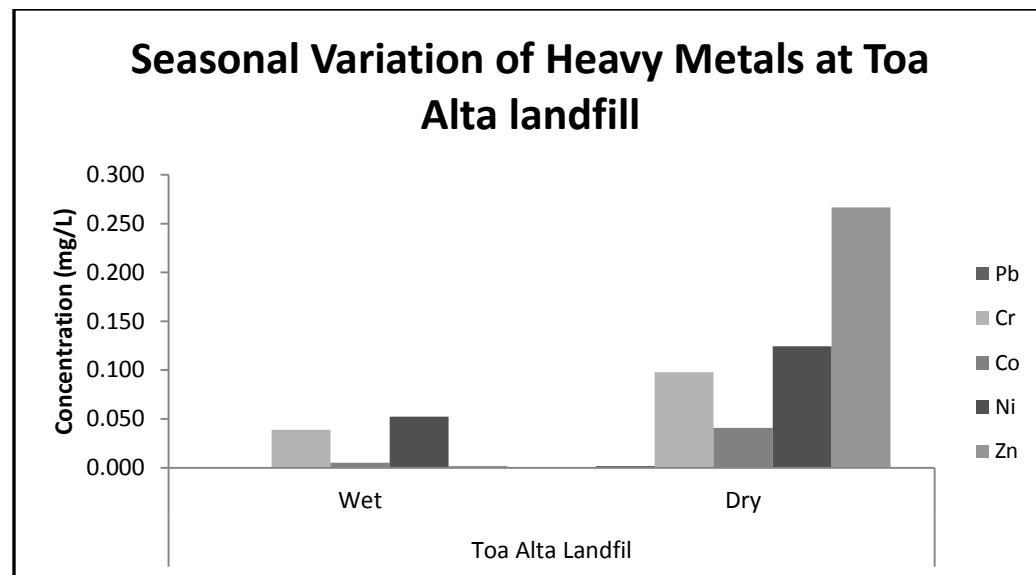


Figure 4.04. Seasonal variations of heavy metals at Toa Alta landfill.

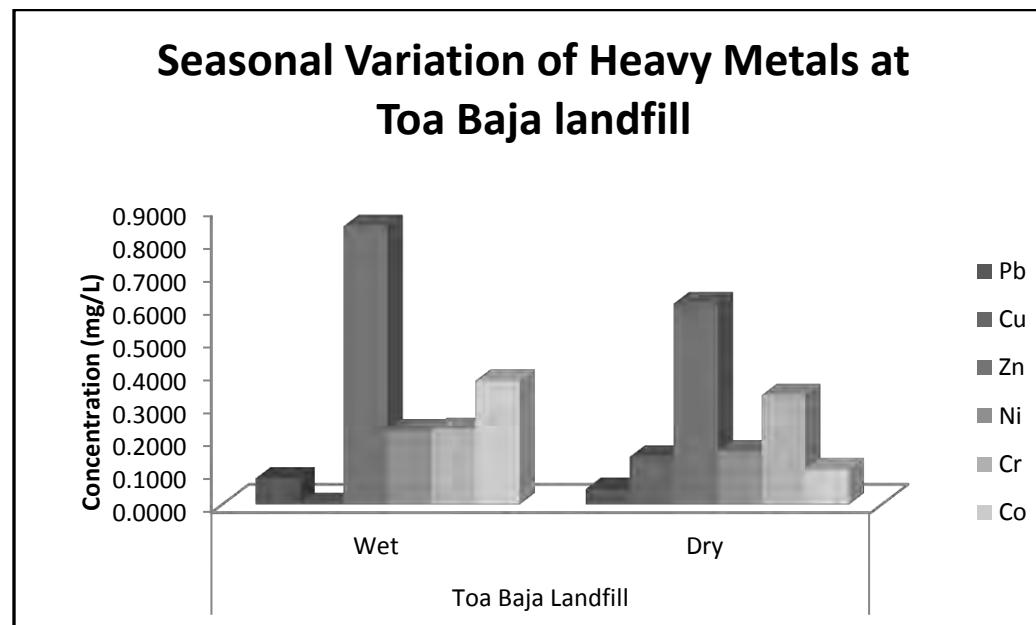


Figure 4.05. Seasonal variations of heavy metals at Toa Baja landfill.

4.2.3 Leachate Characterization at Toa Baja landfill's "Camino" and 'Minga' Points

To determine the influence of the type of waste on leachate heavy metal composition, two different sampling points in the Toa Baja landfill were chosen. These two points differ by the type of waste deposited in them. Point 1 or "Minga" is close to the scrap deposits, whereas Point 2 or "Camino" is in an area far away from the scrap deposits.

Both points were characterized in terms of field parameters, inorganic macrocomponents and heavy metal composition for the purpose of comparison. Results of leachate characterization at each of these points are presented in Tables 4.05 to 4.07.

4.2.3.1 Field Parameter Results

Results for field parameters (temperature, pH and electrical conductivity) are listed in Table 4.05. Leachate temperature for the "Minga" landfill point was found to be in the range between 35.0 °C and 36.0 °C; whereas for the "Camino" point, the temperature ranged from 34.4 °C to 36.9 °C. The pH values ranged from 8.16-8.56 and 7.93-8.20 for Minga and Camino points, respectively. The highest pH value was found in "Minga" point. The EC mean values and standard deviations were 17 295±4528 and 19 674±3670 μ S/cm for "Minga" and "Camino" landfill points, respectively. The EC measurements of the samples collected were found to be in range of 13 650 to 23 350 μ S/cm for "Minga", and 14 300 to 22 300 μ S/cm for "Camino". The relatively high values of EC found in this study indicate the presence of inorganic ions in the leachate samples.

Table 4.05. Leachate field parameters at Minga and Camino landfill points.

Parameter	Mean ± SD of Leachate Landfill Points		Value Range of Leachate Landfill Points	
	Minga	Camino	Minga	Camino
Temperature °C	35.5±0.5	35.9±1.2	35.0-36.0	34.4-36.9
pH	8.33±0.18	8.05 ±0.13	8.16-8.56	7.96-8.20
EC (μ S/cm)	17 295±4528	19 674±3670	13 650-23 350	14 300-22 300

4.2.3.2 Inorganic Macrocomponents Results

Data regarding the inorganic macrocomponents studied (Al, Ca, Mg, Mn, Fe, K and Na) are presented on Table 4.06. At “Minga” landfill point the mean concentrations (with standard deviation) for Al, Ca, Mg, Mn, Fe, K and Na, were: 1.972±1.329; 73.157±61.312; 11.232±2.048 821.250±133.558; 37.553±25.367; 0.394±0.452; 1626.000±51.994 respectively. Leachate values for “Camino” yielded 1.188±0.685; 43.061±10.355; 6.165±3.857; 625.592±322.533; 24.513±11.517; 0.161±0.070; and 1381.900±696.5200 for Al, Ca, Mg, Mn, Fe, K and Na, respectively.

Table 4.06. Inorganic macrocomponents of leachate at Minga and Camino landfill points.

Parameter (mg/L)	Mean ± SD of leachate Landfill Points		Value Range of Leachate Landfill Points	
	Minga	Camino	Minga	Camino
Aluminum (Al)	1.972±1.329	1.188±0.685	0.449-3.671	0.441-2.041
Calcium(Ca)	73.157±61.312	43.061±10.355	28.457-163.833	30.165-53.667
Iron (Fe)	11.232±2.048	6.165±3.857	9.167-14.063	1.041-10.347
Potassium (K)	821.250±133.558	625.592±322.533	663.667-989.333	156.367-884.333
Magnesium (Mg)	37.553±25.367	24.513±11.517	20.107-74.267	14.467-37.613
Manganese (Mn)	0.394±0.452	0.161±0.070	0.024-1.050	0.083-0.247
Sodium (Na)	1626.000±51.994	1381.900±696.5200	1554.000-1667.333	398.933-2025.333

Among all the inorganic macrocomponents studied, with the exception of Na, maximum heavy metal concentrations were found at “Minga” (Al: 3.671 mg/L, Ca : 163.833 mg/L; Fe : 14.063 mg/L; K : 989.333 mg/L; Mg : 74.267 mg/L, and Mn : 1.050 mg/L); whereas the maximum concentration of Na was found at “Camino” (Na : 2025.333 mg/L). Among inorganic concentrations detected in both leachates, Na presented the relatively highest value, followed by K and Ca, whereas the lowest figure is for Mn in both landfill points. For both landfills, the concentration of inorganic macrocomponents follows the same trend, i. e.: [Na] > [K] > [Ca] > [Mg] > [Fe] > [Al] > [Mn] (see Figure 4.06).

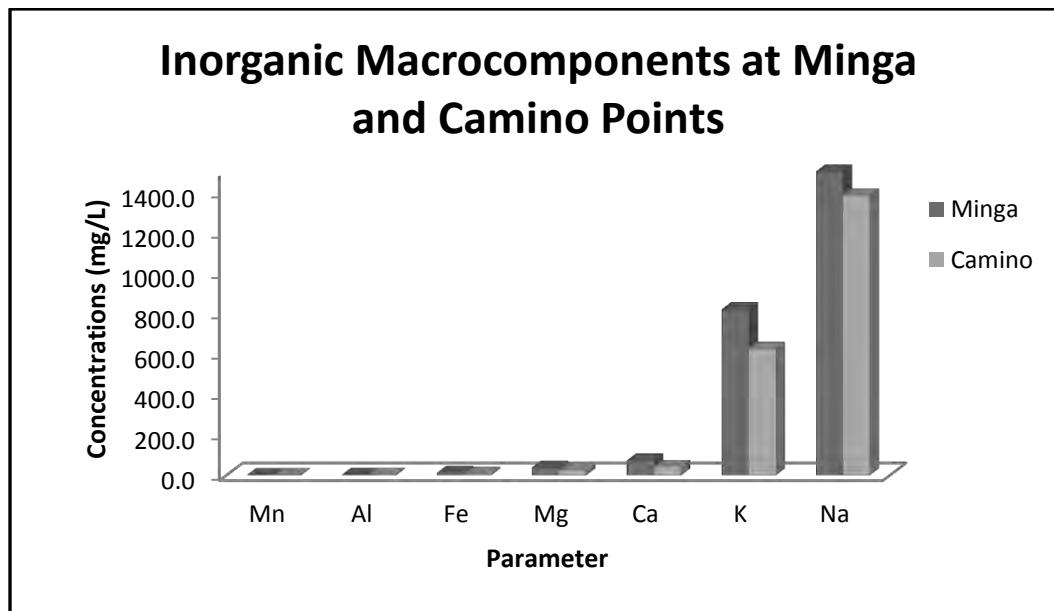


Figure 4.06. Inorganic macrocomponents at Minga and Camino points.

4.2.3.3 Heavy Metal Results

The leachate samples at “Minga” and “Camino” points were analyzed for six heavy metals: Cr, Co, Cu, Ni, Pb and Zn. Data regarding these parameters are shown on Table 4.07. The mean values (in mg/L) for the “Minga” landfill point are: Cr: 0.305 ± 0.107 ; Cu: 0.057 ± 0.073 ; Ni: 0.177 ± 0.146 ; Zn: 0.365 ± 0.341 ; Co: 0.159 ± 0.150 ; and

Pb: 0.034 ± 0.040 ; whereas for "Camino" the mean values obtained were: Cr: 0.255 ± 0.107 ; Cu: 0.087 ± 0.124 ; Ni: 0.151 ± 0.149 ; Zn: 0.795 ± 0.568 ; Co: 0.071 ± 0.048 ; and Pb: 0.044 ± 0.030 .

Table 4.07. Heavy metals in leachate at Minga and Camino landfill points.

Parameter (mg/L)	Mean \pm SD of Leachate		Value Range of Leachate	
	Landfill Points		Landfill Points	
	Minga	Camino	Minga	Camino
Chromium (Cr)	0.305 ± 0.107	0.255 ± 0.165	0.160-0.412	0.022-0.387
Cobalt (Co)	0.159 ± 0.150	0.071 ± 0.048	0.036-0.377	0.007-0.123
Copper (Cu)	0.057 ± 0.073	0.087 ± 0.124	0.000-0.152	0.000-0.264
Lead (Pb)	0.034 ± 0.040	0.044 ± 0.030	0.000-0.078	0.000-0.069
Nickel (Ni)	0.177 ± 0.146	0.151 ± 0.149	0.000-0.346	0.000-0.294
Zinc (Zn)	0.365 ± 0.341	0.795 ± 0.568	0.061-0.845	0.014-1.278

The heavy metal of highest concentration in both "Minga" and "Camino" sampling points was Zn, with values of 0.845 mg/L and 1.278 mg/L, respectively; whereas that of lowest concentration in both landfill points was Pb. With exception of Cu and Zn, value for all other heavy metals at "Minga" were higher than those obtained at the "Camino" landfill point (see Figure 4.07).

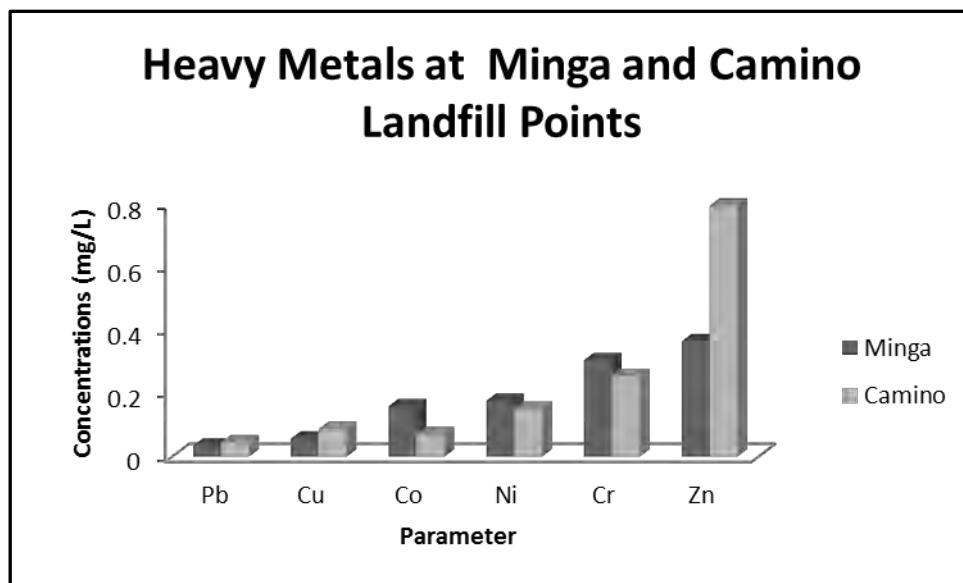


Figure 4.07. Heavy metals at Minga and Camino landfill points.

4.3.0 Groundwater Samples

This section details the results obtained from the analysis of groundwater from Levittown, Campanilla and Primate Center wells. Groundwater samples were characterized for field parameters, inorganic macrocomponents and heavy metals. One of the goals was to determine impact of leachate on groundwater quality.

4.3.1 Levittown, Campanilla and Primate Center Wells Quality Analysis

The groundwater characterization or quality parameters for the Toa Alta Levittown, Campanilla and Primate Center Wells are listed in Tables 4.08 to 4.10. All leachate samples were characterized in terms of field parameters, inorganic macrocomponents and heavy metals. All data obtained are included in Appendix B.

4.3.1.1 Field Parameter Results

The result of all measured field parameters for the Levittown, Campanilla and Primate Center wells are included in Table 4.08. The groundwater sample temperature was found to be in the range of 27.1 °C to 28.1 °C for the Levittown well; 26.5 °C to 27.0 °C for the Campanilla well; and 26.8 °C to 27.0 °C for the Primate Center well. The

mean pH values for samples from these three groundwater wells were found to be 7.38 for the Primate Center, 7.21 for both Campanilla and Levittown. No statistical difference ($p>0.05$) in pH was observed among the three wells.

The results from the analyses of the groundwater samples showed that EC had a mean value (with standard deviation of $576 \pm 24 \mu\text{S}/\text{cm}$ for Levittown; $558 \pm 32 \mu\text{S}/\text{cm}$ for Campanilla; and $773 \pm 79 \mu\text{S}/\text{cm}$ for the Primate Center wells.

Table 4.08. Field parameter of groundwater from Levittown, Campanilla and Primate Center wells.

Parameter	Mean ± SD			Range		
	Levittown	Campanilla	Primate	Levittown	Campanilla	Primate
Temperature (°C)	27.6 ±0.4	26.8±0.2	26.9±0.1	27.1-28.1	26.5-27.0	26.8-27.0
pH	7.21±0.17	7.21±0.17	7.38±0.25	7.03-7.45	7.12-7.51	7.21-7.80
EC (μ S/cm)	558±32	576±24	773±79	517-588	552-603	700-878

The EC measurements for the groundwater samples collected were found to be in the range of 517 to 588 $\mu\text{S}/\text{cm}$ for the Levittown well; 552 to 603 $\mu\text{S}/\text{cm}$ for the Campanilla well; and 700 to 878 $\mu\text{S}/\text{cm}$ for the Primate Center well. From these values it is evident that the Primate Center well's conductivity was consistently higher than that of the Levittown and Campanilla wells.

4.3.1.2 Inorganic Macrocomponents Results

Data for inorganic macrocomponents (including Al, Ca, Mg, Mn, Fe, K and Na) are presented in Table 4.09. Among the three wells reported, the one with the lowest range values for Al, Ca, Fe, K and Na was the Levittown well, which yielded mean values of $0.241 \pm 0.069 \text{ mg/L}$; $68.583 \pm 8.948 \text{ mg/L}$; $0.093 \pm 0.049 \text{ mg/L}$; $3.364 \pm 2.658 \text{ mg/L}$; and $28.229 \pm 3.793 \text{ mg/L}$, respectively, for these parameters. The lowest concentration of Mg was found in the Primate Center well; and Mn was consistently found below limits of detection (value of 0.000, for statistical purposes), except for the March campaign in Levittown, where one of the samples yielded a Mn concentration of 0.008 mg/L. (Appendix B).

Table 4.09. Inorganic macrocomponents in Levittown, Campanilla and the Primate Center wells.

Parameter (mg/L)	Mean ± SD			Range		
	Levittown	Campanilla	Primate	Levittown	Campanilla	Primate
Aluminum (Al)	0.241±0.069	0.347±0.060	0.389±0.054	0.145-0.304	0.295-0.412	0.309-0.426
Calcium (Ca)	68.583±8.948	88.333±4.786	92.408±24.563	63.167-81.967	83.033-92.833	62.633-122.767
Iron (Fe)	0.093±0.049	0.135±0.134	0.000±0.000	0.029-0.145	0.046-0.327	0.000-0.000
Potassium (K)	3.364±2.658	2.016±2.308	5.771±2.456	1.785-7.337	0.563-5.453	4.389-9.443
Magnesium (Mg)	10.271±1.297	6.685±1.974	3.985±1.043	9.473-12.200	3.768-8.063	2.661-5.203
Manganese (Mn)	0.002±0.004	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000
Sodium (Na)	28.229±3.793	18.565±2.419	40.018±9.598	24.820-33.660	15.653-21.037	27.120-50.223

The highest concentrations of Al, Ca, K, and Na were found in the Primate Center well with maximum values of 0.426 mg/L, 122.767 mg/L, 9.443 mg/L, and 50.223 mg/L respectively for these parameters. In the case of Fe, the highest concentration was found in Campanilla with a maximum value of 0.327 mg/L. Compared to Levittown, these results show that groundwater samples collected at the Primate Center well have higher concentrations of inorganic ions with the exception of Fe, Mg and Mn (see Figure 4.08).

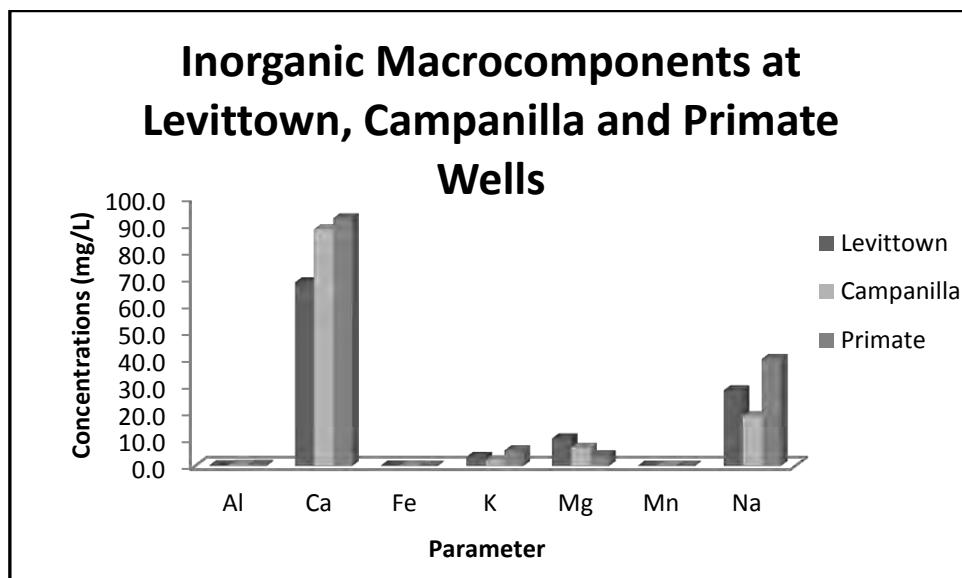


Figure 4.08. Inorganic macrocomponents at Levittown, Campanilla and the Primate Center.

4.3.1.3 Heavy Metal Results

All groundwater samples were analyzed for six heavy metals: Cr, Co, Cu, Ni, Pb and Zn. The results for heavy metal concentrations in groundwater samples from the Levittown, Campanilla and Primate Center wells are shown in Table 4.10. Of the six heavy metals analyzed, only three (Co, Ni, Zn) were detected in groundwater samples collected at these wells, as no Cr, Cu and Pb were found. In Campanilla, the presence of Zn was not observed; whereas in the Primate Center well it exhibits the highest value.

The mean values with standard deviations (in mg/L) for the Levittown well are Ni: 0.008 ± 0.02 mg/L; Zn: 0.006 ± 0.007 mg/L; and Co: 0.0007 ± 0.015 mg/L. For Campanilla, the mean concentrations yielded Ni: 0.088 ± 0.017 mg/L; and Co: 0.003 ± 0.005 mg/L; and for the Primate Center well the values obtained were Ni: 0.012 ± 0.025 mg/L; Zn: 0.011 ± 0.022 mg/L; and Co: 0.008 ± 0.016 mg/L.

In general, heavy metal analysis results of leachate from Levittown, Campanilla and the Primate Center show that the highest concentrations of heavy metals are recorded at the Primate Center well.

Table 4.10. Heavy metals in groundwater samples from Levittown, Campanilla and Primate Center Wells.

Parameter (mg/L)	Mean ± SD)			Range		
	Levittown	Campanilla	Primate	Levittown	Campanilla	Primate
Chromium (Cr)	ND	ND	ND	ND	ND	ND
Copper (Cu)	ND	ND	ND	ND	ND	ND
Nickel (Ni)	0.008±0.017	0.008±0.017	0.012±0.025	0.000-0.033	0.000-0.033	0.000-0.049
Zinc (Zn)	0.006±0.007	ND	0.011±0.022	0.000-0.014	ND	0.000-0.043
Cobalt (Co)	0.007±0.015	0.003±0.005	0.008±0.016	0.000-0.030	0.000-0.010	0.000-0.031
Lead (Pb)	ND	ND	ND	ND	ND	ND

ND: Not Detected

A comparison of Zn, Ni and Co concentrations in groundwater samples collected at the Primate Center well shows a relative abundance in the order of Ni > Zn > Co. For samples collected in the Levittown well, the trend is Ni > Co > Zn; whereas for Campanilla (where no Zn was detected) the concentration of Ni is approximately three times that of Co (see Figure 4.09).

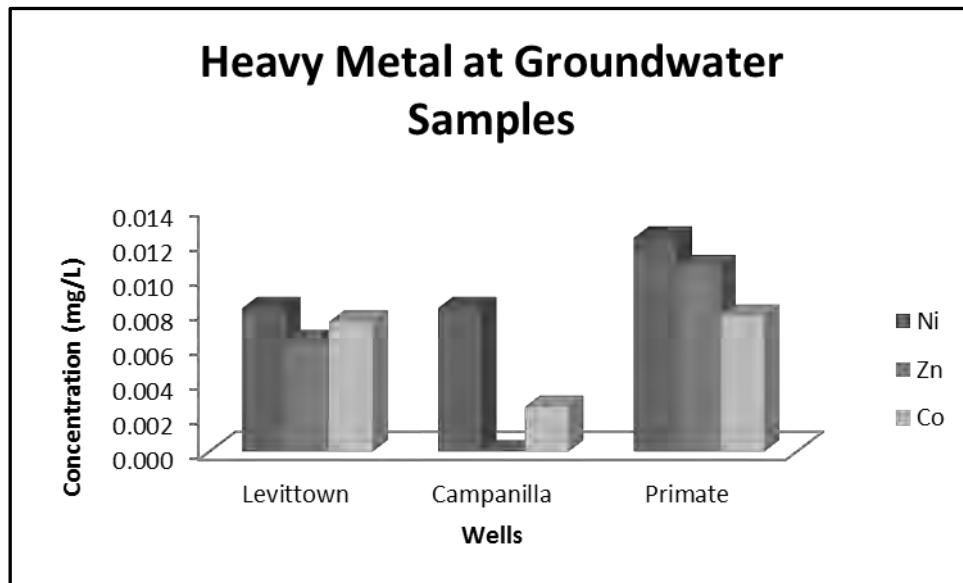


Figure 4.09. Heavy metal content at the three wells.

Chapter 5

Discussion

In this chapter, the significance of the leachate, groundwater and soil characterization results will be discussed and the variations observed among the sample locations and points will be examined. Leachate and groundwater results will also be compared to USEPA effluent limitations guideline (USEPA 2000) and USEPA's water quality criteria guidelines (USEPA 2010) respectively, and groundwater and leachate results will be analyzed in terms of other results reported in the literature. Variations in leachate composition with type of waste deposited and with seasonal changes will also be discussed. For each of these studies mentioned above, statistical analyses were performed in order to either accept or reject the hypothesis tested. These analyses included the t-test for independent and dependent samples, as well as the analysis of variance (ANOVA) test for comparison of means and values obtained for different parameters at each sampling site or point. The results of these analyses will also be discussed.

5.1.0. Characterization of Leachate Samples

The results obtained for the Toa Alta and Toa Baja landfill leachate samples will be discussed in this section and compared with similar data reported in the literature and will also be compared to USEPA effluent limitations guideline (USEPA 2000). This will be followed by a comparison of the values obtained for the Toa Baja landfill's "Camino" and "Minga" points.

5.1.1 Leachate Field Parameters

Table 5.01 presents a comparison of results for landfill leachate quality parameters between this study and others reported in the literature. The pH values for leachate samples collected at the Toa Alta and Toa Baja landfills are in agreement with the typical range values of 4.5 to 9.0 reported by Kjeldsen et al. (2002). These results are also in agreement with the range values obtained by Fatta et al. (1999), Sabahi et al. (2009b) and Yaqout et al. (2003), but higher than those obtained by Mor et al. (2006).

The mean pH values for leachate collected from the Toa Alta and Toa Baja landfills may be used to establish the age or degradation of landfill waste in these facilities. The age of the landfill plays a major role in leachate quality and composition, as it determines the phase that is undergoing the process of stabilization or decomposition of waste (Aziz et al. 2010; Yaquout et al. 2003). The two main phases in leachate are the acid phase and the methanogenic phase. The acid phase usually prevails in a young landfill and the methanogenic phase prevails in a mature landfill. Table 5.02 shows some variations in leachate quality expected during each of these two phases for the parameters most affected, which are pH and concentration of inorganic ions such as Ca, Mg, Fe and Mn. Tchobanoglous and Kreith (1993) classified new landfills as less than 2 years old and mature landfills as more than 10 years old. The relatively high pH values (>7.5) of the leachate samples analyzed suggest that both the Toa Alta and Toa Baja landfills are at the methanogenic phase, since the acid phase is characterized by low pH values and the methanogenic phase is characterized by a pH range from 7.5 to 9.0 and according to the classification by age, both landfill, the Toa Baja and Toa Alta landfill are an old landfills (Tchobanoglous and Kreith 1993).

Table 5.01. Comparison of leachate field parameters values at Toa Baja and Toa Alta landfills with others studies.

Parameter	Landfill values obtained in this study		Typical landfill leachate values		Landfill leachate quality parameters determined by different researchers		
	Toa Alta landfill	Toa Baja Landfill	Kjeldsen et al. (2002)	Fatta et al. (1999) (range)	Mor et al. (2006)	Sabahi et al. (2009b) (range)	Yaqout et al. (2003) (range)
pH	8.05-8.38	7.93-8.56	4.5-9.0	8.30-8.63	6.9	8.42-8.46	6.9-8.2
EC ($\mu\text{S}/\text{cm}$)	4300-19 700	13 975-22 825	2500-35 000	23 000-26 900	24 500	49 600-49 800	5400-16 900

Table 5.02. Typical leachate parameters for the acid and methanogenic phases (Kjeldsen et al.2002).

Leachate Parameter	Acid Phase	Methanogenic Phase
pH	4.5-7.0	7.0-9.0
Calcium	10-2500 mg/L	20-600 mg/L
Magnesium	50-1500 mg/L	40-350 mg/L
Iron	20-2100 mg/L	3-280 mg/L
Manganese	0.3-65 mg/L	0.03-45 mg/L
Zinc	0.1-20 mg/L	0.003-4 mg/L

This increase in pH in methanogenic phase is due to the fact that a steady state has been reached between acid-producing and acid-consuming processes (Yaqout et al. 2003; Kjeldsen et al. 2002). However, another factor that may influence the high pH values in the landfills studied is the fact that both landfills are located in the Northern Karst Region of Puerto Rico.

The slightly alkaline values of pH found in Toa Alta and Toa Baja landfill leachate may have an effect on the concentration of metal cations such as Ca, Mg, Fe, Mn, and others, because alkaline conditions tend to enhance sorption and precipitation processes. In general, the effect of complexation on metal migration in leachate plumes is highly dependent on the plume's pH and varies from metal to metal. For example, for Ni and Zn the speed of migration decreases with increasing pH values; whereas for Cu, the speed of migration increases with increasing pH (Christensen et al. 2001).

Electrical conductivity is used as an indicator of the abundance of dissolved inorganic species or total concentration of ions (Sabahi et al. 2009a). The high conductivity value of leachates from the Toa Alta and Toa Baja landfills (19 700 and 22 850 $\mu\text{S}/\text{cm}$, respectively) indicate the presence of dissolved inorganic materials in the samples. The mean value of EC ($18\ 485 \pm 3782\ \mu\text{S}/\text{cm}$) for leachate collected at the Toa Baja Landfill is higher in comparison to that collected at the Toa Alta Landfill, which suggests that the concentration of soluble inorganic salts in the Toa Baja landfill is greater than that in the Toa Alta landfill. The values of EC for both Toa Alta and Toa Baja leachate are within the typical range, but maximum values of EC in Toa Baja are higher than the maximum values determined by Yaqout et al. (2003) (see Table 5.01).

5.1.2 Leachate Inorganic Macrocomponent Analysis:

Table 5.03 shows a comparison of inorganic macrocomponents in leachate from the Toa Alta and Toa Baja landfills with those obtained from other studies. From the analysis of this table we may conclude that the range of concentrations obtained for Ca,

Mn, K and Na, in both the Toa Alta and Toa Baja landfills, falls within the typical ranges. However, the minimum values of Fe and Mg in Toa Alta landfill and minimum values of Mg in Toa Baja do not fall within the typical ranges expected, or in those reported by Mort et al. (2006) and Sabahi et al. (2009a).

The literature reports that leachate salt content slightly increases with landfill age as a consequence of the decomposition of organic matter, which may explain the high concentration of Na found in the Toa Baja landfill (Chu et al. 1994). In contrast, the concentration of Ca in leachate from both landfills is higher than the values obtained by Fatta et al. (1999), but lower than those reported by Sabali et al. (2009). These variations may be due to age differences between the Toa Baja and Toa Alta landfills. Sabali et al. (2009) and Fatta et al. (1999) explained that, as the landfill moves from the acid phase to the methanogenic phase, the concentration of calcium decreases with time. In contrast with the methanogenic phase, during the acid phase the range of concentrations of Ca, Mg, Mn and Fe normally tend to be much higher and broader (Aziz et al. 2010). This observation again suggests that the leachate could be in the methanogenic phase. Kjeldsen et at. (2002), indicate that high pH values (characteristic of the methanogenic phase), favor processes such as sorption, complexation and precipitation of Ca, Mg and Fe, thus resulting in typically low leachate concentrations of these cations (Tatsi et al. 2002).

Table 5.03. Comparison of leachate inorganic macrocomponents values at Toa Baja and Toa Alta landfill with other studies.

Parameter	Range		Typical leachate concentrations	Landfill leachate concentrations in different studies		
	Toa Alta landfill	Toa Baja Landfill	Kjeldsen et al. (2002) Range	Fatta et al. (1999) Range	Mor et al. (2006)	Sabahi et al. (2009b) Range
Aluminum	0.353-0.531	0.441-3.671	Ns	Ns	Ns	Ns
Calcium	53.233-81.533	20.110-163.833	10-7200	45.4-63.4	Ns	960-1840
Magnesium	14.477-42.837	14.467-74.267	30-15 000	Ns	Ns	136-288
Manganese	0.085-0.203	0.0238-1.050	0.03-1400	Ns	Ns	Ns
Iron	1.216-6.447	6.477-14.107	3-5500	6.35-7.19	Ns	45.7-46.0
Potassium	155.433-494.267	156.367-989.33	50-3700	1499-2,094	1590	4800-4900
Sodium	388.900-624.733	398.933-2025.33	70-7700	1440-3322	545	6200-6300

Ns= Not specified

In general all range values for inorganic macrocomponents are higher in Toa Baja landfill than in Toa Alta landfill, but chemical analysis of leachate samples indicates a same general trend with respect to inorganic macrocomponents abundance in the order of Na>K>Ca>Mg> Fe>Al>Mn at the Toa Alta and Toa Baja landfills. The trend of theoretical solubilities of hydroxides of Ca, Na, Fe, Mn and Mg is Na>Mn>Fe>Ca>Mg (see Table 5.04).

Table 5.04. Theoretical solubilities of hydroxides of selected elements in pure water at 25 °C.^a

Element	Solubility (mg/L)
Calcium	1.85x10 ⁻¹
Chromium	8.4 x 10 ⁻⁴
Cobalt	2.2 x 10 ⁻¹
Copper	2.2 x 10 ⁻²
Iron	8.9 x 10 ⁻¹
Lead	2.1
Manganese	9.0x10 ⁻⁴
Magnesium	1.2
Nickel	6.9x10 ⁻³
Sodium	42.0
Zinc	1.1

5.1.3 Leachate Heavy Metal Analysis

Table 5.05 shows heavy metal concentration values obtained from leachate collected at the Toa Alta and Toa Baja landfills, as well as data from other studies reported in the literature. Comparison with literature values suggests that all heavy metals analyzed were within the typical range. Chemical analysis of leachate samples indicates a general trend with respect to heavy metal abundance in the order of Zn > Cr > Co > Pb at the Toa Alta landfill, and of Zn > Cr > Co > Ni > Cu > Pb for the Toa Baja landfill. The theoretical solubilities of hydroxides is Pb>Zn>Co>Cu>Ni>Cr (see Table 5.04).

Among all heavy metals analyzed, Zn showed the highest relative concentration in both the Toa Alta and Toa Baja landfills. This trend is in agreement with that typical of other landfills and with the Zn trend reported by Mor et al. (2006). These results, however, are higher than those obtained by Fatta et al. (1999) and Oyeku et al. (2000). The presence of Zn usually results from the type of waste deposited in the landfill; that is, to the presence of batteries, fluorescent lamps and raw industrial wastes (Ziyang et al. 2009, Aziz et al. 2010).

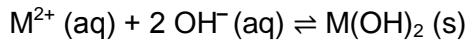
In both the Toa Alta and Toa Baja landfills Cr and Pb were found. These ions are toxic to all forms of life. Possible sources of Pb include batteries, automobile parts, photographic materials, and lead-based paints (Yaquout et al. 2007). The concentrations of heavy metals analyzed in both landfills are lower than those reported by Mort et al.(2006). One possible reason is the effect of pH. Low pH values result in an increase in heavy metal solubility (Esakku, et al. 2003).

Table 5.05. Comparison of leachate heavy metal concentrations in Toa Baja and Toa Alta landfills with other studies.

Parameter	Range in Landfills Studied (mg/L)		Mean ± Standard deviation in landfill studied		Typical leachate concentrations (mg/L)	Landfill leachate concentrations in different studies (mg/L)		
	Toa Alta	Toa Baja	Toa Alta	Toa Baja		Fatta et al. (1999 (range)	Mor et al. (2006)	Oyeku et al. (2010)
Chromium	0.036-0.137	0.022-0.412	0.068±0.047	0.280±0.132	0.02-1.5	1.20-2.44	0.29	NS
Cobalt	0.000-0.050	0.007-0.377	0.023±0.022	0.115±0.113	0.05-1.5	NS	NS	1.03±1.11
Copper	0.000±0.000	0.000-0.264	0.000±0.000	0.072±0.096	0.005-10	0.16-0.31	0.93	0.02±0.04
Lead	0.000-0.004	0.000-0.078	0.001±0.002	0.039±0.034	0.001-1.5	0.24-0.42	1.54	2.4±3.3
Nickel	0.047-0.127	0.000-0.346	0.088±0.042	0.164±0.137	0.015-1.3	0.24-0.97	0.41	NS
Zinc	0.000-0.482	0.014-1.278	0.134±0.233	0.580±0.491	0.03-1,000	0.36-0.79	2.21	0.04±0.06

NS= Not Specified.

Mort et. al. (2006) reported an acid pH of 6.9 for leachate samples; whereas the pH observed for all leachate samples in this study ranged from 7.93 to 8.56, an alkaline pH range. Decreased metal ion solubility due to pH favors processes such as metal ion adsorption or metal ion precipitation as insoluble hydroxides (Reinhart et al. 1998; Tatsi and Zouboulis 2002; Esakku et al. 2003):



where M^{2+} represents any divalent heavy metal ion. According to several authors, the absence or low concentrations of metals is not due to the absence of these metals in the waste deposited, but to their immobilization caused by absorption or precipitation processes which can decrease metal concentration in leachate (Kjeldsen et al. 2002; Longe et al. 2010).

The concentration of Ni in the Toa Baja landfill is higher than that at the Toa Alta landfill. This difference may be due to the fact that the Toa Baja landfill receives a greater amount of nickel waste sources, such as kitchen appliances and steel alloys (Singhet al. 2008).

Some of the parameters found in the Toa Alta and Toa Baja landfill leachates were compared to the guidelines established by USEPA, the limits established by the Humacao Water Treatment Plant (WTP), and the landfill regulations in the Pacific island of Fuji (EMA). In 2000, the USEPA set the limits for some parameters in landfill leachate. These regulations established the maximum allowed levels for landfills that discharge their leachates in federal bodies of water. The maximum levels of Zn found in the Toa Alta and Toa Baja leachates are above the limits established by USEPA. Moreover, the maximum values reported in Toa Baja are also above the limits allowed by the Humacao WTP. For Fe, the maximum values found in the Toa Baja and Toa Alta landfills were above the limits established by both the Humacao WTP and the EMA.

Regulations. In the Toa Baja landfill, the Cr values were above the Humacao WTP limits and the Pb amounts surpassed the levels established by EMA (see Table 5.06).

Table 5.06. Comparison between Leachate from Toa Baja and Toa Alta landfills with other regulations.

Parameter	Toa Alta	Toa Baja	USEPA ^{*1}	Humacao	EMA
	Landfill	Landfill		WTP	Regulations ^{*2}
pH	8.05-8.38	7.93-8.56	6.00-9.00	6.00-9.00	6.00-9.00
Iron (Fe)	1.216-6.447	1.041-14.053	Ns	Ns	5
Chromium (Cr)	0.036-0.137	0.022-0.412	Ns	0.3	Ns
Cobalt (Co)	0.000-0.050	0.007-0.377	Ns	Ns	Ns
Copper (Cu)	BDL	0.000-0.264	Ns	1	Ns
Lead (Pb)	0.000-0.004	0.000-0.078	Ns	0.2	0.05
Nickel (Ni)	0.047-0.127	0.000-0.346	Ns	0.5	Ns
Zinc (Zn)	0.000-0.482	0.014-1.278	0.2	0.5	1

NS: Not specified; BDL: Below Detection Limit. USEPA^{*1} (2000); EMA^{*2} (2008).

5.2.0 Variations in Leachate Composition for Toa Alta and Toa Baja Landfill: Statistical Results

The means values obtained for the leachate quality parameters measured for the Toa Baja and Toa Alta samples were compared using unpaired and paired t-test, in order to determine whether the null or alternate hypotheses should be accepted, and whether seasonal variations had an effect on leachate composition. A similar comparison was performed but only using unpaired t-test, for samples obtained from the Minga and Camino landfill points in order to evaluate whether the type of waste deposited had any effect on leachate composition.

5.2.1 Statistical Approach for Comparing Landfill Leachate Parameters

Hypothesis testing was performed to determine if mean values for landfill leachate quality parameters differed among the Toa Baja and Toa Alta landfills. The first hypothesis is stated as:

H1_o: The mean values of each quality parameter for the leachate landfills studied in Puerto Rico (Toa Alta and Toa Baja) will not differ among themselves.

H1_a: The means values of each quality parameter for the leachate landfills studied in Puerto Rico, (Toa Alta and Toa Baja) will differ among themselves.

Hypothesis Testing

Results of the leachate samples tested for inorganic macrocomponents and heavy metal parameters were analyzed for significant differences among landfills using the t-test for independent samples (unpaired and paired observations). A significance value of $p<0.05$ was used to conclude that differences between landfills were statistically significant. Results to the t-test unpaired and paired, are summarized in Tables 5.07 and 5.08.respectively.

In the case of inorganic macrocomponents, paired t-test showed that there is no significant difference between the two landfills. Application of unpaired t-test showed that there are significant differences between the two landfills, but only observed for Ca and Na during the April 2009 and March 2010 campaigns, which correspond to the dry season. No significant differences were noted for these two leachate parameters during the wet season; or for Mn, Mg and Al, Fe and K for both landfills during any of the two seasons.

Among all heavy metal detected in leachate from both landfills (Cr, Cu, Zn, Co, Pb), significant differences were observed (unpaired t-test) among Toa Alta and Toa Baja during the dry season (April 2009 and March 2010) for all heavy metals ($p<0.05$)

except Ni ($p>0.05$). Application of paired t-test also showed that there are differences when the values of heavy metal in Toa Alta and Toa Baja were compared. For sampling campaigns performed during the wet season (June 2009 and October 2009), significant differences (unpaired t-test, $p<0.05$) were only found for Zn and Co.

Table 5.07. Summary of paired t-Test conducted within 95% confidence interval for Toa Alta and Toa Baja landfills.

Parameter	Wet		Dry	
	t- Test Values	Significance Level (Two- Tailed)	t- Test Values	Significance Level (Two- Tailed)
inorganic- Macrocomponents	1.45	$p> 0.05$	-1.39	$p> 0.05$
Heavy Metal	-2.07	$p> 0.05$	2.87	$p< 0.05$

Table 5.08. Summary of T-test conducted within 95% confidence interval for Toa Alta and Toa Baja landfills.

Parameter	Toa Alta Vs. Toa Baja landfill (campaign April 2009 and March 2010)				Toa Alta Vs. Toa Baja landfill (campaign June 2009 and October 2009)				Significance Level (Two-Tailed)	
	Mean (and SD)		Mean (and SD)		t- Test Values	e Level (Two-Tailed)	Toa Alta Landfill	Toa Baja Landfill		
	Toa Alta Landfill	Toa Baja Landfill	Significanc							
Inorganic Components										
Aluminum (Al)	0.44 (0.14)	1.14 (0.91)	1.86	p>0.05	0.44 (0.05)	1.24(0.94)	2.10	p>0.05		
Calcium (Ca)	67.40(18.90)	34.40(20.60)	-2.89	p<0.05	65.00(10.10)	46.69(7.67)	-3.54	p>0.05		
Iron (Fe)	3.95(2.86)	8.37(5.49)	1.75	p>0.05	1.46(0.29)	5.69(5.11)	2.02	p>0.05		
Potassium (K)	340.00(183.00)	731.00(423.00)	2.08	p>0.05	196.30(49.80)	520.00(399.00)	1.97	p>0.05		
Magnesium (Mg)	30.30(14.90)	23.00(11.90)	-0.94	p>0.05	17.82(3.98)	26.00(12.70)	1.51	p>0.05		
Manganese (Mn)	0.14(0.06)	0.13(0.08)	-0.12	p>0.05	0.15(0.06)	0.19(0.06)	1.02	p>0.05		

Table 5.08., continued.

Sodium (Na)	544.00(288.00)	1742.00(1154.00)	2.47	p<0.05	459.20(88.10)	1022.00(684.00)	2.00	p>0.05
Heavy Metal								
Chromium (Cr)	0.10 (0.05)	0.31 (0.06)	6.68	p<0.05	0.04 (0.01)	0.20 (0.20)	2.02	p>0.05
Copper (Cu)	ID	ID	ID	ID	ID	ID	ID	ID
Nickel (Ni)	0.12 (0.02)	0.15 (0.16)	0.34	p>0.05	0.05 (0.01)	0.16 (0.12)	2.12	p>0.05
Zinc (Zn)	0.27 (0.25)	0.94 (0.28)	4.42	p<0.05	0.00 (0.00)	0.65 (0.69)	2.28	p<0.05
Cobalt (Co)	0.04 (0.01)	0.10 (0.03)	4.63	p<0.05	0.00 (0.01)	0.04 (0.04)	2.33	p<0.05
Lead (Pb)	0.00 (0.00)	0.06 (0.05)	2.79	p<0.05	ID	ID	ID	ID

5.3.0 Variations in leachate composition as a result of type of waste deposited in the Toa Baja landfill

The purpose of this study was to analyze the effect of the type of waste deposited on leachate composition. For this study, two sampling points within the Toa Baja landfill were selected: Minga and Camino. The Minga sampling point is located close to the scrap metal landfill deposits, whereas the Camino sampling point is far away from the scrap wastes but close to the domestic waste deposits.

The null hypothesis was:

H_{1o}: The mean values for each parameter will be similar for both landfill leachate sampling points.

The alternate hypothesis is that mean values for each parameter will differ for both sampling points. The results obtained for inorganic macrocomponents in the samples collected during the dry season indicate that, except for Ca ($p<0.05$) which was higher at Minga, there is no significant difference ($p>0.05$) in mean values for these parameters at the Minga and Camino sampling points. In terms of heavy metal concentrations, except for Zn ($p<0.05$) which was higher at Camino, no significant difference was found between the two sampling points. A summary of the t-test results is shown in Table 5.09.

Table 5.09. Summary of t-Test conducted within 95% confidence interval for Camino and Minga points landfills.

Parameter	Camino Vs. Minga Points landfills (campaign June 2009 and October 2009)								
	Camino Vs. Minga Points landfills (campaign April 2009 and March 2010)				October 2009)				
	Mean (and SD)				Mean (and SD)				
Parameter	Camino	Minga	t- Test Values	Significance Level (Two-Tailed)	Camino	Minga	t- Test Values	Significance Level (Two-Tailed)	
Inorganic Components									
Aluminum (Al)	1.14 (0.91)	2.68 (1.69)	-1.97	p>0.05	1.41(0.85)	1.27 (1.34)	0.23	p>0.05	
Calcium (Ca)	34.40 (20.60)	106.90 (69.60)	-2.45	p<0.05	48.68(7.81)	39.50(14.80)	1.35	p>0.05	
Iron (Fe)	8.37 (5.49)	12.43 (7.82)	-1.04	p>0.05	7.11(4.75)	10.04(1.55)	-1.44	p>0.05	
Potassium (K)	731.00 (423.00)	827.00 (179.00)	-0.51	p>0.05	642.00(380.00)	816.00(39.20)	-1.12	p>0.05	
Magnesium (Mg)	23.00 (11.90)	47.70 (29.40)	-1.91	p>0.05	29.80(12.10)	27.42(8.14)	0.40	p>0.05	
Manganese (Mn)	0.13 (0.08)	0.67 (0.88)	-1.49	p>0.05	0.20(0.06)	0.12(0.11)	1.68	p>0.05	
Sodium (Na)	1742.00 (1154.00)	1607.30 (70.60)	0.28	p>0.05	1235.00(652.00)	1644.70(66.10)	-1.53	p>0.05	

Table 5.09., continued.

Heavy Metal

Chromium (Cr)	0.31 (0.06)	0.36 (0.06)	-1.57	p>0.05	0.20 (0.20)	0.25 (0.13)	-0.49	p>0.05
Copper (Cu)	0.18 (0.11)	0.11 (0.04)	1.29	p>0.05	ID	ID	ID	ID
Nickel (Ni)	0.15 (0.16)	0.17 (0.19)	-0.26	p>0.05	0.16 (0.12)	0.18 (0.09)	-0.41	p>0.05
Zinc (Zn)	0.94 (0.28)	0.28 (0.08)	5.52	p<0.05	0.65 (0.69)	0.45 (0.53)	0.54	p>0.05
Cobalt (Co)	0.10 (0.03)	0.11 (0.01)	-1.10	p>0.05	0.04 (0.04)	0.21 (0.45)	-0.88	p>0.05
Lead (Pb)	0.06 (0.05)	0.03 (0.04)	1.24	p>0.05	0.03 (0.03)	0.04 (0.04)	-0.62	p>0.05

ID: Insufficient data.

5.4.0 Influence of Seasonal Variations in Leachate Quality Parameters for the Toa Alta and Toa Baja Landfills

In order to analyze the seasonal variability of leachate quality for the Toa Alta and Toa Baja landfills, results obtained for samples collected from each landfill during the dry and wet seasons were compared. A summary of the t-test results is shown in Table 5.10.

The null hypothesis was:

$H1_0$: The mean values for leachate quality parameters observed during the dry season for the Toa Alta and Toa Baja landfills will be similar to those observed during the wet season.

5.4.1 Results for the Toa Alta landfill

No significant difference ($p>0.05$) was observed between the mean values of the inorganic macrocomponents during the wet and dry seasons for the Toa Alta landfill. However, significant difference in mean values among wet and dry seasons was found for Cr, Ni, Zn and Co in this same landfill. Other heavy metals were either not detected (Cu) or there was insufficient data (Pb).

5.4.2 Results for the Toa Baja landfill

For the Toa Baja Landfill, except for the mean values of Co which were significantly higher ($p<0.05$) during the dry season, no significant differences ($p>0.05$) were found for the inorganic macrocomponents or heavy metals during the wet and dry seasons.

Table 5.10. Summary of unpaired T-test conducted within 95% confidence interval for Toa Alta and Toa Baja landfills (Influence of seasonal variations).

Parameter	Toa Alta Landfill				Toa Baja Landfill			
	Mean (and SD)		t- Test Values	Significance Level (Two- Tailed)	Mean (and SD)		t- Test Values	Significance Level (Two- Tailed)
	Toa Alta Dry	Toa Alta Wet			Toa Baja Dry	Toa Baja Wet		
Inorganic Components								
Aluminum (Al)	0.44(0.14)	0.44(0.05)	0.04	p>0.05	1.14(0.91)	1.24(0.94)	-0.2	p>0.05
Calcium (Ca)	67.40(18.90)	65.00(10.10)	0.28	p>0.05	34.40(20.60)	46.69(7.67)	-1.37	p>0.05
Iron (Fe)	3.95(2.86)	1.46(0.29)	2.12	p>0.05	8.37(5.49)	5.69(5.11)	0.87	p>0.05
Potassium (K)	340.00(183.00)	196.30(49.80)	1.85	p>0.05	731.00(423.00)	520.00(399.00)	0.89	p>0.05
Magnesium (Mg)	30.30(14.90)	17.82(3.98)	1.99	p>0.05	23.00(11.90)	26.00(12.70)	-0.43	p>0.05
Manganese (Mn)	0.14(0.06)	0.15(0.06)	-0.39	p>0.05	0.13(0.08)	0.19(0.06)	-1.36	p>0.05
Sodium (Na)	544.00(288.00)	459.20(88.10)	0.69	p>0.05	1742.00(1154.00)	1022.00(684.00)	1.31	p>0.05

Table 5.10., continued.

Heavy Metal

Chromium (Cr)	0.10 (0.05)	0.04 (0.01)	3	p<0.05	0.31 (0.06)	0.20 (0.20)	1.18	p>0.05
Copper (Cu)								
Nickel (Ni)	0.12 (0.02)	0.05 (0.01)	8.46	p<0.05	0.15 (0.16)	0.16 (0.12)	-0.1	p>0.05
Zinc (Zn)	0.27 (0.25)	0.00 (0.00)	2.65	p<0.05	0.94 (0.28)	0.65 (0.69)	0.97	p>0.05
Cobalt (Co)	0.04 (0.01)	0.00 (0.01)	5.79	p<0.05	0.10 (0.03)	0.04 (0.04)	2.85	p<0.05
Lead (Pb)	ID	ID	ID	ID	0.06 (0.05)	0.03 (0.03)	1.49	p>0.05

ID: Insufficient data.

In summary, only some parameters exhibit significant differences among seasons. The occurrence of seasonal differences for some parameters and sampling sites may indicate that seasonality may be of importance for some parameters or may not be detected depending on the parameter and the landfill sampled.

5.5.0 Impact of Leachate on Groundwater Quality

In order to assess the impact of leachate from the Toa Baja landfill on groundwater quality, an analysis of groundwater samples from three wells located next to the landfills was conducted. These included the Primate Center well, located downstream and very close (approximately 0.5 Km) from the Toa Baja landfill; and the Campanilla and Levittown wells, located approximately 2.3 and 3.1 Km, respectively, from the landfill. Table 5.11 shows the values obtained for the parameters analyzed in these three wells and in the Toa Baja landfill leachate, as well as the regulatory criteria established by the USEPA for drinking water (USEPA 2011a). Regulatory criteria established by the USEPA for drinking water were used to discuss the results of each one of the parameters at each sampling point. These include field parameters, inorganic macrocomponents and heavy metals.

5.5.1 Overview of USEPA Standards for Drinking Water

EPA's standards classify the drinking water contaminants within the National Primary Drinking Water Regulations (NPDWRs) or National Secondary Drinking Water Regulations (NSDWRs) (USEPA 2011a). A primary standard is set to provide the maximum feasible protection to public health, while the secondary standards regulate the contaminant levels based on aesthetic factors, which do not pose a risk to human health (USEPA 2011a).

Table 5.11. Comparison of various parameter levels in groundwater at different distance and USEPA limits.

	Values Ranges to Wells			Toa Baja Landfill (Range Values) * ¹ USEPA Limits
	Levittown	Campanilla	Primate	
Distance at Landfill (Km)	0.5	2.3	3.1	
Parameter				
Temperature °C	27.1-28.1	26.5-27.0	26.8-27.0	34.9- 36.9
pH	7.03-7.45	7.12-7.51	7.21-7.80	7.93-8.56
EC (μ S/cm)	517-588	552-603	700-878	13 975-22 825
Inorganic Macrocomponents (mg/L)				
Aluminum (Al)	0.145-0.304	0.295-0.412	0.309-0.426	0.441-3.671
Calcium (Ca)	63.167-81.967	83.033-92.833	62.633-122.767	28.457-163.833
Iron (Fe)	0.029-0.145	0.041-0.327	0.000-0.000	1.041-14.063
Potassium (K)	1.785-7.337	0.563-5.453	4.389-9.443	156.367-989.333
Magnesium (Mg)	9.473-12.200	3.768-8.063	2.661-5.203	14.467-74.267
Manganese (Mn)	0.000-0.008	0.000-0.000	0.000-0.000	0.024-1.050
Sodium (Na)	24.820-33.660	15.653-21.037	27.120-50.223	398.933-2025.333
				20 ^{*2}

Table 5.11., continued.

Heavy Metal						Ns
Chromium (Cr)	0.000-0.000	0.000-0.000	0.000-0.000	0.022-0.412	0.01	
Copper (Cu)	0.000-0.000	0.000-0.000	0.000-0.000	0.007-0.377	Ns	
Nickel (Ni)	0.000-0.033	0.000-0.033	0.000-0.049	0.000-0.264	1	
Zinc (Zn)	0.000-0.014	0.000-0.000	0.000-0.043	0.014-1.278	5	
Cobalt (Co)	0.000-0.030	0.000-0.010	0.000-0.031	0.000-0.346	Ns	
Lead (Pb)	0.000-0.000	0.000-0.000	0.000-0.000	0.000-0.078	0	

Ns= Not specified.^{*1} (USEPA 2011a).^{*2}Drinking water contaminant candidate list (USEPA 2011b).

Each primary contaminant is assigned a Maximum Contaminant Level (MCL), which is the highest possible level at which the contaminant is not expected to cause adverse health effects over a lifetime of exposure. For secondary contaminants, the USEPA does not establish MCLs, but assigns a suggested level. Among the primary standards relevant to the discussion of this thesis are chromium (Cr) and lead (Pb), (both heavy metal parameters). The secondary standards relevant to this research are pH (a field parameter), as well as zinc (Zn), iron (Fe), aluminum (Al), copper (Cu) and manganese (Mn) (which are considered inorganic macrocomponent parameters). In addition to the primary and secondary standards, the USEPA has a list of possible contaminants known as “Drinking Water Contaminant Candidate List”, which includes sodium (Na) (USAEPA 2011b; Hill et al. 2005). Effects on human health and environment of these primary and secondary standards and the other metals are presents in Table 5.12.

5.5.2 Field Parameters

The field parameters measured at each well include temperature, pH and electric conductivity. The groundwater temperature was similar for all wells. In terms of pH, the highest value (7.8) was observed in the Primate Center well, whereas the lowest value (7.1) was observed in the Campanilla and Levittown wells. The pH values of all groundwater samples fell within the range of 6.5-9.0, established by USEPA (USEPA 2011).

Statistically significant differences in the electrical conductivity of the groundwater extracted from these three wells is observed ($F=22.12$, $p<0.05$). The samples with highest EC values (700-878 $\mu\text{S}/\text{cm}$) were those obtained at the Primate Center well. This well is located very close (approximately 0.5 Km) to the Toa Baja landfill.

Table 5.12. Toxic effect of metals on health and ecological receptors.

Metal	Health Effect	Ecological Effect
Manganese	Central nervous system effects. Decreased enzymatic activity (Decreased erythrocyte superoxide dismutase). Nausea and vomiting.	Inhibits chlorophyll synthesis, and induces a decline in photosynthetic rate. Alteration in various vital growth processes such as photosynthesis and photosynthetic electron transport and biosynthesis of chlorophyll.
Nickel	Carcinogenic, nausea, vomiting, diarrhea, giddiness, lassitude, headache, and shortness of breath.	Toxicity symptoms in plant (chlorosis or yellowing of leaves followed by necrosis).
Lead	Metal lapse, carcinogenic, death, permanent damage to the central nervous system.	Increasing levels inhibit germination of seeds and exert a wide range of adverse effects on growth and metabolism of plants.
Copper	Carcinogenic, liver and kidney damage, nausea, diarrhea and abdominal pain.	Chlorosis and necrosis.
Chromium	Potent carcinogen	Mutagenesis and toxicity symptoms in plant (stunted growth, poorly developed root system and curled and discolored leaves).

Table 5.12., continued.

Possible implication of		
Aluminum	aluminum in the genesis of Alzheimer's disease.	Growth-limiting factor for plants.
Cobalt	Iodine deficiency disease in humans.	Affect the growth and metabolism of plants. Excess Co induced iron deficiency symptoms, decreased the chlorophyll a and b, and increased that of peroxidase and ribonuclease.
Iron	Oxidative mitochondrial membrane damage and poisoning of enzymes of tricarboxylic acid cycle and energy metabolism.	Growth inhibition, reduced chlorophyll content and an inhibition of photosynthesis.

^aSalem et al. 2000; Goyer et al. 1995.

EC values for the Campanilla well (located close to, but not downstream, from the landfill) were in the range of 552-603 µS/cm; whereas groundwater from the Levittown well (located downstream, but farther away from the landfill) exhibited the lowest values, 517-588 µS/cm. The higher EC values observed at the Primate Center suggest a higher concentration of soluble inorganic salts in this well, compared to the Campanilla and Levittown wells.

5.5.3 Inorganic Macrocomponents

Except for Fe and Mg, all mean values for the inorganic macrocomponents analyzed were higher for groundwater samples collected at the Primate Center well, than those collected at the two other wells (see Figure 5.01). The highest concentration

of Al (0.309-0.426 mg/L) is found at the Primate Center well, followed by that at the Campanilla (0.295-0.295 mg/L) and Levittown (0.145-0.304 mg/L) wells. It should be noted that, at all three wells, these values exceed the maximum permissible limit of 0.05-0.20 mg/L established for drinking water (USEPA 2011a) (Figure 5.02).

Drinking water containing aluminum is considered to be one of the main sources of Al intake for the human body. Although research has shown that is not the prime factor in the initiation of Alzheimer's disease, it is known to exacerbate and accelerate the disease once it is established. Aluminum is also commonly associated with dementia and Parkinson diseases (Othman et al. 2010; Momodu et. al. 2010). Other health and environmental effects of aluminum are presented in Table 5.12.

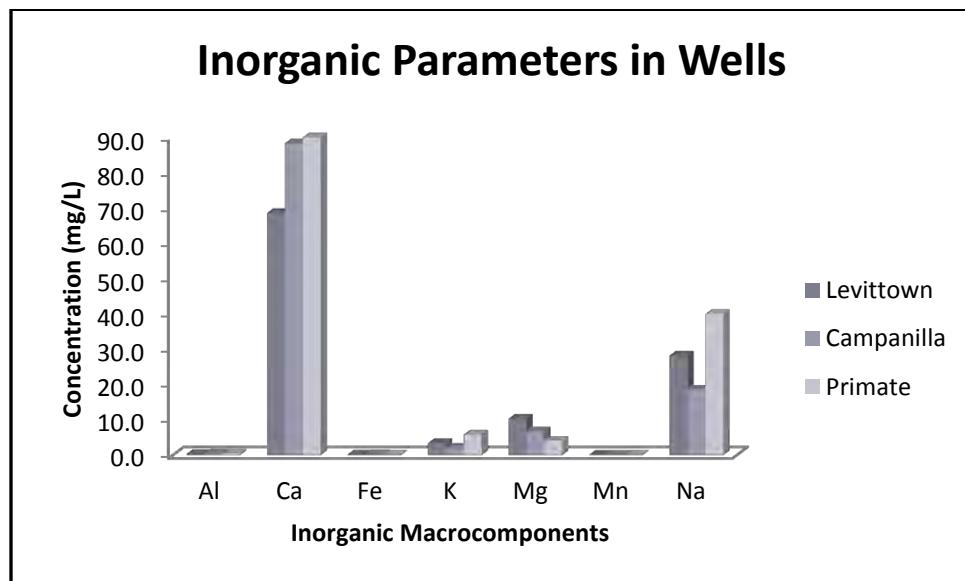


Figure 5.01. Concentrations of inorganic macrocomponents in Levittown, Campanilla and the Primate Center wells.

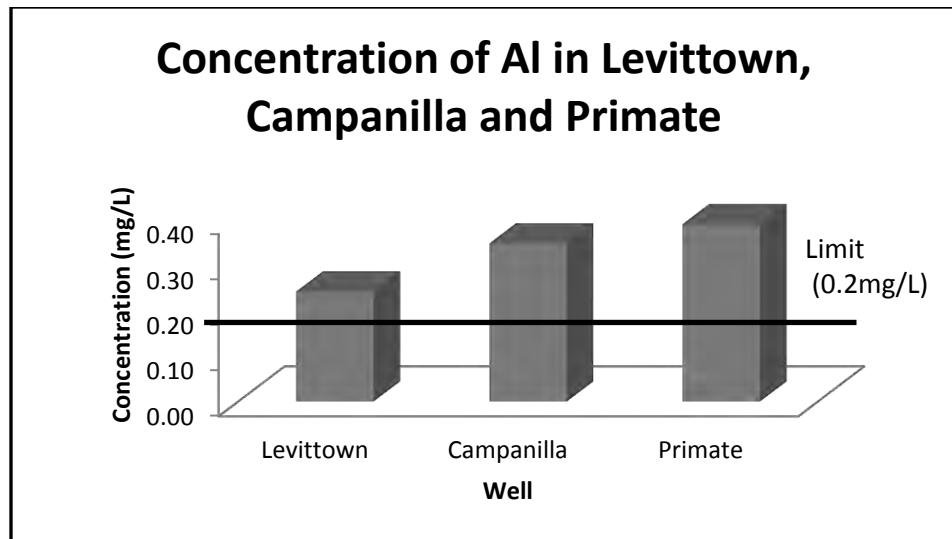


Figure 5.02. Aluminum (Al) concentrations in Levittown, Campanilla and the Primate Center wells and their relation to USEPA standard limits.

The same trend observed for Al (Primate Center > Campanilla > Levittown) is also observed for Ca, K and Na. Increasing concentration of Al, Ca, K and Na in these wells happens to coincide with a decrease in distance to landfill (Primate Center < Campanilla < Levittown) (see Figure 5.03). This observation may seem to suggest that the adverse impact on wells may result from leachate migration from the Toa Baja landfill. Among all inorganic components analyzed, Ca showed the highest values for all groundwater samples. Although the values obtained are lower than those observed by Cecen et al. (2002); Mor et al. (2006), it is important to point out that literature reports indicate that groundwater calcium concentrations are highly dependent on proximity to anthropogenic sources of pollution, such as sewage, leachate and industrial wastes (Longe et. al. 2007). Table 5.13 shows groundwater quality parameters for these wells located close to landfills, and for similar wells studied by other researchers.

In terms of Na, the groundwater concentration range observed at Primate Center, Campanilla and Levittown wells was 27.120-50.223 mg/L; 24.820-33.660 mg/L; and 15.653-21.037mg/L, respectively. These values are lower than those reported by Mor et. al. (2006), but higher than those observed by Cecen et al. (2000). Although Na is not considered a primary pollutant, it is included in the “Drinking Water Contaminant Candidate List”. All wells studied exceeded the maximum permissible limit of 20 mg/L established for Na by USEPA (2011b) (see Figure 5.03).

Table 5.13. Groundwater parameter levels in the wells analyzed in this and other studies.

	Wells analyzed in this study			Other studies		
	Levittown	Campanilla	Primate	Mort et al. (2006)	Longe et al. (2010)	Cecen et al. (2000)
Field Parameters						
Temperature °C	27.1-28.1	26.5-27.0	26.8-27.0	NR	NR	NR
pH	7.03-7.45	7.12-7.51	7.21-7.80	7.02-7.85	5.30-7.07	7.0-7.2
EC ($\mu\text{S}/\text{cm}$)	517-588	552-603	700-878	617-3620	NR	1160-1485
Inorganic Macrocomponents (mg/L)						
Aluminum (Al)	0.145-0.304	0.295-0.412	0.309-0.426	NR	NR	NR
Calcium (Ca)	63.167-81.967	83.033-92.833	62.633-122.767	477	NR	328-383
Iron (Fe)	0.029-0.145	0.041-0.327	ND	0.04	0.07	2-195
Potassium (K)	1.785-7.337	0.563-5.453	4.389-9.443	16.9	NR	1.53-43
Magnesium (Mg)	9.473-12.200	3.768-8.063	2.661-5.203	NR	NR	68-383

Table 5.13., continued.

Manganese (Mn)	0.000-0.008	ND	ND	NR	0.08	0.008-0.090
Sodium (Na)	24.820-33.660	15.653-21.037	27.120-50.223	291	NR	20.4-27
Chromium (Cr)	ND	ND	ND	NR	NR	NR
Heavy Metals (mg/L)						
Chromium (Cr)	ND	ND	ND	NR	0.44	0.002-0.003
Copper (Cu)	ND	ND	ND	NR	NR	NR
Nickel (Ni)	0.000-0.033	0.000-0.033	0.000-0.049	NR	NR	0.002-0.007
Zinc (Zn)	0.000-0.014	ND	0.000-0.043	0.03	0.08	0.008-0.090
Cobalt (Co)	0.000-0.030	0.000-0.010	0.000-0.031	NR	NR	NR
Lead (Pb)	ND	ND	ND	NR	NR	0.003-0.042

*NR= Not reported; ND = Not detected.

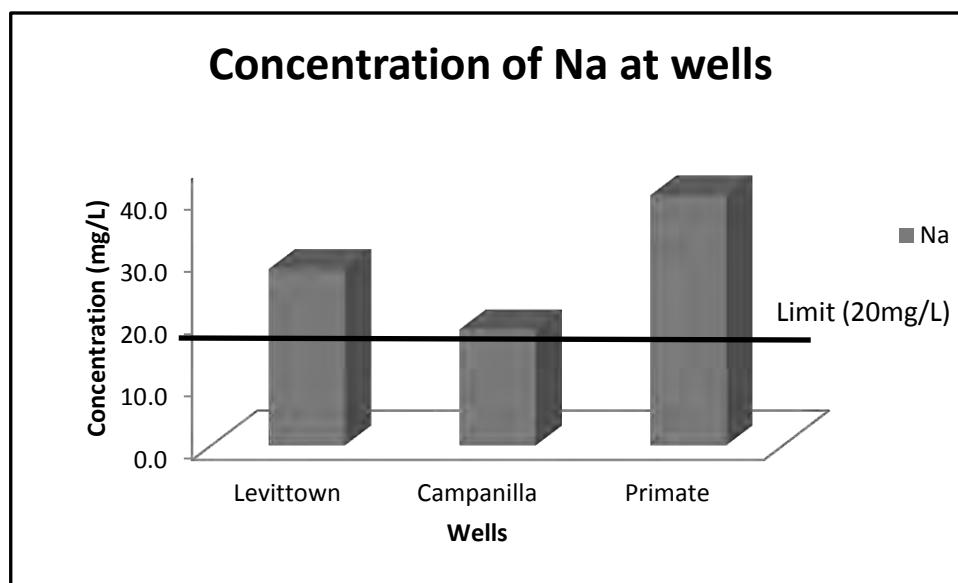


Figure 5.03. Na concentrations in Levittown, Campanilla and the Primate Center wells.

Although Na is commonly found in groundwater because most rock and soils contain sodium compounds, increased intake of sodium in drinking water may be problematic for people with hypertension, heart disease or kidney problems (USEPA 2011b).

Mg and Fe groundwater concentrations did not show the distance decay observed for the parameters discussed above. Mg was not detected in either Primate Center or Campanilla wells. It was found in Levittown, but only in one sample. On the other hand, Fe was not observed in the Primate Center well, but was detected in groundwater extracted from the Campanilla and Levittown wells. In Campanilla, Fe values ranged from 0.029-0.145 mg/L, which were exceeded by those found in groundwater from the Levittown well (0.041-0.327 mg/L). These groundwater Fe concentrations in Campanilla are lower than those found by Cecen et al. in 2006 (1-195 mg/L). However, they are higher than the 0.07 mg/L and 0.04 mg/L reported by Longe et al. (2010) and Mor et al. (2006), respectively.

As mentioned above, among all the inorganic components analyzed, Ca shows the highest concentration levels in all wells. These results are in agreement with those reported by Sabali et al. (2009) who concluded that the increase in Ca groundwater levels is due to leachate migration from landfill. In general terms, the trend in inorganic component concentrations found in Levittown and Campanilla is: Ca > Na > Mg > K > Al > Fe, whereas at the Primate Center it follows the order: Ca > Na > K > Mg > Al.

5.5.4 Heavy Metals

Among the six heavy metals analyzed, Ni, Zn and Co were detected in all the wells, with the highest values detected at the Primate Center well. The maximum value of Zn in the Primate Center well lies within the admissible levels established by USEPA (USEPA 2011), but is higher than the 0.03 mg/L reported by Mor et al. (2006), the 0.08 mg/L reported by Longe et al. (2010) and the 0.008-0.009 mg/L range observed by Cecen et al. (2006). The pattern observed for Zn in wells located downgradient with respect to the Toa Baja landfill (Primate Center and Levittown wells) is the same as that observed for most inorganic macrocomponents; that is, the concentration decreases with distance to landfill. At a distance of 0.5 Km (Primate Center) and 2.3 Km (Levittown), mean values found were 0.011 ± 0.02 mg/L and 0.006 ± 0.01 mg/L, respectively. This suggests that the high concentration of Zn in groundwater from the Primate Center may be related to the high concentration of Zn in the Toa Baja landfill leachate (0.014-1.278 mg/L) as a result of leachate percolation through soil. This would be in agreement with the conclusions reported by Sabali et al. (2009).

Although Ni went undetected in most groundwater samples taken at all three wells, Ni concentrations were highest in some samples collected at the Primate Center well, which exceeded those obtained by Cecen et al. (2000). Pb was not detected in any of the three wells. In general terms, Zn, Ni and Co concentrations in Primate Center are higher than those at Levittown (Figure 5.04).

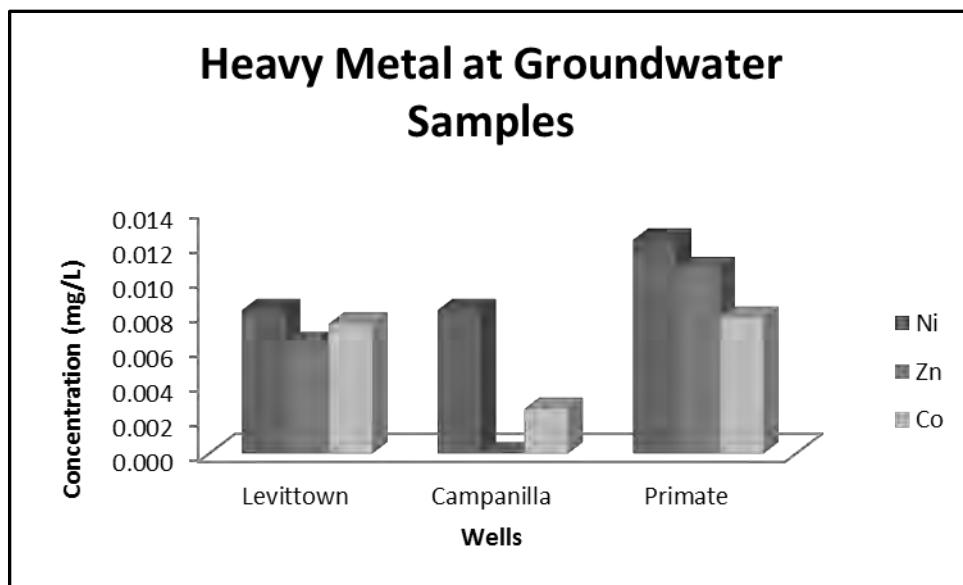


Figure 5.04. Heavy metal content in Levittown, Campanilla and the Primate Center wells.

5.6.0 Statistical Results for the Impact of the Toa Baja Landfill Leachate on Groundwater Quality

Most of the parameters analyzed for this study were found in highest concentrations in samples collected at the Primate Center well (0.5 mi from landfill) than in those collected at the Levittown well (3.1 Km from landfill). These results suggest that increased groundwater contamination around landfill locations seems to be dependent on distance to landfill and on downgradient diffusion potential.

In order to evaluate the impact of landfill leachate on groundwater quality, statistical analyses were performed based on results obtained for the Primate Center, Campanilla and Levittown wells. Results of the groundwater samples tested for inorganic macrocomponents and heavy metal parameters were analyzed for significant differences among wells using the ANOVA one-way test, for the three wells sampled ($n=36$). All tests were performed at the 95% level of significance. Results for these tests are shown in Table 5.14.

Hypothesis Testing:

Statistical analyses comparing the mean parameter from Levittown and Primate wells, were used to evaluate the hypotheses related to impact of landfill on wells

The hypothesis is stated as:

H₀: The mean values of each quality parameter for the well closest to the landfill will not differ from those of the well farthest from the landfill.

Table 5.14. Summary of ANOVA test conducted within 95% confidence interval for the Primate Center, Campanilla and Levittown wells.

Parameter	Wet						Dry					
	Mean (and SD)			F	P	Mean (and SD)			F	P		
	Primate	Campanilla	Levittown			Primate	Campanilla	Levittown				
Inorganic												
Macrocomponents												
(mg/L)												
Aluminum (Al)	0.41(0.02)	0.34(0.06)	0.26(0.02)	21.07	p<0.05	0.32(0.17)	0.35(0.07)	0.22(0.09)	2.02	p>0.05		
Calcium (Ca)	106.98(17.44)	87.47(12.64)	73.35 (9.50)	9.26	p<0.05	77.83 (38.14)	89.20 (4.46)	63.82(1.12)	1.97	p>0.05		
Iron (Fe)	0.00(0.00)	0.19(0.16)	0.09(0.07)	5.31	p<0.05	0.00(0.00)	0.08(0.06)	0.10(0.02)	13.18	p<0.05		
Potassium (K)	6.93(2.76)	3.13(2.58)	4.67(3.09)	2.76	p>0.05	3.88(1.91)	0.90(0.37)	2.06(0.30)	10.45	p<0.05		
Magnesium (Mg)	4.57(0.71)	7.87(1.07)	11.03(1.29)	56.98	p<0.05	3.40(1.67)	5.50(1.91)	9.51(0.12)	26.96	p<0.05		
Manganese (Mn)	ID	ID	ID	ID	ID	ID	ID	ID	ID	ID		
Sodium (Na)	45.26(5.61)	18.79(1.46)	30.47(3.53)	68.76	P<0.05	34.77(17.26)	18.35(2.97)	25.99(1.35)	3.94	p<0.05		

Table 5.14., continued.

Heavy Metals (mg/L)

Chromium (Cr)	ID	ID	ID	ID	ID	ID	ID	ID	ID	ID
Copper (Cu)	ID	ID	ID	ID	ID	ID	ID	ID	ID	ID
Nickel (Ni)	ID	ID	ID	ID	ID	0.03(0.03)	0.02 (0.03)	0.02(0.03)	0.18	p>0.05
Zinc (Zn)	0.02 (0.05)	0.00(0.00)	0.01 (0.01)	0.7	p>0.05	0.02 (0.01)	0.00(0.00)	0.01(0.01)	0.7	p>0.05
Cobalt (Co)	ID	ID	ID	ID	ID	0.02 (0.01)	0.01(0.01)	0.01(0.01)	0.86	p>0.05
Lead (Pb)	ID	ID	ID	ID	ID	ID	ID	ID	ID	ID

ID: Insufficient data

In terms of inorganic macrocomponents, significant differences were found between all three wells for all ions, except K, during the wet season. The trend, however, does not follow the same pattern for every ion, which makes it impossible to explain in terms of distance from landfill.

No significant differences were noted for Al and Ca concentrations in groundwater during the dry season. However, the concentrations of Fe, K, Mg and Na differed significantly for all three wells, with the first three decreasing in the order Levittown > Campanilla > Primate Center. For the heavy metals no significant difference was found during the dry or wet season for the three wells.

Once they reach groundwater, many of the inorganic pollutants analyzed become diluted. Others, however, may be retained in the soil. Because some difference is observed between the Primate Center well and the other two wells, a soil analysis was performed at the Primate Center in order to determine whether contaminants were being retained in the soil matrix. A discussion of the results of this study is presented below.

5.7.0 Impact of the Toa Baja Landfill Leachate on the Quality of Soil at the Primate Center

In order to assess the impact of the Toa Baja landfill on the soil surrounding the Primate Center, an analysis of three sampling points close to the Primate Center and one sampling point within the Toa Baja Landfill was conducted. All sampling points near the Primate Center were located downstream with respect to the Toa Baja landfill, but at different distances from this contaminant source. Point 1 ("Possible soil contamination on the Primate Center") is at an approximate distance of 0.3 Km from the Toa Baja landfill. Point 2 ("Soil Primate") is located farther away (0.5 km) from the landfill, but close to the Primate Center contaminant source (the cages where the Primate are kept). Point 3 ("Control site") was selected as a control site, since it is located far away from both the landfill (0.74 Km) and the animal cages. Analytical data for the soil samples collected at

the Primate Center and in the Toa Baja landfill at depths of 0-15 and 0.30 cm are presented in Tables 5.15 at 5.16. These data include field parameters, inorganic macrocomponents and heavy metals. The complete set of data is listed in Appendix D.

5.7.1 Analysis of Soil Collected at the Primate Center and the Toa Baja landfill

The soils at the Primate Center belong to the Tanamá series. They are clays classified as mixed, active, isohyperthermic, lithic hapludalfs of the order alfisols (Beiroth et al. 2002). The field parameters for the soil samples collected are presented in Table 5.15. For the sample collected at, Points 2 (“Soil Primate”) and 3 (“Control site”), the pH for samples taken at a depth of 0-15 cm were lower than those taken at a 15-30 cm depth. In contrast, for samples taken at Point 3 (“Control site”), the pH at a depth of 0-15 cm was higher.

Except for the soil samples collected at the Toa Baja landfill, the EC for all soil samples decreased with sampling depth. At a depth of 0-15 cm, EC values for sampling points at the Primate Center ranged from 145 µS/cm to 266 µS/cm; whereas for the 15-30 cm layer, the EC ranged from 144 to 219 µS/cm. The highest single EC value away from the landfill was found at Point 1 (266 µS/cm); and the lower value (134 µS/cm) was found at the control site. The Toa Baja landfill yielded the highest single EC values, which were 640 µS/cm for the 0-15 cm layer, and 932 µS/cm for the 15-30 cm layer.

Table 5.15. Field parameters for soil samples collected at the Primate Center and Toa Baja landfill.

Sampling Points	Depth	Distance from landfill	EC ($\mu\text{S}/\text{cm}$)	pH
Primate Point 1	0-15 cm	0.3 km	266	7.60
Primate Point 1	15-30 cm	0.3 Km	219	7.75
Primate Point 2	0-15 cm	0.5 Km	145	7.47
Primate Point 2	15-30 cm	0.5 Km	134	7.57
Primate Control Site	0-15 cm	0.74 Km	144	7.40
Primate Control Site	15-30 cm	0.74 Km	132	7.51
Toa Baja Landfill	0-15 cm	-	570	8.09
Toa Baja Landfill	15-30 cm	-	880	8.65

The results for inorganic macrocomponents in soil are presented in Table 5.15. Variations in the concentration of inorganic macrocomponents with sampling depth were also determined. For soils collected at the Primate Center, the levels of Al, Fe, Mn and Na observed at a sampling depth of 15-30 cm were higher than those obtained at 0-15 cm. With the exception of potassium (K) in soil samples collected at the Primate Center control site, for all samples collected at the Primate Center the levels of Ca, K and Mg observed at a sampling depth of 0-15 cm were higher than those obtained at 0-30 cm.

Table 5.16. Inorganic macrocomponent content of soil samples collected at the Primate Center and Toa Baja landfill.

Point, depth and distance from landfill	Al(mg/g)	Ca(mg/g)	Fe(mg/g)	K(mg/g)	Mg(mg/g)	Mn(mg/g)	Na(mg/g)
Point 1 (0-15 cm) (0.18 mi)	16.553±0.875 (15.568-17.699)	72.606±27.230 (47.127-111.178)	34.026±5.483 (30.337-42.150)	0.995±0.104 (0.847-1.069)	2.291±0.347 (1.814-2.624)	0.682±0.344 (0.475-1.192)	0.305±0.011 (0.293-0.317)
Point 1 (15-30 cm) (0.18 mi)	17.724±0.483 (17.369-18.404)	41.711±29.818 (9.744-74.589)	42.991±6.209 (36.175-48.476)	0.605±0.135 (0.442-0.743)	1.211±0.306 (0.921-1.602)	1.832±0.663 (1.244-2.562)	0.338±0.056 (0.257-0.381)
Point 2 (0-15 cm) (0.31mi)	11.113±0.672 (10.341-11.860)	4.312±2.626 (1.350-7.735)	30.194±6.099 (22.419-37.324)	0.133±0.041 (0.073-0.163)	0.717±0.206 (0.450-0.926)	0.963±0.400 (0.454-1.375)	0.119±0.094 (0.046-0.251)
Point 2 (15-30 cm) (0.31mi)	11.166±1.675 (8.671-12.259)	4.011±1.477 (2.712-6.136)	34.161±5.813 (25.537-37.801)	0.098±0.021 (0.077-0.126)	0.513±0.150 (0.329-0.674)	1.314±0.265 (0.975-1.589)	0.146±0.095 (0.040-0.246)
Control Site (0-15cm) (0.46 mi)	9.299±0.844 (8.513-10.466)	35.298±57.609 (1.224-15.660)	17.430±4.143 (11.735-21.490)	0.429±0.734 (0.047-1.530)	1.154±1.193 (0.403-2.930)	0.330±0.074 (0.247-0.406)	0.417±0.732 (0.023-1.515)
Control Site (0-30cm) (0.46 mi)	9.995±0.885 (9.153-11.244)	3.452±3.436 (1.223-8.498)	21.550±2.087 (18.893-23.374)	0.058±0.024 (0.029-0.088)	0.619±0.281 (0.302-0.876)	0.340±0.074 (0.235-0.398)	0.059±0.028 (0.028-0.090)

Table 5.16., continued.

Point Toa Baja Landfill (0-15 cm)	9.564 ± 0.548 (8.979-10.176)	82.267 ± 57.780 (3.652-141.567)	15.974 ± 9.303 (10.037-29.842)	1.225 ± 0.902 (0.069-2.169)	2.157 ± 1.195 (0.369-2.882)	0.565 ± 0.661 (0.222-1.555)	1.127 ± 0.805 (0.159-2.030)
Point Toa Baja Landfill (15-30 cm)	9.935 ± 0.826 (8.703-10.420)	107.687 ± 35.573 (72.106-156.262)	12.223 ± 1.907 (10.580-14.561)	1.172 ± 0.341 (0.844-1.629)	5.659 ± 0.238 (2.421-2.908)	0.242 ± 0.030 (0.199-0.065)	0.796 ± 0.208 (0.605-1.089)

For soil samples collected at the Toa Baja landfill, the levels of Al, Ca and Mg at a 15-30 cm sampling depth were higher than those at 0-15 cm. In contrast, the levels of Fe, K, Mn and Na at a sampling depth of 0-15 cm were higher than those collected at 15-30 cm.

The results for heavy metal characterization of the soil samples collected at each of these points are presented in Table 5.17. Upon analysis of these results, no specific pattern is observed with respect to variations in heavy metal content for these samples.

5.7.2 Comparison of Soil Characteristics between Sites

The pH values for soils collected at all three sampling points of Primate Center ranged from 7.40 to 7.75, indicating neutrality to slight alkalinity of the soils. These values are in the same range as those reported by Akpoeta et al. (2010). The highest value range 7.60-7.75 was found at Point 1 ("Possible soil contamination on Primate Center") (0.3 Km from the landfill), whereas the lowest value range of 7.40-7.51 was reported in the Point 3 "Control site" (0.74 Km from the landfill). Heavy metal adsorption on soil particles is considered the major contributing factor for the accumulation of heavy metals in soil. Soil pH has a significant effect on this process and on solute concentration. In general terms, high soil pH promotes greater heavy metal retention and lower heavy metal solubility (Akpoeta et al. 2010).

Statistically significant variations with respect to electrical conductivity (EC) of soil samples collected in the area between the landfill and the Primate Center were observed ($F= 17.406$; $p<0.05$), with the EC decreasing with increasing distance from the landfill. Akpoeta et al. (2010) report that high conductivity values (165 to 201 $\mu\text{s}/\text{cm}$) indicate significant presence of soluble inorganic salts in the soils studied.

Table 5.17. Heavy metal content of soil samples collected at the Primate Center and Toa Baja landfill.

Site, depth and distance from landfill	Cr (mg/g)	Cu (mg/g)	Ni (mg/g)	Zn (mg/g)	Co (mg/g)	Pb (mg/g)
Point 1 (0-15 cm) (0.18 mi)	0.048±0.028 (0.032-0.090)	0.071±0.020 (0.056-0.1010)	0.014±0.002 (0.012-0.016)	0.107±0.020 (0.092-0.135)	0.005±0.003 (0.002-0.0080)	0.075±0.059 (0.043-0.163)
Point 1 (15-30 cm) (0.18 mi)	0.106±0.025 (0.079-0.135)	0.056±0.009 (0.044-0.064)	0.022±0.001 (0.020-0.023)	0.156±0.051 (0.114-0.229)	0.010±0.003 (0.006-0.012)	0.064±0.026 (0.037-0.089)
Point 2 (0-15 cm) (0.31 mi)	0.031±0.014 (0.011-0.044)	0.031±0.041 (0.009-0.092)	0.002±0.002 (0.000-0.005)	0.024±0.011 (0.015-0.038)	0.000±0.000 (0.000-0.000)	0.018±0.002 (0.017-0.022)
Point 2 (15-30 cm) (0.31mi)	0.042±0.004 (0.037-0.047)	0.014±0.003 (0.011-0.018)	0.003±0.002 (0.000-0.005)	0.017±0.002 (0.015-0.020)	0.000±0.000 (0.000-0.000)	0.018±0.002 (0.017-0.020)
Control Site (0-15cm) (0.46 mi)	0.060±0.012 (0.044-0.074)	0.021±0.005 (0.015-0.026)	0.005±0.001 (0.004-0.007)	0.140±0.147 (0.018-0.353)	0.003±0.002 (0.000-0.005)	0.024±0.003 (0.020-0.027)
Control Site (0-30cm) (0.46 mi)	0.069±0.011 (0.053-0.053)	0.024±0.003 (0.020-0.027)	0.006±0.001 (0.005-0.007)	0.202±0.207 (0.061-0.503)	0.005±0.002 (0.004-0.007)	0.025±0.002 (0.022-0.028)

Table 5.17., continued.

Point Toa Baja Landfill (0-15 cm)	0.020±0.027 (0.006-0.060)	0.110±0.129 (0.022-0.302)	0.002±0.003 (0.000-0.006)	0.093±0.105 (0.034-0.251)	0.001±0.003 (0.000-0.005)	0.022±0.004 (0.018-0.027)
Point Toa Baja Landfill (15-30 cm)	0.009±0.002 (0.007-0.0120)	0.109±0.078 (0.035-0.206)	0.000±0.000 (0.000-0.000)	0.034±0.008 (0.029-0.045)	0.000±0.000 (0.000-0.000)	0.021±0.004 (0.017-0.027)

Besides those samples collected at the landfill, which yielded very high electrical conductivity, the samples with highest EC values (219-266 µS/cm) were those obtained at Point 1 ("Possible soil contamination on the Primate Center", 0.3 km from landfill). EC values for Point 2 ("Primate Soil", 0.5 Km from landfill) and Point 3 ("Control site", 0.74 Km from landfill) yielded very similar results (134-45 µS/cm and 132-144 µS/cm, respectively) suggesting that the high ionic concentrations presumably caused by leachate dispersion have already decayed at a distance of 0.5 Km from the landfill.

In a similar manner, all mean values for the inorganic macrocomponents analyzed were higher for soil samples collected at Point 1 than for other samples collected at the Point 2. The trend of increasing concentration for all inorganic macrocomponents in soil happens to coincide with a decrease in distance to landfill from Point 1 to Point 2 (Point 1 > Point 2 \cong Control site). This observation again suggests that the adverse impact on soil may result from leachate migration from the Toa Baja landfill.

For soil samples collected at Point 1, the relative abundance follows the order Ca > Fe > Al > Mg > K > Mn > Na, whereas for Point 2, the trend is Fe > Al > Ca > Mg > Mn > K > Na, and at the control site it follows the order Fe > Al > Ca > Mn > Mg > K > Na. For the Toa Baja landfill sample, the trend is Ca > Fe > Al > Mg > K > Na > Mn, which is very similar to that for Point 1. It is important to point out that leachate at the Toa Baja landfill runs in streams, while at the Primate Center it forms ponds during some times of the year, thus allowing more extensive interaction with the soil's aqueous layer.

Table 5.15 shows the concentration of heavy metals in soil at all sampling sites. Zupanc et al (2010) indicate that soil characteristics can be affected by landfill leachate, and Chiemchaisri et al. (2004) report that leachate can have a significant impact on plant growth due to nutrient imbalances.

Heavy metals considered in this study included micronutrients (Cu, Mg, Fe, Ni), non-essential elements (Zn) and toxic metals (Pb, Cr, Co). Although Cu, Zn and Ni are

essential micronutrient for plants, these are toxic to organisms at high concentrations. (Li et al. 2005) All heavy metals were detected in all sampling points, with the exception of Co at the control site. Among all heavy metals detected at the Primate Center and Toa Baja landfill, the highest concentrations were recorded at Point 1 (0.3 Km from landfill). Based on the results obtained, there was a gradual decrease in the concentration of heavy metals with increasing in distance from the Toa Baja Landfill (Point 1 > Point 2 > Control site).

5.7.3 Comparison between Heavy Metal Concentrations in Primate Center Soils and USEPA Standard Regulations

To minimize the risk of heavy metal contamination of the food chain and the environment, USEPA has established maximum concentration limits in sludge as well as background concentrations for nine heavy metals, including Zn, Cr, Cu, Ni and Pb (USEPA). Since these heavy metals were found at all sampling sites of the present study, the results obtained were compared to both the Maximum Acceptable Values in sludge and the typical background heavy metal soil concentrations (Table 5.18).

All mean values of heavy metals found were below the permissible limit for sludge, but above background concentrations of these metals. Excess heavy metal accumulation in soils is toxic to humans and other animals. For example, prolonged exposure to copper, lead, nickel and zinc can cause deleterious health effects in humans, and can adversely affect plant growth and yields when toxic concentrations are exceeded (Mwegoha et al. 2010).

Table 5.18. Comparison with standard regulations (concentrations in mg/g)

	Cr	Cu	Ni	Zn	Pb
Point 1 (0-15 cm) (0.3 Km)	0.077	0.063	0.018	0.132	0.069
Point 2 (0-15 cm) (0.5 Km)	0.061	0.047	0.012	0.087	0.049
Control Site (0-15 cm) (0.74 Km)	0.053	0.027	0.006	0.094	0.027
Toa Baja Landfill (0-15 cm)	0.042	0.052	0.004	0.113	0.024
* ^a Maximum concentration allowed in sludge (mg/g)	3.0	4.3	0.045	7.5	0.42
* ^b Typical background concentration for non-contaminated soils	ND	0.017- 0.065	0.007- 0.045	0.019- 2	0.008- 0.022

Ns: Not specified; *^a USEPA; *^bEvanylo 2009.

5.7.4 Statistical Analysis of Impact of the Toa Baja Landfill Leachate on the Quality of Soils at the Primate Center

Most of the parameters analyzed in this study were found in highest concentrations in the Point 1 (“Possible soil contamination on the Primate Center 0.3 Km away from Toa Baja landfill) than in the Point 3 (“Control site”, 0.48 Km away from Toa Baja landfill). These results indicate that increased soil contamination around landfill locations seem to also be dependent on distance to landfill and on downgradient diffusion potential.

In order to evaluate the impact of landfill leachate in soil quality, a statistical analysis was performed based on results obtained for soil samples collected at the Primate Center (Points 1 and 2), and the control site. Results of the soil samples tested for inorganic macrocomponents and heavy metal parameters were tested for significant differences among these three sampling points ($n=16$) using the ANOVA one-way test. When differences were found, a Tukey comparison test was performed to determine whether individual differences between each site were significant. Tests were performed at the 95% level of significance (Table 5.19).

Hypothesis Testing:

Statistical analyses comparing mean values for each parameter detected at the Primate Center (Points 1 and 2) and the control site were used to evaluate the hypotheses related to impact of landfill leachate on Primate Center soil.

The hypothesis is stated as:

H_{1o}: The mean values for each parameter of soil samples collected close to the landfill will not differ from those collected farther away from the landfill.

Except for Na ($p>0.05$), all inorganic macrocomponents and heavy metal in soils collected at these three sites showed a statistically significant difference ($p<0.05$). In case of inorganic macrocomponents, tukey comparison tests indicate that, except for Na, the

mean values for samples collected at the Point 1 ("Possible soil contamination on the Primate Center") differ from those obtained at the "Control site" and comparison tests between Point 1 and Point 2, also indicate that, except for Fe, Mn and Na, the mean values do not differ.

For all heavy metals Tukey comparison test indicates that the mean values for samples collected at the Point 1("Possible soil contamination on the Primate Center"), differ from those obtained at the "Control site". Tukey comparison also indicate that for Cu, Pb and Ni, the mean values for samples collected at Point1 not differ from those obtained at Point 2.

Table 5.19. Results of ANOVA tests for soil parameters.

	Mean (and SD)			Significance	
	Control Site	Point 2	Point 1	F Values	Level
Inorganic Components					
Aluminum (Al)	9.65(0.88)	11.14 (1,18)	17,14(0.91)	125.94	(p<0.05)
Calcium (Ca)	19.37 (41.44)	4.16 (1,98)	57.16 (31.17)	6.64	(p<0.05)
Iron (Fe)	19.49(3.75)	32.18 (5.91)	38.51(7.24)	22.21	(p<0.05)
Potassium (K)	0.24(0.52)	0.12(0.04)	0.80(0.24)	9.71	(p<0.05)
Magnesium (Mg)	0.89(0.85)	0.62(0.20)	1.75(0.65)	7.09	(p<0.05)
Manganese (Mn)	0.34(0.07)	1.14(0.37)	1.26(0.79)	7.99	(p<0.05)
Sodium (Na)	0.24(0.52)	0.13(0.09)	0.32(0.04)	0.78	(p>0.05)
Heavy Metal					
Chromium (Cr)	0.04(0.01)	0.06(0.01)	0.08(0.04)	5.65	(p<0.05)
Copper (Cu)	0.02(0.03)	0.02(0.00)	0.06(0.02)	12.20	(p<0.05)
Nickel (Ni)	0.00(0.00)	0.01(0.00)	0.02(0.00)	65.44	(p<0.05)
Zinc (Zn)	0.02(0.01)	0.17(0.17)	0.13(0.04)	4.74	(p<0.05)
Cobalt (Co)	0.00(0.00)	0.00(0.00)	0.01(0.00)	17.45	(p<0.05)
Lead (Pb)	0.02(0.01)	0.02(0.01)	0.07(0.11)	10.34	(p<0.05)

Conclusions

Based on the analysis and the results obtained, the following conclusions are reached:

1. The leachate from both the Toa Baja and Toa Alta landfills is most likely in the methanogenic phase, because the range of pH values observed (7.93 and 8.56) falls within the alkaline range, which is typical of this phase.
2. With the exception of two parameters (Zn and Ca), no significant difference is observed with respect to leachate composition between landfill areas that receive wastes from different sources (metal scrap versus domestic waste).
3. Although no significant changes in the inorganic macrocomponents composition of leachate was observed as a result of seasonal variations at the Toa Alta landfill, the Toa Alta landfill showed significantly higher concentrations of certain parameters during the dry season.
4. In general terms, significant seasonal changes in the concentration of heavy metal parameters in leachate was observed for the Toa Alta landfill, with higher concentrations obtained during the dry season.
5. With the exception of a single parameter (Co), no significant difference in the concentration of heavy metals in leachate was observed for the Toa Baja landfill during both the dry and wet seasons.
6. Although the groundwater from the wells included in this study meets the drinking water standards for most parameters, all groundwater samples collected exceeded the maximum allowed limit for at least one primary or secondary drinking water standard, making it unsuitable for human consumption.
7. Groundwater samples from wells located near the Toa Baja landfill were analyzed to evaluate the potential impact of leachate on nearby wells. Although a statistically significant ($p<0.05$) distance effect was found for several of the water quality parameters

measured, the direct impact of leachate on these wells could not be clearly established on the basis of the results obtained.

8. In general terms, although with some notable exceptions, the concentration of inorganic macrocomponents and heavy metal parameters in leachate, groundwater and soil samples seems to decay with distance to landfill as well as with the site's downgradient diffusion potential.

9. Results obtained from the analysis of soil samples collected near the Toa Baja landfill, and extending towards the Caribbean Primates Research Center facility in Sabana Seca, suggest that the contamination of soils close to this facility is related to leachate from the Toa Baja municipal landfill.

10. Because landfill leachate may cause adverse effects to nearby communities and natural systems, it is important for environmental agencies (such as the PREQB) to gain a better understanding of its composition and diffusion patterns in order to make more sound decisions with regards to the location, lifespan and long-term management of current and future facilities, as well as to the need for leachate pre-treatment prior to its discharge in wastewater treatment plants or its direct release to the environment. Based on the analysis and the results obtained, the following conclusions are reached:

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Appendix A:

PROCEDIMIENTO OPERACIONAL ESTANDAR

PARA

**TOMA DE MUESTRA DE LIXIVIADOS EN SISTEMA DE RELLENOS SANITARIOS
PARA ANALISIS DE METALES**

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Lista de Abreviaciones

ICPES: Espectroscopia de Plasma de Inducción Acoplada

JCA: Junta de Calidad Ambiental

SRS: Sistema de Relleno Sanitario

SOPs: Procedimientos operacional estándar

USEPA: Agencia de Protección Ambiental Federal

A. Propósito

El objetivo de este Procedimiento de Operación Estándar (SOP, por sus siglas en inglés) es describir los procedimientos para colección de muestras representativas de lixiviados. Esta guía es principalmente para ser usada en la toma de muestras de lixiviado en los sistemas de rellenos sanitarios.

B. Definiciones

SRS: Instalación para la disposición final de desperdicios sólidos no peligrosos.

SW 846: Manual, publicado por la EPA para proveer la guía y métodos físicos y químicos para la evaluación de desperdicios sólidos.

Método 3010: Procedimiento incluido en los SW846 para la digestión de las muestras antes de ser analizadas para metales usando espectroscopía de plasma de inducción acoplada.

Metales Totales: Concentración de metales disueltos y suspendidos en una muestra. Los mismos se determinan luego de someter la muestra a los métodos de digestión tales como 3010A, 3015, 3020, 3050, 3051, 3052.

Muestras discretas (grab): Una muestra discreta que es colectada individualmente en una localidad específica en un punto determinado en tiempo. La muestra es recolectada toda de una sola vez, en el punto de muestreo.

Métodos Series 6000: Métodos para analizar metales incluidos en SW 846

Condiciones de Preservación: Temperatura de 4 °C y a un pH<2 con HNO₃ concentrado.

Puntos de muestreo: Lugar escogido dentro del sitio de muestreo para tomar cada muestra.

Campaña de muestreo: Cada evento de muestreo durante un día

Control de Temperatura: Envase con agua desionizada o destilada que se coloca en cada nevera en la cual se almacenan las muestras y se utiliza para verificar no solo la

temperatura en la cual se reciben las muestras en el laboratorio, sino también durante la campaña de muestreo.

Blanco de Viaje: Envase con agua desionizada o destilada que se coloca en cada nevera en la cual se almacenan las muestras y se utiliza para verificar contaminación cruzada.

Blanco de Campo: (Field Blank): Envase con agua desionizada o destilada que se lleva al punto de muestreo. Sirve para evaluar no solo la contaminación en el sitio de muestreo sino también la pureza de los reactivos empleados.

Triplificados de Muestras: Triplificados de muestras son muestras recolectadas consecutivamente en envases separados, en la misma fuente o punto de muestreo, bajo idénticas condiciones

C. Materiales Equipos

Los siguientes materiales y equipos son requeridos para toma de muestras de lixiviados

-Guantes de látex

-Mascarilla

-Neveras portátiles con hielo

-Termómetros calibrados con escala de -10 a 100 °C

-Botella de polietileno de 500 ml, con tapa del mismo material con certificado de análisis

- Ácido nítrico HNO₃ (5ml/L)

-Papel Tornasol (Litmus) con rango de 0-2.5 y de 0-14

-Metro de pH para pruebas de Campo

- Metro de conductividad

-Vasos de precipitado de 500 ml y 100 ml “Beaker” y probetas-clase A 15 ml

-Bolsas Plásticas 16 x 11 pulgadas

- Gotero plástico
- Agua destilada o desionizada.
- Hojas de registros para cadena de custodia y para descripción general del sitio de muestreo.

D. Procedimientos

Los procedimientos siguientes son para muestras de lixiviados de tipo “grab” (muestras discretas).

D.1 Prevención de Contaminación y Medidas de Seguridad

- El uso de guantes látex, en todo momento, es requerido con el propósito de proteger el personal y evitar contaminación accidental de la muestra (por parte del personal de muestreo).
- Utilizar mascarilla, zapatos y gafas de seguridad durante todas las actividades de muestreo.
- No tocar ni el interior de los envases de muestras ni tampoco las tapas de los mismos, esto con el propósito de evitar contaminación de la muestra.
- Proceso de descontaminación: todos los equipos o materiales son lavados con agua desionizada y solución de detergente alconox (1 cucharada de alconox por cada galón de agua) y luego enjuagados con una solución de ácido nítrico 10 a 15 % (1 volumen de ácido por 5 volumen de agua) y se finaliza enjugando tres veces con agua desionizada. Una vez descontaminados los equipos y materiales son envueltos de papel aluminio hasta su uso.

D.2 Organización de Equipo de muestro

El siguiente procedimiento se llevará a cabo en el laboratorio antes de partir para cada campaña o día de muestreo:

- Todos los envases y neveras se inspeccionan para detectar imperfecciones (grietas, manchas, dobleces, etc.) antes de ser usados. Los envases o neveras con defectos

visibles no serán utilizados. El día del muestreo se prepara las neveras con hielo y en cada una de las campañas de muestreo se llevará una nevera adicional con suficiente hielo.

D.3 Toma de Muestreo de Lixiviados para el Análisis de Metales

Antes de tomar la muestra, el recipiente se debe enjuagar tres veces con lixiviado antes de efectuar el muestreo. La muestra es recogida en los envases directamente de la fuente de lixiviado. Coloque el envase en dirección del flujo de lixiviado, llene el envase y retire. Cuando no sea posible colocar el envase directamente de la fuente, éste será sumergido con el cuello en posición vertical, en la charca de lixiviado. Este procedimiento debe hacerse con mucho cuidado para evitar el disturbio de la muestra.

D.4 Preservación, Manipulación y Almacenaje de Muestras

D.4.1 Preservación de las Muestras

Con el propósito de minimizar cualquier proceso físico, biológico y químico que pueda ocurrir en la muestra antes del análisis, las muestras son preservadas.

Los requerimientos de preservación para análisis de metales, son temperatura de 4 °C y pH >2 (con ácido nítrico concentrado de alto grado químico). Inmediatamente después de la recolección de la muestra, el ácido es adicionado en cada uno de los envases de las muestras. El ácido para la muestra se transporta en botella de plástico dentro de un envase de protección. En el momento en que se vaya a utilizar el ácido, para ajustar el pH, se coloca inicialmente 5 ml en una la probeta y de ahí se adiciona a la muestra con ayuda de un gotero hasta lograr un pH menor de 2 en la muestra. Luego de adicionar el preservativo, las muestras preservadas son agitadas y el pH es verificado. Para verificar si el pH es menor de 2, aproximadamente 5 ml de muestra preservada es vertida en vaso de precipitación ('beaker') y se procede a medir pH utilizando papel de tornasol. El preservativo es adicionado hasta que las muestras alcancen los requerimientos de pH.

La misma cantidad de preservativo utilizado para las muestras es adicionado a los blancos de campo. El ácido debe ser transportado al campo de muestreo en un recipiente plástico o de teflón, adecuados para este fin.

D.4.2. Manipulación y Almacenaje de Muestras

Todos los envases para blancos son enjuagadas con agua desionizada antes de ser llenados con los 500 ml de agua desionizada. Los envases de las muestras son enjuagados con lixiviados antes de recolectar las muestras finales. Las muestras son colocadas en una nevera con hielo inmediatamente después de su recolección, satisfaciendo los requerimientos de bajas temperatura y transportadas al laboratorio una vez terminada las actividades del día de la campaña de muestreo.

Las mediciones de pH y de conductividad son determinadas en cada punto de muestreo y luego de la recolección de la muestra. Para medir el pH y la conductividad en cada punto de muestreo emplea el siguiente procedimiento: se enjuaga tres veces con agua desionizada el electrodo, luego se sumerge el mismo en aproximadamente 30 ml de muestra bien homogenizada y se registra el valor de la medida.

D.5 Procedimiento para la Certeza de Calidad

Las muestras de campo para certeza de calidad son colectadas y analizadas para asegurar la consistencia en la ejecución de todas las actividades de muestreo de lixiviado.

D.5.1-Equipos: Para cada campaña de muestreo la calibración de los equipos de pH y conductividad debe ser verificada antes de salir del laboratorio.

D.5.2 -Control de calidad en el campo de muestreo: incluyen los blancos de viaje (trip blanks), blancos de campos (field blank) and triplicados de muestras. Todos los envases son colocados en una bolsa plástica (tipo zip-loc) y colocados en la nevera de la siguiente manera: se coloca una capa de hielo en la parte inferior de la nevera, se

colocan las bolsas con los envases de tal forma que queden completamente rodeadas de hielo.

D.5.2.1 Blanco de Temperatura

El procedimiento de preparación de blancos de temperatura se realiza en el laboratorio antes de salir para cada campaña de muestreo. Para los envases de control de temperatura se emplea un recipiente de polietileno de 500 ml, debidamente identificado, se introduce en una bolsa tipo zip-loc de 1 galón y se coloca en cada una de las neveras utilizadas para transportar las muestras. La temperatura en el envase del blanco de temperatura es verificada durante la campaña de muestreo (en cada sitio y punto de muestreo) y al llegar al laboratorio. El envase del blanco de temperatura es destapado y un termómetro calibrado es introducido y al pasar 1 a 2 minutos (tiempo para que se estabilice la temperatura), se procede a tomar y reportar la lectura la temperatura.

El blanco de temperatura no es analizado debido a que su propósito es para verificar y asegura que durante toda la campaña de muestreo y hasta el arribo al laboratorio, las muestras cumplieron con los requerimientos de temperatura. Se emplea un recipiente de blanco temperatura para cada una de las neveras utilizadas para el transporte de muestras de lixiviado.

D.5.2.2 Blanco de Viaje

El blanco de viaje es preparado en el laboratorio, al adicionar 500 ml de agua desionizada en un envase de polietileno del mismo tipo utilizado para recolectar las muestras de lixiviado. El envase es tapado, sellado y colocado en cada una de las neveras utilizadas para transportar las muestras. El blanco de viaje cumple con el propósito de verificar se ocurre contaminación cruzada durante la campaña de muestreo. El blanco de vieja no es destapada en ningún momento, durante las

actividades de campo pero es manipulado y analizado de la misma forma que las muestras.

D.5.2.3 Blancos de Campo

Recolección y análisis de blancos de campos son con el propósito de asegurar el control de calidad en la integridad en los procedimientos de recolección y manipulación de la muestra. El blanco de campo es preparado en el laboratorio, al adicionar 500 ml de agua desionizada en el mismo tipo de envase de polietileno utilizado para recolectar las muestras de lixiviado. Al llegar al punto de muestreo, el envase de blanco de campo se destapa y se coloca lo más próximo al punto de muestreo mientras se realiza la recolección en triplicada de las muestras de lixiviado. Una vez finalizada la recolección de las muestras de lixiviado el blanco de campo es tapado, sellado y trasportado junto con las muestras de lixiviado. El blanco de campo es sujeto al mismo procedimiento de preservación, manipulación y análisis que sufren las muestras de lixiviado.

D.5.2.4 Triplicados de Muestras

Triplicado de muestras son tres muestras consecutivas recolectadas en un mismo punto de muestreo utilizando el mismo procedimiento. Triplicado de muestras son usadas para evaluar la precisión de todo el proceso de muestreo y análisis de las muestras. Los triplicados de muestras serán colectados en cada uno de los puntos de muestreo.

D.5.2.5 Documentación

Hojas de formas para documentar las actividades durante una campaña de muestreo incluyen, cadena de custodia, hoja de descripción de área, hoja de descripción general de las condiciones climáticas y hojas de verificación de calibración de los equipos.

D.5.2.6 Identificación de muestras

Todas las muestras serán identificadas usando la nomenclatura asignada y la fecha del muestreo o campana de muestreo.

Nomenclatura para la Identificación de muestras

Se asignará la nomenclatura para la identificación de cada una de las muestras conforme a los siguientes puntos:

Muestras de lixiviados:

La nomenclatura de cada muestras comenzara con la letra L:

L= Lixiviado

Después de la letra inicial, separado por un guion, va un número que corresponden a las dos últimas siglas del año en curso (por ejemplo: 07 para el año 2007) y le antecede un número de uno o dos dígitos (según el caso) que indique en forma consecutiva si es la primera, segunda, etc., campaña de muestreo tomada en ese sitio, esto para identificar cada campaña de muestreo.

A lo anterior le sigue un código que indica el sitio de muestreo.

Para las muestras tomadas en los SRS de Toa Baja y Toa Alta, por ejemplo, se emplean los siguientes códigos:

Toa Baja: SRSTB

Toa Alta: SRSTA

Todas las muestras se toman en triplicado por lo que después del código anterior se adiciona el número 1, 2 o 3 según el caso para indicar el triplicado de cada muestra. En el caso donde en un mismo SRS, se escogen dos o más puntos diferentes de muestreo, el primer punto de muestreo se le asigna la letra A y al segundo punto de muestreo la letra B y así sucesivamente. Estas letras preceden la secuencia anterior de identificación para las muestras de lixiviados.

El siguiente es un ejemplo de una nomenclatura para la identificación de las muestras de lixiviado del SRS de Toa Baja durante la primera campaña de muestreo en el 2007 y recolectadas en el punto A y en el punto B:

Para el punto A:

L-01-07-SRSTB-1-A

L-01-07-SRSTB -2-A

L-01-07-SRSTB -3-A

Para el punto B:

L-01-07-SRSTB -1-B

L-01-07-SRSTB -2-B

L-01-07-SRSTB -3-B

Blancos de Muestras

Los blancos serán identificados de la siguiente manera:

Las letras iniciales para cada uno de los blancos son las siguientes:

BTL = blanco de temperatura para el lixiviado

BCL = blanco de campo para las muestras de lixiviado (field blank)

BVL: blanco de viaje para cada nevera que transporta muestras de lixiviado (trip blank).

A cada una de las letras iniciales es seguida por un número que indique la campaña y por dos números que indiquen el año en que se realiza cada una de las campañas de muestreo (por ejemplo para una campaña realizada en el 2007 se utiliza el código: 07 y 08 para el año 2008). Por último, al igual que para las muestras de lixiviado, se adiciona un código que indica el sitio y punto de muestreo.

La Tabla A-1 presenta un ejemplo de la nomenclatura utilizada para la identificación de blancos tomados en una primera campaña de muestreo realizada en el 2007 en el SRS de Toa Baja.

Tabla A-1 Nomenclatura para la Identificación de blancos para la primera campaña.

Tipo de Blanco	Número de Campaña y Año	Sitio de Muestreo	Punto de Muestreo
BVL	07	SRATB	A
BVL	07	SRATB	B
BTL	07	SRATB	A
BTL	07	SRATB	B
BCL	07	SRATB	A
BCL	07	SRATB	B

D.5.2.7 Rotulación de los Envases

Para rotular los envases de las muestras y los blancos, se pega al envase antes o en el momento de muestreo, papel engomado o etiquetas adhesivas en las que se anota, con tinta a prueba de agua la siguiente información:

Nomenclatura asignada para la identificación de la muestra (como se explicó anteriormente)

Nombre del recolector de la muestra

Fecha, hora y lugar de muestreo

Preservación realizada

D.5.2.8 Cadena de Custodia

El proceso de control y vigilancia del muestreo, preservación y análisis (cadena de custodia) es esencial para asegurar la integridad de la muestra desde su recolección

hasta el reporte de los resultados. Para la cadena de custodia se emplea un registro (ver apéndice 1), con la siguiente información:

- Número de secuencia para identificar cada uno de los envases de las muestras y los blancos
- Identificación de la muestra
- Descripción de la muestra
- Tipo de Muestra
- - Parámetros
- Tipo de preservación
- Firma, fecha y hora del personal que realizó el muestreo y de la persona que recibe la muestra en el laboratorio.
- Sitio fecha y hora de muestreo

Una vez diligenciado el formato de cadena de custodia las muestras son almacenadas en el laboratorio hasta su análisis mediante ICP-AES usando el método 6010 de la serie 6000 de la USEPA u otro método aprobado por la USEPA (ver Tabla A-2).

Tabla A-2 Método analítico para metales.

Parámetro	Método	Longitud de onda (nm)	Límite de Detección Estimado ($\mu\text{g/L}$)
Cobalto	EPA SW 846 6010 C	226.502	4.7
Cromo	EPA SW 846 6010 C	227.716	4.7
Hierro	EPA SW 846 6010 C	259.94	4.1
Nickel	EPA SW 846 6010 C	231.604	10
Zinc	EPA SW 846 6010 C	213.856x2	1.2
Plomo	EPA SW 846 6010 C	220.353	28
Cobre	EPA SW 846 6010 C	324.754	3.6

D.5.2.9 Requerimientos Adicionales

La cantidad o volumen y preservación de la muestra, el, tipo de envase y tiempo máximo de análisis (holding time), son requisitos adicionales, necesario para cumplir con un plan de certeza de calidad (see Tabla A-3).

Tabla A-3. Requisitos Adicionales para cumplir con el plan de certeza de calidad.

Parámetro		Volumen	Tiempo
	Envase de Recolección	mínimo requerido de Muestra (ml)	máximo de espera
Metales	Platico (polietileno de alta densidad)	Refrigeración a 4 °C, pH<2 con HNO ₃	6 meses
Totales			

Referencias

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Appendix B:

Results of Laboratory Data for Inorganic- Macrocomponents

Table B.01. Laboratory Report of Leachate Samples for Inorganic- Macrocomponents (April and June 2009)

USDA Forest Service. International Institute of Tropical Forestry

IITF Laboratory Report

Heavy Metal Characterization of Leachate from Two Municipal Waste Disposal Landfills in Puerto Rico and its impact on Nearby Groundwater Wells

Investigator: Luz S. Betancourt (Ph.D. Dissertation - Turabo University)

#-Sequence	ID	Al(ppm)	Ca(ppm)	Fe(ppm)	K(ppm)	Mg(ppm)	Mn(ppm)	Na(ppm)
HS		100	100	100	100	100	100	50
LS		0.015	0.040	0.020	0.017	0.002	0.003	0.038
1	Trip Blank Pozo-abril-09	<	0.753	<	<	<	<	<
2	Trip Blank SRS-abril-09	<	<	<	<	<	<	2.392
3	Field Blank Levitown-abril-09	<	<	<	<	<	<	2.402
4	Lev-Sample 1-A abril-09	0.155	61.800	0.102	1.741	9.300	<	26.770
5	Lev-Sample 1-B abril-09	0.115	63.800	0.134	1.783	9.560	<	27.290
6	Lev-Sample 1-C abril-09	0.165	63.900	0.092	1.830	9.560	<	27.390
7	Field Blank Campanilla-abril-09	<	<	<	<	<	<	2.437
8	Campanilla Sample 2-A-abril-09	0.297	94.300	0.129	0.581	3.924	<	20.990
9	Campanilla Sample 2-B-abril-09	0.278	90.400	0.103	0.539	3.593	<	20.760
10	Campanilla Sample 2-C-abril-09	0.309	93.800	0.139	0.568	3.787	<	21.360
11	Field Blank Primate-abril-09	<	<	<	<	<	<	2.403
12	Primate-Sample 3-A-abril-09	0.315	94.000	<	4.368	4.087	<	40.800
13	Primate-Sample 3-B-abril-09	<	<	<	<	<	<	<
14	Primate-Sample 3-C-abril-09	0.304	93.900	<	4.409	3.897	<	40.560
15	Field Blank Toa Baja Punto 1-abril-09	<	0.432	<	<	<	<	<
16	Toa Baja Punto1-1A-Sample-abril-09	1.414	23.820	13.370	1149.000	22.090	0.089	2994.000
17	Toa Baja Punto1-1B-Sample-abril-09	<	<	<	<	<	<	<

Table B.01., continued.

18	Toa Baja Punto 1-1C-Sample-abril-09	2.722	36.510	15.500	1156.000	23.560	0.159	3082.00
19	Field Blank Toa Baja Punto 2-abril-09	<	<	<	<	<	<	2.791
20	Toa Baja Punto2-2A-Sample-abril-09	3.042	134.300	6.310	997.000	68.700	0.309	1650.000
21	Toa Baja Punto2-2B-Sample-abril-09	5.250	212.300	8.480	990.000	73.200	0.394	1711.000
22	Toa Baja Punto2-2C-Sample-abril-09	2.702	1449.000	27.400	981.000	80.900	2.447	1621.000
23	Field Blank Toa Baja Punto 3-abril-09	<	<	<	<	<	<	2.591
24	Toa Baja Punto 3-3A-Sample-abril-09	4.724	104.100	15.780	1181.000	51.100	0.692	2830.000
25	Toa Baja Punto 3-3B-Sample-abril-09	6.670	128.000	18.660	1180.000	50.800	0.964	2818.000
26	Toa Baja Punto 3-3C-Sample-abril-09	7.110	114.600	18.320	1136.000	51.000	0.806	2858.000
27	Field Blank Toa Alta-abril-09	<	<	<	<	<	<	2.467
28	Toa Alta-Sample-1-A-abril-09	0.702	101.100	7.940	622.000	53.300	0.119	124.200
29	Toa Alta-Sample-1-A-abril-09	0.454	72.800	5.720	428.400	37.220	0.068	850.000
30	Toa Alta-Sample-1-A-abril-09	0.437	70.700	5.680	432.400	37.990	0.068	900.000
31	Trip Blank Pozo-junio-09	<	<	<	<	<	<	2.430
32	Trip Blank SRS-junio-09	<	<	<	<	<	<	2.767
33	Field Blank Toa Baja-Minga-junio-09	<	<	<	<	<	<	2.494
34	Toa Baja-Minga-Sample 4-A-junio-09	0.614	30.420	11.810	844.000	20.850	0.030	1757.000
35	Toa Baja-Minga-Sample 4-B-junio-09	0.333	26.940	10.250	768.000	19.150	0.018	1586.000
36	Toa Baja-Minga-Sample 4-C-junio-09	0.400	28.010	10.670	795.000	20.320	0.024	1659.000
37	Field Blanik Toa Baja-Camino-junio-09	<	<	0.027	<	<	<	2.185
38	Toa Baja Camino-Sample-5-A-junio-09	1.464	53.900	9.570	895.000	37.650	0.221	1683.000
39	Toa Baja Camino-Sample-5-B-junio-09	2.468	53.500	10.730	862.000	37.540	0.253	1557.000
40	Toa Baja Camino-Sample-5-C-junio-09	2.191	53.600	10.740	896.000	37.650	0.266	1696.000
41	Field Blank Toa Alta-junio-09	<	<	<	<	<	<	2.399
42	Toa Alta-Sample-1-A-junio-09	0.444	79.600	1.767	264.300	22.740	0.229	566.000
43	Toa Alta-Sample-1-B-junio-09	0.448	66.600	1.595	210.100	18.970	0.173	476.600
44	Toa Alta-Sample-1-C-junio-09	0.472	73.500	1.763	237.200	21.800	0.208	546.000
45	Field Blank Levitown-junio-09	0.252	<	<	<	<	<	2.287

Table B.01., continued.

46	Lev-Sample-1-A-junio-09	0.235	81.000	0.027	8.720	12.240	<	34.200
47	Lev-Sample-1-B-junio-09	0.242	83.800	0.030	7.640	12.200	<	33.660
48	Field Blank Campanilla-junio-09	<	<	<	<	<	<	2.392
49	Campanilla-Sample-2-A-junio-09	0.247	79.400	0.072	6.270	6.990	<	19.290
50	Campanilla-Sample-2-A-junio-09	0.276	83.300	0.067	4.830	7.240	<	19.510
51	Campanilla-Sample-2-C-junio-09	0.368	113.000	<	5.260	9.960	<	21.150
52	Field Blank-Primate-junio-09	<	<	<	<	<	<	2.472
53	Prmiates-Sample-3-A-junio-09	0.433	124.800	<	9.780	5.330	<	51.000
54	Prmiates-Sample-3-B-junio-09	0.420	124.100	<	9.470	5.180	<	50.100
55	Prmiates-Sample-3-C-junio-09	0.397	119.400	<	9.080	5.100	<	49.570
56	Lev-Sample-1-C-junio-09	0.245	81.100	0.030	5.650	12.160	<	33.120
55	Prmiates-Sample-3-C-junio-09	0.397	119,400	<	9,080	5,100	<	49,570
56	Lev-Sample-1-C-junio-09	0.245	81,100	0.03	5,650	12,160	<	33,120

Table B.02. Laboratory Report of Leachate Samples for Inorganic- Macrocomponents (October 2009)

#-Sequence	ID	Al(ppm)	Ca(ppm)	Fe(ppm)	K(ppm)	Mg(ppm)	Mn(ppm)	Na(ppm)
HS		100	100	100	100	100	100	50
LS		0.003	0.006	0.000	0.010	0.003	0.001	0.004
1	Trip Blank SRS-octubre-09	<	<	<	<	<	<	2.730
2	Trip Blank Pozo-octubre-09	<	<	<	<	<	<	2.602
3	Field Blank Primate-octubre-09	<	<	<	<	<	<	2.554
9	Primate-Sample 1-A-octubre-09	0.422	90.500	<	4.424	3.910	<	40.850
10	Primate-Sample 1-B-octubre-09	0.411	93.600	<	4.604	4.162	<	42.090
11	Primate-Sample 1-C-octubre-09	0.378	89.500	<	4.234	3.731	<	37.970
4	Field Blank Levitown-octubre-09	<	<	<	<	<	<	<
12	Lev-Sample 2-A octubre-09	0.273	65.200	0.127	1.973	10.120	<	27.910
13	Lev-Sample 2-B octubre-09	0.256	65.100	0.135	1.908	9.710	<	27.160
14	Lev-Sample 2-C octubre-09	0.301	63.900	0.172	2.115	9.760	<	26.790
5	Field Blank Campanilla-octubre-09	<	<	<	<	<	<	2.510
15	Campanilla Sample 3-A-octubre-09	0.380	81.100	0.290	0.800	7.720	<	17.590
16	Campanilla Sample 3-B-octubre-09	0.371	84.500	0.305	0.823	7.570	<	17.690
17	Campanilla Sample 3-C-octubre-09	0.399	83.500	0.386	0.822	7.750	<	17.480
6	Field Blank Toa Alta-octubre-09	<	<	<	<	<	<	2.929
18	Toa Alta-Sample-4-A-octubre-09	0.477	57.000	1.187	131.000	12.950	0.081	333.200
19	Toa Alta-Sample-4-B-octubre-09	0.459	59.100	1.336	171.200	15.800	0.117	424.500
20	Toa Alta-Sample-4-C-octubre-09	0.335	54.100	1.125	164.100	14.680	0.107	409.000

Table B.02., continued.

8	Field Blank Toa Baja Camino-octubre-09	0.091	0.713	<	<	<	<	3.459
21	Toa Baja Camino-Sample-5A-octubre-09	0.440	40.700	1.053	159.000	14.460	0.134	403.000
22	Toa Baja Camino-Sample-5B-octubre-09	0.444	39.860	1.057	158.300	14.730	0.134	398.700
23	Toa Baja Camino-Sample-5C-octubre-09	0.441	38.600	1.014	151.800	14.210	0.127	395.100
7	Field Blank Toa Baja Minga-octubre-09	<	0.691	<	<	<	<	3.370
24	Toa Baja Minga-Sample-6A-octubre-09	1.194	40.980	7.970	781.000	32.310	0.173	1577.000
25	Toa Baja Minga-Sample-6B-octubre-09	3.896	65.900	11.180	858.000	36.370	0.270	1667.000
26	Toa Baja Minga-Sample-6C-octubre-09	1.153	44.510	8.350	850.000	35.500	0.191	1622.000
	Duplicada Toa Baja Minga 6-B	2.937	64.500	10.650	838.000	34.630	0.263	1598.000

Table B.03. Laboratory Report of Leachate Samples for Inorganic- Macrocomponents (March 2009)

#Tube	Nomenclatura Muestras- Lixiviado	Al(ppm)	Ca(ppm)	Fe(ppm)	K(ppm)	Mg(ppm)	Mn(ppm)	Na(ppm)
HS		100	100	100	100	100	100	50
LS		0.002	0.011	0.006	0.057	0.007	0.006	0.005
H2O-Di		<	<	<	<	<	<	<
1	Trip Blank SRS-Marzo-10	<	<	<	0.175	<	<	0.162
2	Trip Blank Pozo-Marzo-10	<	<	<	0.144	<	<	<
3	Fiel Blank Primate-Marzo-10	<	<	0.127	0.140	<	<	<
9	Primate-Sample 1-A-Marzo-10	0.434	92.300		4.756	4.201	<	47.080
10	Primate-Sample 1-B-Marzo-10	0.431	94.400	<	4.937	4.244	<	39.110
11	Primate-Sample 1-C-Marzo-10	0.415	92.400	<	4.807	3.972	<	41.090
4	Field Blank Levitown-Marzo-10	<	<	<	0.178	<	<	<
12	Lev-Sample 2-A -Marzo-10	0.306	63.900	0.071	2.362	9.540	0.007	24.170
13	Lev-Sample 2-B- Marzo-10	0.298	64.300	0.106	2.308	9.650	0.008	24.890
14	Lev-Sample 2-C- Marzo-10	0.307	65.200	0.087	2.335	9.450	0.008	25.400

Table B.03., continued.

5	Field Blank Campanilla-Marzo-10	<	<	<	0.218	<	<	<
15	Campanilla Sample 3-A-Marzo-10	0.401	87.800	0.102	1.253	7.410	<	15.540
16	Campanilla Sample 3-B-Marzo-10	0.428	85.800	0.021	1.216	7.310	<	16.160
17	Campanilla Sample 3-C-Marzo-10	0.408	83.100	<	1.227	6.970	<	15.260
6	Field Blank Toa Alta-Marzo-10	<	<	<	0.198	<	<	<
18	Toa Alta-Sample-4-A-Marzo-10	0.345	53.100	1.427	183.400	17.880	0.192	463.000
19	Toa Alta-Sample-4-B-Marzo-10	0.372	53.100	1.476	185.300	17.830	0.191	461.600
20	Toa Alta-Sample-4-C-Marzo-10	0.341	53.500	1.455	186.100	17.660	0.195	468.000
8	Field Blank Toa Baja Camino-Marzo-10	<	<	<	0.200	<	<	<
21	Toa Baja Camino-Sample-5A-Marzo-10	0.800	41.910	6.870	678.000	29.630	0.169	1357.000
22	Toa Baja Camino-Sample-5B-Marzo-10	1.043	60.600	7.290	705.000	31.720	0.208	1486.000
23	Toa Baja Camino-Sample-5C-Marzo-10	0.835	43.570	7.160	697.000	30.910	0.178	1531.000
7	Field Blank Toa Baja Minga-Marzo-10	<	<	<	0.206	<	<	<
24	Toa Baja Minga-Sample-6A-Marzo-10	0.658	33.020	8.670	656.000	20.190	0.186	1531.000
25	Toa Baja Minga-Sample-6B-Marzo-10	3.424	77.400	14.440	674.000	22.420	0.467	1603.000
26	Toa Baja Minga-Sample-6C-Marzo-10	0.977	39.200	9.250	661.000	20.730	0.215	1528.000
27	Duplicada Toa Baja Minga 6-B	3.516	78.100	14.500	676.000	22.240	0.474	1577.000
Fortificado	Spike(fortificado) de Toa baja Minga 6-8	3.589	75.200	14.690	663.000	22.270	0.466	1515.000

Appendix C

Results of Laboratory Data for Heavy Metal

Table C.01. Laboratory Report of Leachate Samples for Heavy Metal (April and June 2009)

USDA Forest Service. International Institute of Tropical Forestry

IITF Laboratory Report

Heavy Metal Characterization of Leachate from Two Municipal Waste Disposal Landfills in Puerto Rico and its impact on
Nearby Groundwater Wells

Investigator: Luz S. Betancourt (Ph.D. Dissertation - Turabo University)

#-Secuencia	ID	Cr(ppm)	Cu(ppm)	Ni(ppm)	Zn(ppm)	Co(ppm)	Pb(ppm)
HS		10	10	10	10	10	10
LS		0.003	0.004	0.006	0.010	0.001	0.015
Blank		<	<	<	<	<	<
1	Trip Blank Pozo-abril-09	<	<	<	<	<	<
2	Trip Blank SRS-abril-09	<	<	<	<	<	<
3	Field Blank Levitown-abril-09	<	<	<	<	<	<
4	Lev-Sample 1-A abril-09	<	<	<	<	<	<
5	Lev-Sample 1-B abril-09	<	<	<	<	<	<
6	Lev-Sample 1-C abril-09	<	<	<	<	<	<
7	Field Blank Campanilla-abril-09	<	<	<	<	<	<
8	Campanilla Sample 2-A-abril-09	<	<	<	<	<	<
9	Campanilla Sample 2-B-abril-09	<	<	<	<	<	<
10	Campanilla Sample 2-C-abril-09	<	<	<	<	<	<
11	Field Blank Primate-abril-09	<	<	<	<	<	<
12	Primate-Sample 3-A-abril-09	<	<	<	<	<	<

Table C.01., continued.

13	Primate-Sample 3-B-abril-09	<	<	<	<	<	<
14	Primate-Sample 3-C-abril-09	<	<	<	<	<	<
15	Field Blank Toa Baja Punto 1-abril-09	<	<	<	<	<	<
16	Toa Baja Punto1-1A-Sample-abril-09	0.417	0.087	0.354	0.202	0.105	<
17	Toa Baja Punto1-1B-Sample-abril-09	0.410	0.072	0.338	0.199	0.100	<
18	Toa Baja Punto1-1C-Sample-abril-09	0.408	0.067	0.347	0.211	0.099	<
19	Field Blank Toa Baja Punto 2-abril-09	<	<	<	<	<	<
20	Toa Baja Punto2-2A-Sample-abril-09	0.254	0.227	0.302	0.582	0.072	0.019
21	Toa Baja Punto2-2B-Sample-abril-09	0.280	0.220	0.289	0.582	0.069	0.0221
22	Toa Baja Punto2-2C-Sample-abril-09	0.228	0.345	0.290	1.060	0.081	0.1646
27	Field Blank Toa Alta-abril-09	<	<	<	<	<	<
28	Toa Alta-Sample-1-A-abril-09	0.170	<	0.157	0.601	0.043	<
29	Toa Alta-Sample-1-A-abril-09	0.107	<	0.103	0.405	0.019	<
30	Toa Alta-Sample-1-A-abril-09	0.134	<	0.120	0.440	0.031	<
31	Trip Blank Pozo-junio-09	<	<	<	<	<	<
32	Trip Blank SRS-junio-09	<	<	<	<	<	<
33	Field Blank Toa Baja-Minga-junio-09	<	<	<	<	<	<
34	Toa Baja-Minga-Sample 4-A-junio-09	<	<	<	<	<	<
35	Toa Baja-Minga-Sample 4-B-junio-09	0.237	<	0.194	0.088	0.050	<
36	Toa Baja-Minga-Sample 4-C-junio-09	0.241	<	0.213	0.097	0.058	<
37	Field Blanik Toa Baja-Camino-junio-09	<	<	<	<	<	<

Table C.01., continued.

38	Toa Baja Camino-Sample-5-A-junio-09	0.366	<	0.259	1.255	0.077	0.0547
39	Toa Baja Camino-Sample-5-B-junio-09	0.396	<	0.264	1.269	0.079	0.0513
40	Toa Baja Camino-Sample-5-C-junio-09	0.398	<	0.264	1.310	0.079	0.05
41	Fiel Blank Toa Alta-junio-09	<	<	<	<	<	<
42	Toa Alta-Sample-1-A-junio-09	0.043	<	0.069	0.012	0.017	<
43	Toa Alta-Sample-1-B-junio-09	0.037	<	0.049	<	<	<
44	Toa Alta-Sample-1-C-junio-09	0.046	<	0.055	<	0.013	<
45	Field Blank Levitown-junio-09	<	0.254	<	<	<	<
46	Lev-Sample-1-A-junio-09	<	<	<	<	<	<
47	Lev-Sample-1-B-junio-09	<	<	<	<	<	<
48	Field Blank Campanilla-junio-09	<	<	<	<	<	<
49	Campanilla-Sample-2-A-junio-09	<	<	<	<	<	<
50	Campanilla-Sample-2-A-junio-09	<	<	<	<	<	<
51	Campanilla-Sample-2-C-junio-09	<	<	<	<	<	<
52	Field Blank-Primate-junio-09	<	<	<	<	<	<
53	Prmiates-Sample-3-A-junio-09	<	<	<	<	<	<
54	Prmiates-Sample-3-B-junio-09	<	<	<	<	<	<
55	Prmiates-Sample-3-C-junio-09	<	<	<	<	<	<
56	Lev-Sample-1-C-junio-09	<	<	<	<	<	<

Table C.02. Laboratory Report of Leachate Samples for Heavy Metal (October 2009)

#-Sequence	ID	Cr(ppm)	Cu(ppm)	Ni(ppm)	Zn(ppm)	Co(ppm)	Pb(ppm)
HS		10	10	10	10	10	10
LS		0.013	0.028	0.007	0.011	0.010	0.0066
Blank		v	v	v	v	v	v
1	Trip Blank SRS-octubre-09	v	v	v	0.056	v	v
2	Trip Blank Pozo-octubre-09	v	v	v	v	v	v
3	Fiel Blank Primate-octubre-09	v	v	v	v	v	v
9	Primate-Sample 1-A-octubre-09	v	v	v	v	v	v
10	Primate-Sample 1-B-octubre-09	v	v	v	v	v	v
11	Primate-Sample 1-C-octubre-09	v	v	v	v	v	v
4	Field Blank Levitown-octubre-09	v	v	v	v	v	v
12	Lev-Sample 2-A octubre-09	v	v	v	v	v	v
13	Lev-Sample 2-B octubre-09	v	v	v	v	v	v
14	Lev-Sample 2-C octubre-09	v	v	v	v	v	v
5	Field Blank Campanilla-octubre-09	v	v	v	v	v	v
15	Campanilla Sample 3-A-octubre-09	v	v	v	v	v	v
16	Campanilla Sample 3-B-octubre-09	v	v	v	v	v	v

Table C.02., continued.

17	Campanilla Sample 3-C-octubre-09							
6	Field Blank Toa Alta-octubre-09	<	<					
18	Toa Alta-Sample-4-A-octubre-09	0.027		0.034				
19	Toa Alta-Sample-4-B-octubre-09	0.043		0.055				
20	Toa Alta-Sample-4-C-octubre-09	0.037	<	0.051	<			
8	Field Blank Toa Baja Camino-octubre-09	<	<	<	0.428			
21	Toa Baja Camino-Sample-5A-octubre-09	0.021	<	0.046	0.043	0.011		
22	Toa Baja Camino-Sample-5B-octubre-09	0.023	<	0.047	<			
23	Toa Baja Camino-Sample-5C-octubre-09	0.021	<	0.048	<	0.011		
7	Field Blank Toa Baja Minga-octubre-09	<	<	<	<			
24	Toa Baja Minga-Sample-6A-octubre-09	0.338	<	0.231	1.120			0.074
25	Toa Baja Minga-Sample-6B-octubre-09	0.352	<	0.251	1.134	<		0.0894
26	Toa Baja Minga-Sample-6C-octubre-09	0.346	<	0.192	0.280	1.130	0.0715	
	Duplicada Toa Baja Minga 6-B	0.362	<	0.250	1.182	0.080		0.0844

Table C.03. Laboratory Report of Leachate Samples for Heavy Metal (March 2009)

#-Sequence	HS	ID	Cr(ppm)	Cu(ppm)	Ni(ppm)	Zn(ppm)	Co(ppm)	Pb(ppm)
	LS		10	10	10	10	10	10
	H ₂ O-Di		0.026	0.045	0.048	0.010	0.029	0.007
1			<	<	<	<	<	<
2		Trip Blank SRS-Marzo-10	0.031	<	<	<	<	<
3		Trip Blank Pozo-Marzo-10	0.031	<	<	<	<	<
9		Fiel Blank Primate-Marzo-10	0.032	<	<	<	<	<
10		Primate-Sample 1-A-Marzo-10	0.032	<	0.051	<	0.033	<
11		Primate-Sample 1-B-Marzo-10	0.032	<	0.049	<	0.033	<
4		Primate-Sample 1-C-Marzo-10	0.030	<	0.048	<	0.028	<
12		Field Blank Levitown-Marzo-10	0.033	<	<	<	0.031	<
13		Lev-Sample 2-A -Marzo-10	0.031	<	<	<	0.031	<
14		Lev-Sample 2-B- Marzo-10	0.038	<	0.050	0.011	0.030	<
5		Lev-Sample 2-C- Marzo-10	0.033	<	0.050	0.023	0.029	<
15		Field Blank Campanilla-Marzo-10	0.034	<	<	<	<	<
16		Campanilla Sample 3-A-Marzo-10	0.035	<	<	<	<	<

Table C.03., continued.

17	Campanilla Sample 3-B-Marzo-10	0.033	<	0.051	<	<	<
6	Campanilla Sample 3-C-Marzo-10	0.036	<	0.049	<	0.031	<
18	Field Blank Toa Alta-Marzo-10	0.033	<	<	<	<	<
19	Toa Alta-Sample-4-A-Marzo-10	0.091	<	0.125	0.057	0.050	<
20	Toa Alta-Sample-4-B-Marzo-10	0.091	<	0.122	0.048	0.049	0.011
8	Toa Alta-Sample-4-C-Marzo-10	0.092	<	0.118	0.049	0.052	<
21	Field Blank Toa Baja Camino-Marzo-10	0.033	<	0.052	<	0.031	<
22	Toa Baja Camino-Sample-5A-Marzo-10	0.372	0.082	<	1.091	0.115	0.055
23	Toa Baja Camino-Sample-5B-Marzo-10	0.387	0.089	<	1.153	0.125	0.056
7	Toa Baja Camino-Sample-5C-Marzo-10	0.408	0.086	<	1.196	0.131	0.060
24	Field Blank Toa Baja Minga-Marzo-10	0.034	0.040	<	<	0.027	<
25	Toa Baja Minga-Sample-6A-Marzo-10	0.330	0.141	<	0.340	0.122	0.039
26	Toa Baja Minga-Sample-6B-Marzo-10	0.337	0.163	<	0.383	0.125	0.096
27	Toa Baja Minga-Sample-6C-Marzo-10	0.351	0.153	<	0.327	0.123	0.042
Fortificado	Duplicada Toa Baja Minga 6-B	0.354	0.166	<	0.396	0.123	0.075
	Spike(fortificado) de Toa baja Minga 6-8	0.545	0.347	0.558	0.593	0.329	0.262

Appendix D

Results of Laboratory Data for Soil

Table D.01. Laboratory Report of Soil Samples for Inorganic Macrocomponnts (April 2009)

Lab.	Site description	Depth (cm)	Al(mg/g)	Ca(mg/g)	Fe(mg/g)	K(mg/g)	Mg(mg/g)	Mn(mg/g)	Na(mg/g)
1	Possible site contaminate -Primate	0-15	15.568	65.139	30.337	0.847	2.286	0.479	0.309
3	Possible site contaminate -Primate	0-15	16.491	111.178	31.192	1.066	2.624	0.475	0.317
5	Possible site contaminate -Primate	0-15	16.454	66.980	32.426	0.998	2.441	0.581	0.299
7	Possible site contaminate -Primate	0-15	17.699	47.127	42.150	1.069	1.814	1.192	0.293
9	Background-Primate	0-15	10.466	121.175	11.735	1.530	2.930	0.247	1.515
11	Background-Primate	0-15	9.318	3.132	17.463	0.047	0.403	0.288	0.051
13	Background-Primate	0-15	8.901	15.660	21.490	0.075	0.754	0.406	0.078
15	Background-Primate	0-15	8.513	1.224	19.034	0.064	0.529	0.378	0.023
17	Field Blank - Monos- Primate	0-15	10.341	1.350	22.419	0.073	0.926	0.454	0.057
19	Field Blank - Monos- Primate	0-15	10.808	7.735	30.724	0.158	0.672	1.375	0.251
21	Field Blank - Monos- Primate	0-15	11.443	3.860	30.310	0.141	0.450	1.164	0.121
23	Field Blank - Monos- Primate	0-15	11.860	4.304	37.324	0.163	0.822	0.858	0.046
25	Toa Baja - Near Primate	0-15	10.176	141.567	10.037	1.022	2.882	0.250	0.853
27	Toa Baja - Near Primate	0-15	9.855	3.652	29.842	0.069	0.369	1.555	0.159
29	Toa Baja - Near Primate	0-15	8.979	100.051	11.460	1.641	2.684	0.222	1.467
31	Toa Baja - Near Primate	0-15	9.247	83.800	12.555	2.169	2.693	0.232	2.030

Table D.02. Laboratory Report of Soil Samples for Heavy Metals (April 2009)

USDA Forest Service. International Institute of Tropical Forestry. IITF Laboratory Report

Heavy Metal Characterization of Leachate from Two Municipal Waste Disposal Landfills in Puerto Rico and its impact on
Nearby Groundwater Wells

Investigator: Luz S. Betancourt (Ph.D. Dissertation - Turabo University)

ID#		Depth(cm)	Cr(mg/g)	Cu(mg/g)	Ni(mg/g)	Zn(mg/g)	Co(mg/g)	Pb(mg/g)
2	Possible site contaminant -Primate	15-30	0.094	0.044	0.023	0.128	0.012	0.037
4	Possible site contaminant -Primate	15-30	0.079	0.064	0.020	0.229	0.006	0.047
6	Possible site contaminant -Primate	15-30	0.117	0.063	0.022	0.155	0.011	0.089
8	Possible site contaminant -Primate	15-30	0.135	0.053	0.022	0.114	0.012	0.084
10	Background-Primate	15-30	0.047	0.018	0.005	0.016	0.000	0.020
12	Background-Primate	15-30	0.037	0.011	0.000	0.018	0.000	0.017
14	Background-Primate	15-30	0.040	0.011	0.002	0.020	0.000	0.019
16	Background-Primate	15-30	0.045	0.014	0.004	0.015	0.000	0.017
18	Field Blank - Monos- Primate	15-30	0.053	0.020	0.006	0.503	0.004	0.024
20	Field Blank - Monos- Primate	15-30	0.074	0.025	0.007	0.177	0.007	0.028
22	Field Blank - Monos- Primate	15-30	0.077	0.027	0.006	0.069	0.006	0.026
24	Field Blank - Monos- Primate	15-30	0.071	0.024	0.005	0.061	0.004	0.022
26	Toa Baja - Near Primate	15-30	0.007	0.206	0.000	0.030	0.000	0.022
28	Toa Baja - Near Primate	15-30	0.007	0.139	0.000	0.032	0.000	0.017
30	Toa Baja - Near Primate	15-30	0.009	0.035	0.000	0.029	0.000	0.019
32	Toa Baja - Near Primate	15-30	0.012	0.058	0.000	0.045	0.000	0.027