

EXECUTIVE SUMMARY

ASSESSING THE FATE AND TRANSPORT OF LANDFILL LEACHATE CONTAMINANTS IN THE SURFACE WATER AND GROUNDWATER IN RODRIGUEZ, RIZAL, PHILIPPINES

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One of the main environmental concerns regarding the operation of landfills is the leaching and transport of contaminants from the landfill into nearby surface water and into groundwater. The Montalban Solid Waste Disposal Facility (MSWDF) located in Rodriguez, Rizal, (referred to in this work as the "landfill"), has been perceived to pose serious and immediate problems. A concern arises from the selection of the site, being situated on a mountain ridge, around 250 m elevation, with a heavily fractured volcanic geology. Surface water affected by the landfill comprises one of the headwaters of the Marikina River system which drains the Marikina river watershed. In view of the hydrologic setting, the operators and regulators are faced with the challenge of implementing adequate precautionary measures to protect the water supply from deterioration. To determine the degree of mitigation required to ensure that the water sources are adequately protected, and to ensure that resources are spent in the most cost-effective manner, a risk assessment of the MSWDF is necessary. The MSWDF is considered to be a contaminated site which may pose a risk if toxic substances that may be present in the leachate reach a receptor. Risk assessments of contaminated sites are usually based on source- pathway- receptor concept where the pathway is the mechanism by which a contaminant gets from the source to the receptor. A given source is considered a risk if a complete pathway-linkage exists between the source and the receptor. In this case, a complete pathway consists of a leachate release from the landfill, a transport media (surface water, groundwater, and soil), and an exposure route at the receptor contact point. In this case, the contaminant can reach a human being through ingestion or dermal contact. The goal of this thesis is to provide suitable scientific basis for risk assessment of the landfill. It focuses primarily on the **"source-pathway"** part of the risk assessment. A number of factors and processes influence the distribution, fate and transport of the contaminants in the environment. Among these are the hydrologic setting, which determines the prevalent pathways of contaminant migration, the composition of the soils and geologic materials in the unsaturated zone, which influences the mobility of contaminants, and the potential for biodegradation of the waste materials in the prevailing environment. The approach in this thesis is to conduct site investigations to characterize the source and to determine the spatial and temporal contamination of surface water and groundwater from landfill leachate, and to perform sorption and degradation experiments to assess the attenuation potential of the system. The results of these studies will provide information needed for future modeling efforts to predict the resulting contaminant impact on the surface water and groundwater downstream of the source. The characterization of the contaminant source, i.e., the leachate, focuses on the isotopic composition of hydrogen and oxygen, major ions, and selected metals. These components are similarly investigated in the surface water and groundwater. These components are meant to merely indicate the potential occurrence of groundwater contamination from the landfill, which may be hazardous due to their toxicity and/or persistency if they move through the aquifer towards the water supply. The detection of these indicators of leachate contamination in the freshwater should provide impetus for further investigations on specific hazardous contaminants that may be present in the leachate and may have reached the water

supply. Field investigations were conducted in Rodriguez and San Mateo in Rizal from 2003 to 2008. The isotopic (oxygen and hydrogen) and chemical composition (major ions and heavy metals) of groundwater, surface water, and precipitation were determined before and after the rainy season, whenever possible, to assess seasonal variations. In October 2009, one month after typhoon Ondoy, the production wells in Rodriguez were monitored for major ions only. Tritium (^3H), the radioactive isotope of hydrogen, was detected in the leachate at concentrations more than 200 times higher than current atmospheric concentration in this region which is around 2 Tritium Units (TU). The elevated tritium concentration in the leachate is attributed to some manufactured products that could be disposed as municipal waste such as gaseous tritium light devices (GTLDs), watches and clocks containing GTLs, luminous paints, compasses, and electron tubes. The concentrations of the major ions, sodium (Na), potassium (K), magnesium (Mg), and chloride (Cl), in the leachate, were higher by at least an order of magnitude than their concentrations in non-impacted surface water. Sulfate was low in the leachate, in the order of 10 mg/L, due to microbial degradation of SO_4^{2-} to S_2^{2-} under anoxic conditions. This was not significantly distinct from the concentrations detected in the surface water. Bicarbonate concentration in the leachate, was significantly higher than that in the non-impacted surface water, although the levels in these media were in the same order of magnitude. The pathway of leachate contamination along the Lukutan River, located downstream of the landfill, could be traced from the concentration gradient of tritium and the major ions, Na, K, Mg, Ca, and Cl along the river stream, following a negative exponential relationship with distance from the leachate source. This provided unequivocal evidence of leachate finding its way into the Lukutan River. Heavy metals detected in the leachate: Ti, V, Cr, Ni, Cu, Zn, and Pb were generally below ≤ 1 mg/L and were not significantly different from those in stream water not impacted by leachate. Leachate in the holding pond was more enriched in the heavier stable hydrogen isotope, deuterium, than the freshwater sources in the study area by as much as 65 ‰. Enrichment in the heavier isotope of oxygen, ^{18}O , occurs at a lesser extent, by as much as 4‰. The higher degree of enrichment in deuterium than in ^{18}O in the leachate is attributed to anaerobic biodegradation of organic matter in the waste. During biodegradation at the methanogenic stage, isotopic fractionation occurs with the preferential association of lighter hydrogen isotope with the gas phase, CH_4 , leaving the heavier isotope in the liquid phase. Enrichment in ^{18}O of leachate in the collection pond is due to evaporation which also contributes to enrichment in deuterium. Dilution by stream water, however, adequately masked the isotopic signature of leachate in surface water, precluding its utility as an indicator of leachate contamination in this medium. Dilution similarly masked the effect of leachate in the shallow groundwater which was strongly influenced by precipitation. Deep groundwater is expected to contain low or no tritium because when water infiltrates the ground, it becomes isolated from the atmospheric tritium source, thus, its tritium concentration decreases over time due to radioactive decay. However, isolated cases of significant tritium concentrations, as high as 6 TU in one well and about 2 TU in two wells, were detected in 2003 when the average amount of rainfall exceeded that measured in the succeeding sampling periods, except in 2009, by about 40%. This coincided with corresponding enrichment in deuterium of groundwater in these wells. Two of the wells now produce water that has low tritium but one has constantly shown tritium concentrations above 1 TU in the period 2005 to 2008. The presence of tritium in concentrations similar to and even above the present day atmospheric concentration in the deep groundwater indicates hydraulic connection with surface water and its susceptibility to contamination from the surface including leachate from the landfill. The major ion composition of the deep groundwater from 2003 to 2008 has evolved to be approximately 20% richer in both chloride and sulfate. This composition now lies closer to the leachate end of the mixing line between freshwater and leachate. This corroborates further the hypothesis that the groundwater in Rodriguez is not fully protected from leachate contamination. Depletion in deuterium in groundwater in the drier months is observed and is attributed to the effect on the groundwater of methane produced within the landfill. The sporadic occurrence and the apparent rapid infiltration

in the groundwater can be attributed to the inherent complex nature of flow in fractured rocks. For contaminated sites, knowledge of the potential impacts of natural attenuating processes on contaminant release and migration would be useful in achieving site specific remediation objectives within available resources and timeframe that is reasonable compared to that offered by other more active methods. Natural processes that influence the distribution, fate and transport of contaminants in the environment such as sorption and biodegradation were investigated in the laboratory. The field investigations have found the leachate to be highly enriched in deuterium, the enrichment attributed to microbial degradation. A microcosm study was conducted to assess the potential for the isotopic fractionation effects of biodegradation of organic matter leachate as an indicator of leachate contamination and consequently, as a tool for determining the degree of biodegradation in the leachate. The differentiation between the isotopic fractionation effects of biodegradation and of evaporation is an essential part of this study because both processes result in enrichment in the heavy isotope of hydrogen. The experiment demonstrated that isotopic fractionation due to biodegradation can be distinguished from evaporative enrichment. Evaporative enrichment resulted in progressive fractionation of both hydrogen and oxygen isotopes, with resulting isotope ratios that could be traced along an evaporation line. Isotopic fractionation from biodegradation was observed for both oxygen and hydrogen. The isotopic ratios of oxygen in the leachate generally became more enriched in ^{18}O with time. On the other hand, the isotopic ratio of hydrogen fluctuated between depletion and enrichment in deuterium depending on the stage of degradation. A net enrichment in deuterium, about 10 ‰, was observed after 63 days of incubation. Lactic acid and acetic acid were identified to be among the degradation products in the leachate. As observed for the isotopic ratio of hydrogen, the concentrations of these acids fluctuated during the incubation period, but tended to decrease after 63 days of incubation. The decrease in the concentration of these acids is attributed to the onset of methanogenesis which correlates with the enrichment in deuterium. While no attempt was done to quantify the degree of degradation or to evaluate the kinetics of biodegradation, the study has provided insights on potential studies that could be undertaken in the future to better understand and assess the extent of biodegradation of organic contaminants in water environments affected by municipal waste disposal facilities. With proper experimental design, useful information may be obtained in the context of risk assessment, management of contaminated land, and bioremediation measures. The degree of deuterium enrichment that was observed in the leachate in this experiment was much lower than that exhibited by the leachate in the landfill simply because of the difference in the volume and nature of the substrate, the nature of organisms, the amount of moisture, and the environmental conditions. However, this experiment demonstrated the enrichment in deuterium in relation to biodegradation and may serve as a tool, in conjunction with other parameters, to monitor degradation processes in the landfill environment. Sorption is a major process responsible for accumulation of heavy metals, thus, the study of sorption processes is of utmost importance for understanding the transfer of heavy metals from a liquid mobile phase to the surface of a solid phase. Sorption, as referred to in this study, represents the process of the binding of chemicals to surfaces of soils. It does not distinguish between chemical and physical adsorption and other processes involving surface catalyzed degradation, bulk adsorption or chemical reactions. While the heavy metal composition of the leachate from the Montalban disposal facility was generally low, proper evaluation of the attenuation process of metals will be useful for the assessment of the environmental effects of the long term operation of the landfill. This study determined the competitive sorption/desorption characteristics of the heavy metals Pb, Zn, and Ni in low to moderate (1 mg/L to 100 mg/L) concentrations, onto landfill affected soils. These metals were selected since these are among the parameters included in the Philippine National Standards for Drinking Water (PNSDW 2007). Pb and Ni are among the inorganic constituents considered for their significance to health, while Zn is included among those constituents that would affect the aesthetic quality of water. Furthermore, these metals were detected in the leachate and freshwater sources studied, although generally in

concentrations below the standard limits. The study aims to obtain empirical sorption values that may be used to predict the partitioning of the heavy metals between the soil and the aquatic environment in the landfill affected area. To this end, equilibrium sorption and desorption coefficients for the metals under study were determined. Batch experiments were conducted involving simultaneous presence of Pb, Zn, and Ni (competitive), with initial concentrations, C_0 , ranging from 1 mg/L to 100 mg/L, in sulfate fortified rainwater solutions. These were carried out in ambient temperature and in unadjusted and close to soil field pH conditions. The kinetics of adsorption fitted a pseudo second-order model, providing rate constants for predicting sorption of Pb, Zn, and Ni at a given time. The equilibrium sorption capacities for the heavy metals in the clay and sandy loam soils were estimated using the Linear, Freundlich, and Langmuir isotherm models. Adsorption coefficients of Pb and Zn on clay showed variability with C_0 , K values decreasing with increasing C_0 . At the lower C_0 range of 1-30 mg/L, the linear isotherm applies while at higher C_0 range, the Freundlich model applies. This indicates changes in the nature of the sites and interactions involved in the sorption process as the metal concentrations increase. For Ni, the Freundlich model provided a better fit for the clay soil covering the entire range of C_0 studied, indicating a highly selective adsorption for Ni. Based on the K values, adsorption of the metals onto the clay soil follows the order $Zn > Pb > Ni$. In the sandy loam soil, the sorption capacity for the metals under the same conditions followed the order $Pb > Zn > Ni$. The sorption capacities for the metals were in the order of 1 mg/g in both the landfill clay soil and the Lukutan River sandy loam soil, although higher by about 50% in the clay soil than in the sandy loam soil. Desorption was minimal, less than 1% in the clay soil and about 2% in the sandy loam soil. Sorption reversibility tests showed that the retention of the metals follows the order $Ni > Pb > Zn$ in the clay soil and $Ni \approx Pb > Zn$ in the sandy loam soil. The sorption/desorption experiments provided information that may be used for modeling pollutants transport in the surface water soil interface. These will be useful in predicting the effect of the leachate on downstream pumping wells and to identify efficient remedial actions. While numerous studies on the sorption characteristics of soils for heavy metals have already been conducted, parameters obtained are not invariable and will always be affected by the type of soil and other environmental conditions that may vary with location. The dissertation has provided useful information for the assessment of the risk of contamination from leachate of water resources in Rodriguez, particularly, in the development of a pollutant fate and transport model. Integrating the results of this thesis, a conceptual model of the possible flow paths associated with the landfill is developed. In this model, the waste disposal site sits on an unsaturated geological media which overlies an unconfined aquifer. The quantity of the leachate generated and its ability to infiltrate depends on the water budget. The effective rainfall percolating through the waste is an important control on the volume of leachate generated by the landfill and in the recharge to the aquifer. Leachate run-off to the river occurs and the concentrations of the contaminants are affected by dilution, evaporation, and sorption. The study showed that the concentration of the major ions along the flow path in the river follows a negative exponential curve that fits a general hydrodynamic dispersion model of toxicants in flowing streams. The river infiltrates into the unsaturated zone and is directly affected by precipitation. Leachate from the landfill infiltrates through the unsaturated zone and, depending on the volume of rainfall, penetrates the deeper aquifer and migrates downstream to the well field in Rodriguez. Farther downstream of the Marikina River, other contaminant source may load the river through surface run-off. The soils in the landfill environment exhibit significant sorption and retention capacities for the metals Zn, Pb, and Ni in near neutral pH, and the degradation of organic contaminants provides opportunity that will lead to their attenuation along the river stream and along the groundwater flow. Contaminant concentration along pathways decreases depending on the retardation factor which represents the lumped behavior of sorption and decay processes. This study will be the first in the country to incorporate environmental chemical and isotope techniques in assessing the contamination of water resources by landfill leachate. This approach has improved the

understanding of the transport of leachate contaminants in the freshwater environment affected by the Montalban Solid Waste Disposal Facility in Rodriguez, Rizal. It facilitated the distinction of hydrochemically different regimes, and detection of possible indications of the mixing of leachate with surface water and groundwater. The results obtained provide information that unequivocally identifies leachate as a source of contamination in the surface water and in groundwater. These could provide impetus for further research and for regulatory agencies to evaluate further the impact of long term operation of the landfill and for other landfills in the country. With the evidence of leachate contamination of the groundwater occurring during periods of excessive rainfall events, one measure that could immediately be implemented by regulators would be the inspection of potential leachate production towards the end of wet seasons or following excessive rainfall events such as when floods occur. Measures to minimize infiltration should be implemented by the operators to prevent water from percolating through the waste and forming leachate, which can pollute underlying soil and groundwater.