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Environmental monitoring of a landfill area through the application of carbon stable isotopes, chemical parameters and multivariate analysis

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ABSTRACT

Leachate produced during an organic matter decomposition process has a complex composition and can cause contamination of surface and groundwaters adjacent to a landfill area. The monitoring of these areas is extremely important for the characterization of the leachate produced and to avoid or mitigate environmental damages. Thus, the present study has the objective of monitoring the area of a Brazilian landfill using conventional parameters (dissolved metals and anions in water) and alternative, stable carbon isotopes parameters ($\delta^{13}C$ of dissolved organic and inorganic carbons in water) in addition to multivariate analysis techniques. The use of conventional and alternative parameters together with multivariate analysis showed that cells of the residues are at different phases of stabilization of the organic matter and probably already at C3 of the methanogenic phase of decomposition. In addition, the data showed that organic matter stabilization ponds present in the landfill are efficient and improve the quality of the leachate. Enrichment of the heavy ^{13}C isotope in both surface and groundwater suggested contamination in two sampling sites.

1. Introduction

Population growth, coupled with industrialization and urbanization, are primarily responsible for an increase in the indiscriminant final disposal of urban solid waste (Lange et al., 2006; Syafalni et al., 2014). Incorrect disposal practices and the inappropriate management of these wastes represents a great threat to the environment, especially regarding the quality of nearby water resources (Syafalni et al., 2014; Van Breukelen et al., 2003). Nowadays, sanitary landfills are the most environmentally appropriate final destination of waste, but it is recommended that only waste with no potential for reuse, recycling and recovery of energy should be disposed of at such sites (Aderemi et al., 2011; Manzur et al., 2016). However, the leachate from the biological and physico-chemical decomposition of waste can eventually cause damage to the environment in cases of percolation of this liquid (Castañeda et al., 2012; Kjeldsen et al., 2002; Qin et al., 2016).

Landfill leachate is a dark liquid with a foul smell and complex composition; it contains a wide range of organic and inorganic compounds including dissolved organic matter, inorganic compounds (e.g. ammonium, calcium, magnesium, sodium, potassium, iron, sulfates, chlorides), heavy metals (e.g. cadmium, chromium, copper, lead, zinc, nickel) and xenobiotic organic compounds (Aderemi et al., 2012; Christensen et al., 2001; Liu et al., 2015; Moravia et al., 2013; Qin et al., 2016). The chemical and microbiological composition of the leachate varies between landfills and depends on the characteristics of the residues, age of the landfill, environmental conditions, landfill operational mode and decomposition mechanism of the organic matter (Kjeldsen et al., 2002; Moravia et al., 2013).

The degradation of the organic and inorganic compounds present in the residues in more stable substances occurs from a series of complex reactions, via biological and physico-chemical mechanisms (Kjeldsen et al., 2002; Pohland and Harper, 1985; Warith et al., 2005; Widory et al., 2012). The first phase of decomposition of a landfill consists of the aerobic oxidation of organic matter with the consumption of free oxygen present in the residues. This phase is followed by reactions such as oxidation, hydrolysis and anaerobic acidification that result in the accumulation of CO_2 and organic acids and decrease the pH of the medium. With the continuation of anaerobic degradation, methanogenesis becomes the predominant phase in the landfill, where a decrease in acetic acid and other organic acids is associated with increased pH and methane

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production during the development of this phase (Castello et al., 2008; Christensen et al., 2001; Kjeldsen et al., 2002; Pohland and Harper, 1985; Porowska, 2015; Wimmer et al., 2013).

Since percolation of the leachate can compromise the quality of water (Barbieri et al., 2014; Kjeldsen et al., 2002), the assessment of the contamination of surface and groundwater surrounding a landfill is one of the main environmental concerns of these areas (Castañeda et al., 2012). Thus, these sites need environmental monitoring programs that are capable of identifying the influence of the leachate in water resources adjacent to the landfill area (Aderemi et al., 2011; North et al., 2006). Conventional monitoring programs typically involve periodic sampling of surface and groundwater for the determination of chemical parameters such as the quantity of inorganic ions, heavy metals, hardness, alkalinity, chloride, pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), total dissolved solids (TSS), total suspended solids (TSS), suspended solids (SS), ammonium nitrogen (NH_4^+-N) and total Kjeldahl nitrogen (TKN) (Castañeda et al., 2012; Kjeldsen et al., 2002; Mukherjee et al., 2015; North et al., 2006).

These conventional parameters are important for monitoring programs; however, they are sometimes limited or ineffective in scenarios where they are strongly influenced by environmental biogeochemistry (e.g., chloride level in coastal areas) or multiple polluting sources (Castañeda et al., 2012; North et al., 2004; Porowska, 2015). Sometimes, the use of chemical analysis alone or univariate characterizations are not enough to explain the spatial and temporal variation of the contamination load and its concentration in water (Porowska, 2015; Tonjes, 2013). Even in studies where conventional parameters have been found to be adequate to assess the environmental impact of the leachate, the use of additional tools such as stable isotopes can provide additional information, such as an assessment of the maturity stage of the landfill site, and provide more in-depth insight in the area (Bjerg et al., 2014; Minet et al., 2017; North et al., 2006).

Moreover, due the complexity of the environmental samples, large datasets and intrinsic multivariate nature, the use of chemometrics tools have been widely applied in monitoring programs (Peré-Trepat et al., 2007; Reid and Spencer, 2009; Terrado et al., 2006). Multivariate statistical techniques are especially important to evaluate the established relationship between the variables and samples through simultaneous processing of large datasets (Hair et al., 2009). The aim of these methods in the environmental studies is to proceed data mining and project the data into a smaller and more interpretable dimension with the aim of taking a comprehensive understanding about the studied system and provide information for the decision making.

In our previous work, environmental monitoring of a municipal landfill in the state of Rio Grande do Sul was conducted. The efficiency of the stabilization process, as well as the quality of surface water and groundwater resources in adjacent areas, were evaluated through the analysis of conventional parameters (cations and anions) combined with multivariate statistical tools. As the main results, high concentrations of metals and anions in a piezometer and evidence of leachate percolation into surface water near the landfill were identified. The conventional parameters, evaluated in a multivariate approach, were important for carrying out environmental monitoring in the region, but were not sufficient to confirm the occurrence of leachate percolation into the surrounding water resources. Once evidence of contamination has been observed, it is necessary to obtain additional information to increase the reliability of the conducted environmental assessment (Engelmann et al., 2017). Therefore, the use of other contamination indicators is extremely important in order to allow for the precise monitoring of areas that are influenced by landfills (Benbow et al., 2008). In this way, the use of stable isotopes is a viable alternative that is able to overcome the deficiencies of conventional parameters used to assess leachate intrusion in adjacent waters (Mostapa et al., 2011; Tazioli and Tazioli, 2005). The use of isotopic methods in studies of water contamination by landfill leachates have provided important information on contaminants. Since the isotopic composition of a substance is unique, this allows us to differentiate substances that are chemically identical (Benbow et al., 2008; Miljević and Golobocanin, 2007; Mostapa et al., 2011; Raco et al., 2013; Tazioli and Tazioli, 2005).

The evaluation of landfills based on the isotopic analysis of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) are important to evaluate the efficiency of stabilization processes and assist in identifying contamination in surrounding areas (Atkins et al., 2017; Kojima et al., 2017; Pastén-zapata et al., 2014; Porowska, 2017a, 2017b; Schwarz et al., 2011). More comprehensive approaches such as compound-specific isotopic analysis (CSIA) complement bulk isotopic analyses and allow for obtaining more refined information about the isotopic fractionation processes present (Mohammadzadeh et al., 2005; Mohammadzadeha and Clark, 2008). However, even if they are very useful, the $\delta^{13}C$ and $\delta^{15}N$ parameters cannot be directly related to other contaminants species such as heavy metals, i.e. Cl^- and Ca^{2+}, among others. In these cases, specific studies on the stable isotopes of other elements, such as heavy metals, could be applied as an important tool to evaluate other biogeochemical processes that may be present (Economou-eliopoulos et al., 2014; Villalobos-aragón et al., 2012). In general, isotopic parameters must be interpreted together with conventional parameters to avoid misinterpretations and to increase the extraction of useful information (Mostapa et al., 2011; Tonjes, 2013).

Thus, stable carbon isotopes are widely used in studies of this nature, since the carbon isotope composition provides valuable information on carbon transfer between the natural environment and landfills; this is because of the distinct carbon isotope signatures of these two sources (Grossman et al., 2002; Porowska, 2015; Van Breukelen et al., 2003; Wimmer et al., 2013). One approach for tracing pollution sources is the estimation of carbon pollutant flow and the determination of its origin (Porowska, 2015). All soluble carbon species and their transformations are controlled by redox and acid-base processes and are divided into two categories: (1) dissolved inorganic carbon (DIC) and (2) dissolved organic carbon (DOC) (Mohan et al., 2016; St-Jean, 2003). Therefore, the analysis of DIC and DOC and their stable isotope ratios ($\delta^{13}C$-DIC and $\delta^{13}C$-DOC) plays an important role in obtaining a better understanding of the carbon cycle, biogeochemical processes and pollutant flow to surface water and groundwater resources (Raco et al., 2013; St-Jean, 2003; Zhou et al., 2015). The isotopic signatures of DOC and DIC can also be used to describe and characterize the phase of a municipal solid waste landfill (Wimmer et al., 2013).

Studies show that the leachate from landfills is normally enriched in $\delta^{13}C$-DIC (dissolved inorganic carbon), with values between 0 and 20‰ (Hackley et al., 1996; North et al., 2006; Porowska, 2015; Van Breukelen et al., 2003; Walsh et al., 1993). The evolution of $\delta^{13}C$-DIC in the leachate is affected by a number of physical, chemical and biological processes (Wimmer et al., 2013). During the initial phases of the landfill, the isotopic composition of $\delta^{13}C$-DIC in the landfill leachate is between −20 and −25‰ and with the advance of decomposition of the residues and the establishment of the methanogenic phase, the $\delta^{13}C$-DIC in the leachate becomes enriched and reaches positive values around 20‰ (Hackley et al., 1996; Mohammadzadeh and Clark, 2011; Wimmer et al., 2013). This is because one of the ways of producing methane is from the reduction of CO_2. During this process, microorganisms prefer to use the isotopically light carbon available in CO_2, which consequently leads to the production of