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Evolution of nitrogen species in landfill leachates under various stabilization states

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ABSTRACT

In this study, nitrogen species in landfill leachates under various stabilization states were investigated with emphasis on organic nitrogen. Ammonium nitrogen was found to be approximately 1300 mg/L in leachates from younger landfill units (less than 10 years old), and approximately 500 mg/L in leachates from older landfill units (up to 30 years old). The concentration and aerobic biodegradability of organic nitrogen decreased with landfill age. A size distribution study showed that most organic nitrogen in landfill leachates is <1 kDa. The Lowry protein concentration (mg/L-N) was analyzed and showed a strong correlation with the total organic nitrogen (TON, mg/L-N, $R^2 = 0.88$ and 0.98 for untreated and treated samples, respectively). The slopes of the regression curves of untreated (protein = 0.45TON) and treated (protein = 0.31TON) leachates indicated that the protein is more biodegradable than the other organic nitrogen species in landfill leachates. XAD-8 resin was employed to isolate the hydrophilic fraction of leachate samples, and it was found that the hydrophilic fraction proportion in terms of organic nitrogen decreased with landfill age. Solid-state ^{15}N nuclear magnetic resonance (NMR) was utilized to identify the nitrogen species. Proteinaceous materials were found to be readily biodegradable, while heterocyclic nitrogen species were found to be resistant to biodegradation.

1. Introduction

Landfilling as an ultimate disposal method for municipal solid waste is commonly used worldwide (van Nooten et al., 2008). Considerable quantities of landfill leachate can be generated by percolation and filtration of rainwater into the waste layers (Anglada et al., 2009). The potential environmental impacts of landfill leachate are mainly pollution of groundwater (Kjeldsen et al., 2002), contamination of surface water (Kjeldsen et al., 2002), nutrient overloading or UV disinfection interference with wastewater treatment when directly discharged (Zhao et al., 2012). Historically, landfills were built without engineered liners and leachate collection systems. To prevent the seepage of landfill leachate into aquifers, sanitary landfills with installed liners and leachate collection systems have been and continue to be strongly recommended. Consequently, a large volume of leachate needs to be discharged into the sewer systems with pretreatment (Primo et al., 2008) or discharged into surface water (Anglada et al., 2009) with complete treatment. Landfill leachate has the potential to impact on water bodies with direct discharge and/or indirect discharge through wastewater treatment facilities. Therefore, the composition of landfill leachate is critical factor, impacting on groundwater, publicly owned treatment works (POTWs) and surface waters.

Many factors can affect the composition of landfill leachate (Renou et al., 2008; Kurniawan et al., 2006; Åkesson and Nilsson, 1997), including the stabilization stage, the nature of the incoming waste, precipitation pattern and seasonal weather variation. The stabilization stage is widely accepted to be the major influencing factor for the landfill leachate composition (Kjeldsen et al., 2002; Baig et al., 1999; Bookter and Ham, 1982).

Municipal solid waste (MSW) is decomposed within the landfill in three major phases (Kjeldsen et al., 2002): the aerobic phase, the acidogenic phase and the methanogenic phase. Leachates in the acidogenic phase contain a high concentration of volatile fatty acids (Ehrig, 1984), which accounts for up to 95% of organic content and results in a low pH value of the leachate. This acidic environment promotes an increasing concentration of metal species in leachates (Erses et al., 2005). Acidogenic phase leachates

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are usually characterized by a high concentration of biological oxygen demand (BOD) and chemical oxygen demand (COD), a moderately high concentration of ammonium nitrogen and a high biodegradability (BOD/COD ratio ranges from 0.4 to 0.7) (Zouboulis et al., 2001; Morais and Zamora, 2005). In methanogenic phase leachates, most of the remaining organic materials are bio-refractory compounds, such as humic substances (Weis et al., 1989), resulting in a moderately high level of COD, a low BOD/COD ratio of less than 0.1 and an alkaline range pH, which drives the metal species to a low level through precipitation of metals (such as iron, zinc, etc.) and hydroxide.

Ammonium nitrogen concentrations in landfill leachates have been reported to be in the range of 500–2000 mg/L (Kjeldsen et al., 2002). When high concentrations of ammonium nitrogen are discharged to wastewater treatment plants (WWTP), this can lead to inhibition of the biological processes (Shiskowski and Mavinic, 1998). High level of ammonium nitrogen can also increase oxygen requirements and require high concentrations of organic matter if denitrification is practiced. When released to surface waters, there is a risk of eutrophication (Jokela et al., 2002).

In recent years, organic nitrogen has been recognized as an emerging issue for the water environment. Stricter discharge limits for total nitrogen have increased the importance of organic nitrogen. With the wider use of nitrification/denitrification, organic nitrogen can account for up to 80% of dissolved nitrogen in the municipal WWTP nitrification-denitrification effluents (Qasim, 1999), adversely impacting many coastal and estuarine ecosystems as well as certain freshwater ecosystems (Pehlivanoglu and Sedlak, 2004). Dissolved organic nitrogen (DON) can also be a potential source of nitrogenous disinfection by-products, such as N-Nitrosodimethylamine (Krasner et al., 2009; Mitch and Sedlak, 2004). There is little agreement on the composition of organic nitrogen in WWTP effluents. As indicated by Pehlivanoglu-Mantas and Sedlak (2008), the sum of the specific compounds that can be quantified in wastewater effluents normally accounts for less than 10% of the total organic nitrogen, leaving most of the organic nitrogen unidentified. Westgate and Park (2010) showed that proteinaceous substances are significantly correlated with organic nitrogen and could comprise up to 60% of the WWTP effluent organic nitrogen.

Even though the effect of the stabilization state on the properties of landfill leachate is well documented, information of the amount and characteristics of organic nitrogen in landfill leachates under different stabilization stages is limited. Zhao et al. (2012) detected and characterized the organic nitrogen in a landfill leachate. The results show that organic nitrogen in landfill leachate is more bio-refractory than other organic matter, and that biologically treated landfill leachate contains up to 60 mg/L organic nitrogen. The discharge of landfill leachates to WWTPs is economically attractive, however organic nitrogen in landfill leachates can contribute significantly to the total nitrogen in WWTP effluents. Hence, a better understanding of organic nitrogen in landfill leachates is beneficial for controlling the nitrogen loading to water bodies and the subsequent adverse effects.

The objectives of this study were to:

(1) Evaluate the effect of the stabilization stage on the concentration, biodegradability and size distribution of organic nitrogen in landfill leachates;
(2) Determine the relationship between protein/amino acids and organic nitrogen in landfill leachates and evaluate the contribution of protein/amino acids degradation to the ammonia concentration;
(3) Investigate the hydrophobicity distribution of organic nitrogen in landfill leachates to evaluate the bioavailability/biodegradability of landfill leachate based on organic nitrogen and its eutrophication potential.
(4) Identify and characterize the chemical structures of nitrogen species in leachate samples with spectroscopic tools, such as solid state ^{15}N NMR.

2. Materials and methods

2.1. Leachate and landfill

All leachate samples in this study were collected from a landfill located in Kentucky (KY), USA. The landfill is comprised of eight individual cells, designated as Units 1 through to 8. Leachate samples collected for this study were from Units 3, 5, 7 and 8, and designated KY-3, KY-5, KY-7 and KY-8, respectively. One leachate sample was collected from each unit. Unit 3 is an inactive landfill unit that was closed and stopped accepting solid waste. Units 5, 7 and 8 are active permitted landfill units that were still accepting municipal solid waste. The average landfilling ages of landfill units 3, 5, 7 and 8 are 30, 16, 9 and 2.5 years, respectively (Table 1). These ages are for landfill units, not for leachate samples. The landfill consisting of the 8 units has a total coverage of approximately 3.2 km^2. Part of the landfill in the study was operated as a "bio-reactor landfill" by the US EPA National Risk Management Research Laboratory (National Risk Management Research Laboratory, 2006). In the "bio-reactor landfill" operation, liquids, such as nitrified leachate, industrial liquids, water from under drains, etc., were added to some units. Unit 5 was selected to operate "bio-reactor landfill", part of Unit 7 was selected as "control" without liquid addition. Unit 3 was closed and Unit 8 was built after the "bio-reactor landfill" study. More details of the landfill can be found in Gupta et al. (2014b), Abichou et al. (2013a, 2013b). The leachate samples were shipped directly from the landfill to the lab in 20-l polyethylene buckets. The leachates were stored in a refrigerator at 4 °C to reduce microbial activity. Leachate buckets were agitated to re-suspend settled particles before sampling.

It should be noted that there are many factors that may affect the leachate characteristics, including landfill age, solid waste accepted, water precipitation level, bioreactor landfill operation, etc. Landfill age is a major but not the only factor that plays a role. Although the experimental set up in this study was designed deliberately to highlight the effect of landfill age and eliminate the influences of other factors by collecting leachate samples from waste cells with different ages in the same landfill, it is almost impossible to completely exclude the impact of other factors because of the complexity and unpredictability of full scale landfills.

2.2. Biological treatment

Biological treatment of landfill leachate was conducted by continuous aeration. Since leachates contain microorganisms from the waste layer and daily soil cover of the landfill, no external seed was added. Microbial floc similar in appearance to activated sludge was formed during the aeration process. Four liters of each leachate was aerated using a porous ceramic diffuser (void volume is 27–32%). Distilled water was added to compensate the water lost by evaporation. The KY-8 and KY-7 leachate samples were aerated for 53 days and aerated leachates were sampled on the 21st, 38th and 53rd days for fractionation and analysis. The KY-3 and KY-5 samples were aerated for 21 days, followed by fractionation and analysis. After 21 days of aeration little additional total organic carbon reduction occurred for the KY-3 and KY-5 samples so aeration was discontinued.