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Organophosphorus flame retardants and heavy metals in municipal landfill leachate treatment system in Guangzhou, China

Mingjun Deng [a], Dave T.F. Kuo [b, c], Qihang Wu [d, *], Ying Zhang [e], Xinyu Liu [e], Shengyu Liu [e], Xiaodong Hu [a], Bixian Mai [f], Zhineng Liu [a], Haozhi Zhang [a]

[a] School of Civil Engineering, Guangzhou University, Guangzhou 510006, China
[b] Department of Architecture and Civil Engineering, City University of Hong Kong, Hong Kong Special Administrative Region
[c] City University of Hong Kong, Shenzhen Research Institute, Shenzhen 518057, China
[d] Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Center for Water Quality and Conservation of the Pearl River Delta, Guangzhou University, Guangzhou 510006, China
[e] Monitoring Centre of Pearl River Valley Aquatic Environment, Guangzhou 510611, China
[f] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

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ABSTRACT

The occurrence, distribution and removal efficiencies of organophosphorus flame retardants (OPFRs) and metals were examined in a municipal landfill leachate treatment system in Guangzhou, China. Five OPFRs and thirty-five metals were detected in wastewater samples collected at different treatment stages. ∑OPFRs was reduced from 4807.02 ng L^{-1} to 103.91 ng L^{-1} through the treatment system, with close to 98% removed from the dissolved phase. Tris(clorisopropyl) phosphates (TCPPs) dominated through the treatment process and accounted for over 80% and 50% of ∑OPFRs at the influent and the effluent, respectively. TCPPs were most efficiently removed (98.6%) followed by tris(2-chloroethyl) phosphate (TCEP) (96.6%) and triphenyl phosphate (TPP) (88.5%). For metals, Fe, Cr, and Rb were dominant in the raw leachate, detected at 7.55, 2.82, and 4.50 mg L^{-1}, respectively. Thirteen regulated heavy metals – including eight major pollutants (i.e., As. Cd, Cr, Cu, Hg, Ni, Pb, and Zn) – have been detected in all wastewater samples at sub-mg L^{-1} levels. Over 99.5% removal was achieved for Cr, Ni, and Fe, and close to 95% removal efficiency was observed for Rb. For the eight major heavy metals, over 99% removal was observed; the only exception was Cu, which was removed at 89%. It was found that microfiltration/reverse osmosis was critical for the removal of OPFRs and heavy metals while the core biological treatment played a minor role towards their removal. Remobilization of Co, Cu, Fe, Hg, Mn, Ni, Sb, and Sr from the returned sludge occurred during the second denitrification, indicating the need for additional post-biological process for effective removal of both contaminants. This study highlights the critical need to develop cheap, effective treatment technologies for contaminants-laden leachate generated from open dumps and under-designed landfills.

1. Introduction

Management of municipal solid waste (MSW) is one of the major environmental and public health challenges for cities in the developing regions (Renou et al., 2008). A recent report published by Waste Atlas has estimated that the safety and health of some 64 million people worldwide may be impacted by 50 biggest dumpsites (D-Waste, 2014). Sanitary landfill is widely used for municipal solid waste management around the world and generates leachate that contains a large variety of organic contaminants and heavy metals (Renou et al., 2008), and can contaminate surface water (Nartey et al., 2012), groundwater (David and Oluyege, 2014) and soil (Idehai, 2015). Organophosphate esters (OPEs) in landfills are mainly associated with plastic, textile, furniture, electronic appliances, building materials and other industrial applications (Rodil et al., 2005). With polybrominated diphenyl ethers (PBDEs) gradually phased out, the application of OPEs as flame retardants has been growing steadily (Stapleton et al., 2009). In 2006, over

* Corresponding author.
E-mail address: wuqihang@gzhu.edu.cn (Q. Wu).

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470,000 t of flame retardants were consumed in Europe with 20% as organophosphorus flame retardants (OPFRs) and half of that as chlorinated compounds (EFRA, 2007; Veen and Boer, 2012). In China, approximately 70,000 t of OPFRs are produced annually with over 40,000 t for export (Wang et al., 2010). Since most OPFRs are mixed rather than bonded in the products, they may be leached from the product matrices during usage or after its disposal. This implies that landfill leachate can act as critical pollution sources of OPFRs to surface and subsurface water resources. Toxicological studies have revealed that OPFRs can induce carcinogenic, neurotoxic, mutagenic, and endocrinal disruptive responses in animals and humans (Craig and Barth, 1999; Meeker and Stapleton, 2010). Furthermore, chlorinated organophosphates, such as tris(2-chloroethyl) phosphate (TCEP) and tris(clorisopropyl) phosphate (TCPP), are suspected carcinogens (WHO, 1998).

Heavy metals are also often present in leachates from both hazardous waste dumpsites and municipal solid waste landfills (Pan et al., 2015; Yan et al., 2009). They pose serious threat to public health as they can cause various physiological damages to human (Jaishankar et al., 2014; Järup, 2003) and ecotoxicological impacts on aquatic and terrestrial ecosystems (Biney et al., 1994; Nagajyoti et al., 2010). For instance, long-term exposure to As can lead to internal cancers, neurological problems, hypertension and cardiovascular disease (Smith et al., 2000). Heavy metals can also inhibit growth and synthesis of photosynthetic pigments on the *Lemna gibba* (Demim et al., 2013). This problem is worsened with the improper disposal of electronic products in the developing nations, leading to the release of high levels of metals in various places (Awasthi et al., 2016; Wittsiepe et al., 2017; Zhang et al., 2012).

With large number of open dumps and under-engineered landfills in developing regions, landfill leachate can pollute downstream water resources. Although various studies have tracked the fate of OPFRs through municipal sewage treatment system (Green et al., 2008; Qi, 2015; Rodil et al., 2012), few have examined their fate in landfill leachate treatment facility. Marklund et al. (2005). reported that only 50% of the OPFRs in the influent were separated during the sewage treatment process. Meyer and Bester (2004) found that 55%, 89%, and 75% of tributyl phosphate (TBP), tris(2-butoxyethyl) phosphate (TBEP), and triphenyl phosphate (TPP), respectively, was removed through the treatment process though chlorinated OPFRs were hardly reduced. The efficacy of the biological process – a core element in standard wastewater treatment facility – can be further complicated by the presence of heavy metals, which can weaken the microorganisms' capacity to mediate nitrification, denitrification, and biodegradation of organic contaminants.

Various treatment strategies have been examined for removing heavy metals or organic contaminants from landfill leachate and wastewater. Effective removal of heavy metals from wastewater can be achieved via biosorption (Gabr et al., 2008; Pan et al., 2007; Souiri et al., 2009), micellar enhanced ultrafiltration (Landaburu-Aguirre et al., 2009). Modern high-rejection reverse osmosis membranes can also retain dissolved both organic and inorganic contaminants with rejection rates as high as 98–99% (Peters, 1998). Efficient removal of metals via adsorption onto chitosan-montmorillonite (Assaad et al., 2007), activated carbon (Foul et al., 2009), and composite materials (Mojiri et al., 2014) have also been reported. Advanced oxidation processes have also been explored for removing organic contaminants in wastewater (Chemlal et al., 2014; Chenna et al., 2016).

The objective of this study is to examine the occurrence of landfill-originated OPFRs and heavy metals in a leachate treatment facility in the city of Guangzhou. A total of nine OPFRs and fifty-five metals were targeted for analysis in composite wastewater samples collected at different treatment stages. Change in distribution and compositional profiles of OPFRs and heavy metals were also examined. Data resolution by treatment phase also enabled the removal efficiencies of these contaminants be assessed. This assessment will help identify treatment processes/units that are critical towards OPFRs and metals removal.

2. Materials and methods

2.1. Refuse landfill leachate

Guangzhou city is a major industrial hub in southern China. Home to 13 million of residents and the Pearl River Delta, the city currently generates waste at approximately 8000 t d^{-1}. Roughly half of the produced waste originates from households; the rest is contributed from various commercial, institutional, and industrial sources. The city supports a wide range of industries with products that include plastics, textiles, photoelectric components, electronics, biomedical products, and telecommunication components (Guangzhou, 2016). As a result of the intensive manufacturing activities in the city and its large residential population, OPFRs and heavy metals are likely to present in the city's landfill leachate.

Approximately 7000 t d^{-1} waste generated in Guangzhou are disposed at the XinFeng Landfill – the site from which the raw and treated leachate originated. With a design disposal capacity of approximately 1.8 million t, the 230-acre site is one of the largest landfills in Asia (Worldatlas, 2017). Constructed as a sanitary landfill with a 20-year operational lifetime, the site has been managed run by the French transnational corporation Veolia since its operation in 2003. The XinFeng Landfill has a leachate collection-treatment system and a facility for methane recovery.

The studied leachate treatment plant had a daily processing capacity of 1600 t of leachate. A membrane bioreactor (MBR), a continuous microfiltration unit (CMF), and a reverse osmosis process (RO) constituted the core treatment of the facility (Kuang, 2012). A regulating pond was installed at the facility for flow equalization. The MBR was installed for advanced nitrogen removal through a three-stage denitrification-nitrification-denitrification process (Fig. 1) and achieved a removal efficiency of 98–99%. The CMF was a closed-circuit continuous filtration system with hollow fiber ultrafiltration/microfiltration module as the centerpiece. The RO was a standard, pressure-driven membrane separation unit to achieve the treatment effluent targets for the leachate. Sludge was returned to the first denitrification unit at a return flow to influent ratio of approximately 6–7.

2.2. Chemicals

For OPFRs, standards for triethyl phosphate (TEP), tripropyl phosphate (TPrP), tris(clorisopropyl)Phosphate (TCPP), tris(1,3-Dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP) were purchased from AccuStandard (New Haven, CT, USA); standards for tributyl phosphate (TBP) and triphenyl phosphate (TPP) were purchased from o2si smart solutions (Charleston, South Carolina, USA); standards for tris(2-chloroethyl) phosphate (TCEP) was obtained from Dr. Ehrensorfer (Augsburg, Bavaria, Germany) while the standard for tricresyl phosphate (TCP) was acquired from Chem Service (West Chester, PA, USA). For metals, a multi-element standard solution (1000 mg L^{-1}) was purchased from SPEX (Norcross Avenue Metuchen, NJ, USA). Organic solvents used included dichloromethane, ethyl acetate, and methanol and were all of chromatography grade. Ultrapure water (Milli-Q, MA, USA) was used for all solution preparation and vessel cleaning in this study.

Standard solutions for OPFRs and metals were prepared by mixing all OPFR standards and the multi-element standard. The