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# Occurrence and treatment efficiency of pharmaceuticals in landfill leachates

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ABSTRACT

Landfill leachates might contain pharmaceuticals due to the expired or unwanted drugs were disposed of at landfills. These pharmaceuticals might pose a threat to soil and groundwater. Therefore, this study investigated the distributions of pharmaceutical residues and toxicities among four typical municipal landfill leachates. Twenty six pharmaceuticals were investigated in this study and fifteen of them were found in all samples from four leachates. In addition, ampicillin and methylenedioxymethamphetamine (MDMA) were detected in urban landfills ($A_1$ and $A_2$) but were not in rural and suburb landfills (B and C). On the other hand, some compounds were much more abundant in suburb/rural landfill leachates than those in urban landfills including diclofenac, gemfibrozil and amphetamine. Landfill leachate treatment plants could not remove most of the pharmaceuticals effectively. Landfill leachates without proper treatments would have significant adverse health impacts on human and aquatic life.



## 1. Introduction

Pharmaceuticals have attracted growing attentions in recent years (Daughton and Ruhoy, 2009; Kumar and Xagoraraki, 2010; Sui et al., 2015; Wang et al., 2015). Potential pathways of pharmaceutical discharged into environment might include (1) the excretion of pharmaceuticals through the human or animals, (2) wastewaters generated from pharmaceutical manufacturing plants or hospitals, and (3) disposal of expired or unwanted drugs into landfills (Heberer, 2002; Gros et al., 2007; S.D. Kim et al., 2007; Lin et al., 2008; Lin and Tsai, 2009). Disposal of expired or unwanted drugs into environment might cause significant environmental impacts (Kumar and Xagoraraki, 2010). For examples, ibuprofen and naproxen, diclofenac, ibuprofen, naproxen, acetaminophen, and carbamazepine (Cleuvers, 2004; S.D. Kim et al, 2007; Eggen et al., 2010) have been reported to present in the environment and have significant health adverse impacts on human and aquatic life.

In Taiwan, infectious medical waste requires to be disinfected before disposed of Taiwan EPA (2016). The primary methods of treatment and disposal of medical waste are incineration and autoclaves. However, disposal of expired or unwanted drugs (except anticancer drugs) into household trash is a common practice in Taiwan. Unused anticancer drugs need to be collected through drug take-back programs through hospitals. Therefore, there is a significant amount of pharmaceuticals entering municipal solid wastes (MSW) landfills in Taiwan. In addition, Bound and Voulvoulis (2005) stated that there were about 63% of pharmaceuticals ended up in household trash in United Kingdom. Musson and Townsend (2009) estimated that active pharmaceutical ingredient concentration in MSW were 7.4–45 mg/kg of MSW.

Most of the literature investigated the occurrence, fate, biological effects, pollution prevention and risk management of pharmaceuticals in ground water and wastewater (Barnes et al., 2008; Buszka et al., 2009; Del Rosario et al., 2014; Sui et al., 2015). Fewer researches addressed the aspects of expired or unwanted drugs and their disposal (Daughton and Ruhoy, 2009; Musson and Townsend, 2009). Only a limited number of studies had investigated the presence of pharmaceutical compounds in landfill leachates. For example, Eggen et al. (2010) and Clarke et al. (2015) investigated new emerging pollutants and trace organic pollutants in landfill leachates, respectively. Both researches focused on certain pharmaceuticals in landfill leachate. Pharmaceuticals associated with the addition of drugs such as ketoprofen, ketamine, flunitrazepam (FM2), heroin, and codeine were not investigated in these researches. Therefore, a wide range of pharmaceuticals (26 chemicals) in four landfills were investigated in this study. Currently, there are no legislations regarding the Taiwanese law for discharge limits of these pharmaceuticals. In addition, Luo et al. (2014) stated that pharmaceutical and personal care products (PPCPs) are not included in the list of regulated substances yet.

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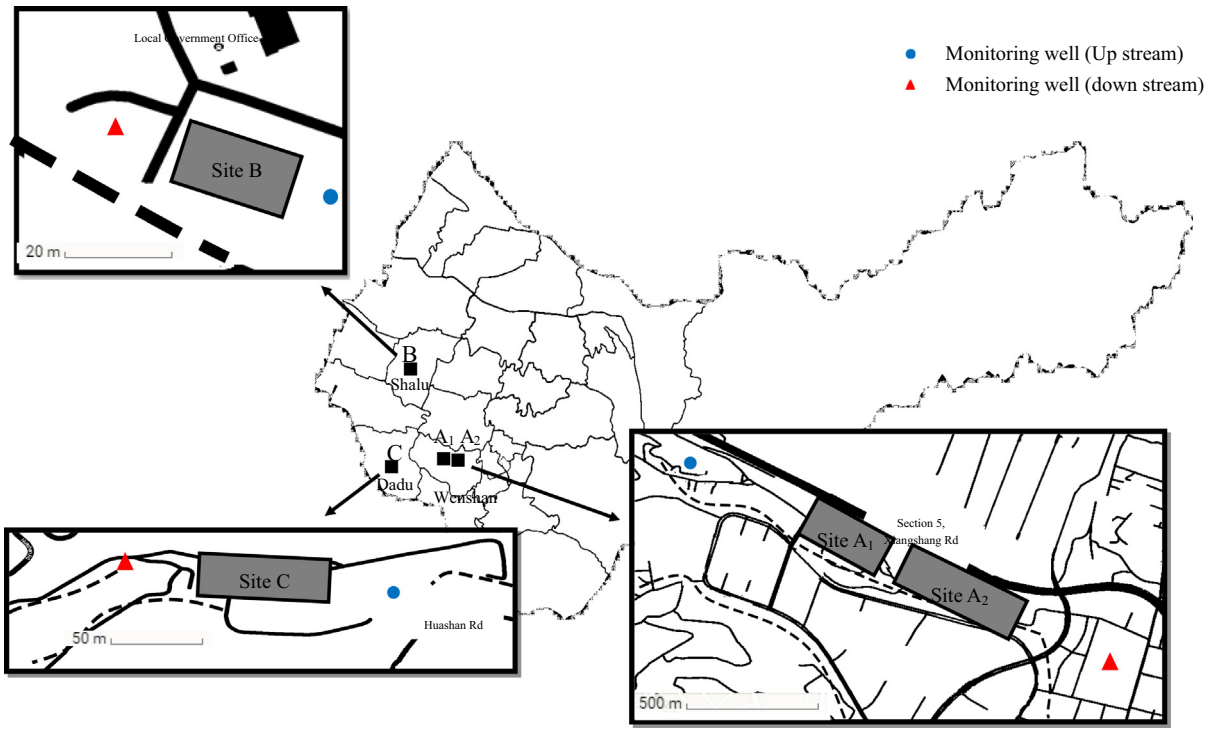


**Fig. 1.** Sketch map of the municipal landfills and monitoring wells.

To set regulatory limits for these compounds is of particular importance. Pharmaceuticals contents in raw leachates, treated leachates and groundwater of monitoring wells were investigated in this research.

## 2. Materials and methods

### 2.1. Landfills

Four landfills (Sites $A_1$, $A_2$, B and C) in central Taiwan were selected for the investigation due to their characteristics and comparative advantages (Fig. 1). Two sites were in urban areas (Sites $A_1$, $A_2$), one in rural area (Site B), and one in suburb (Site C). Both sites $A_1$ and $A_2$ were located in Wenshan, Taichung, Taiwan. Site $A_1$ was a closed landfill (operation period 1988–1994) and the site received mainly the city's MSW (population served: 830,000). Site $A_2$ has been accepting both MSW (about 24%) and incineration bottom ashes (about 76%) from MSW incinerator since 1995 (population served 1,050,000). Site A ($A_1$ and $A_2$) covered an area of 12.1 ha with capacity of 3,600,000 tons. Sites B and C were typical landfills for rural and suburb areas in Taiwan, respectively. Site B was located in remote area (Dadu, Taichung; population served 56,000, site area 8.2 ha, capacity 250,000 tons) and received MSW (100%) (operation period 1988–1994). Site C received MSW (100%) from a small town (Shalu, Taichung; population served 87,000, site area 9.4 ha, capacity 940,000 tons) and was operated between 1993 and 2004. Raw leachates collected from sites $A_1$ and $A_2$ were treated by leachate treatment plant A. Raw leachates collected from sites B and C were treated by leachate treatment plants B and C, respectively.

### 2.2. Sampling procedure

Raw leachates were collected at the sumps of four landfills (Sites $A_1$, $A_2$, B and C) in spring and fall seasons. Spring (March–May) and fall (September–November) seasons were corresponding to dry and wet seasons in Taiwan. Ground water samples were collected at both upstream and downstream monitoring wells of landfills. Influent and final effluent (treated) leachates of the treatment plants were collected according to the hydraulic retention time at each treatment plants. The removal efficiency was calculated using the following equation.

$$\text{Removal efficiency}\,(\%) = (C_{in} - C_e)/C_{in} * 100$$

where $C_{in}$ and $C_e$ are influent and effluent concentrations of a compound.

Triplicate samples were collected and maintained under conditions with minimized exposure to oxygen. Each sample was collected into a 1-L amber glass bottle with Teflon-lined cap and was sample-rinsed immediately prior to collection. In the laboratory, the leachates were filtered through a 0.2 μm membrane and stored at 4 °C in the dark.

### 2.3. Analysis

#### 2.3.1. Sampling preparation

The collected leachate samples were extracted using OASIS HLB cartridge from Waters (Millford, MA, USA). Such cartridges were preconditioned with 15 mL of MeOH and 18 mL of distilled water. The samples (400 mL) passed through the cartridges at 3–4 mL/min. The analytes were eluted using 12 mL of MeOH. The extracts were then concentrated under a flow of $N_2$ to an approximate volume of 0.1 mL. The resulting solutions were made to 1 mL with 50:50% (vol/vol) MeOH: $H_2O_2$ and filtered with 0.2 μm membrane before performing tests. (Nylon, Micron Separatçns Inc., West Borough, MA, U.S.A.)

#### 2.3.2. Chemical analysis

API 4000 LC/MS/MS system (Ab Sciex, Canada) was used to identify pharmaceuticals. Two sets of mobile phases were applied in this study, including 0.1% formic acid/acetonitrile and $H_2O_2$/acetonitrile for positive ion electrospray ionization