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# Comparing volatile organic compound emissions during equalization in wastewater treatment between the flux-chamber and mass-transfer methods

Wei-Hsiang Chen<sup>a,\*</sup>, Sian-Jhang Lin<sup>a</sup>, Feng-Chi Lee<sup>b</sup>, Mei-Hsia Chen<sup>b</sup>,  
T.Y. Yeh<sup>c</sup>, C.M. Kao<sup>a</sup>

<sup>a</sup> Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan

<sup>b</sup> Arouding-You Environmental Eng. Co., Kaohsiung 804, Taiwan

<sup>c</sup> Department of Civil and Environmental Engineering, National University of Kaohsiung, Kaohsiung 804, Taiwan

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## ABSTRACT

The emission of volatile organic compounds (VOCs) during equalization in wastewater treatment plants (WWTPs) is a particular source of concern. In this study, VOC emissions during equalization in three industrial WWTPs were analyzed by two different approaches. The flux-chamber method is a standard method used in many countries including Taiwan, as the theory behind the mass-transfer method is well-established. The objective was to investigate whether different outcomes were generated between two estimation methods and to determine potential overestimation of VOC, chemical oxygen demand (COD), or total organic carbon (TOC) removals in the WWTPs due to VOC emission during equalization. In the results, the estimated VOC fluxes during equalization were similar between two approaches. Recognizable amounts of VOCs were emitted during equalization (up to 28.2%, 13.6%, and 7.6% in three WWTPs). Their impacts on the COD (e.g., less than 0.1% in three WWTPs) or TOC removals (e.g., less than 11.4% in three WWTPs) were rather limited. Through the correlation analysis, the estimated VOC emission flux was not dependent upon individual but on co-influence of the compound's physicochemical characteristics, water quality, and operation during equalization. Although two approaches generated similar outcomes, the results by the flux-chamber method seemed to be more relevant to the operation during equalization, while the water quality were more important to the results by the mass-transfer method. Both methods were effective to quantify VOC emission during wastewater equalization, as the flux-chamber method is possibly a preferable option given their applicability and economic comparison.

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## 1. Introduction

Volatile organic compounds (VOCs) are typically defined as organic chemicals that have elevated vapor pressures due to their low boiling points (USEPA, 2016a; USGS, 2016). VOCs are numerous and include

both naturally-occurring compounds and those originating in human activities. These compounds, including both outdoors and indoors, are ubiquitous. VOCs are typically released via volatilization as raw materials or intermediate byproducts in industrial and commercial processes and from the use of products containing VOCs. Consequently, they are

\* Corresponding author.

E-mail addresses: [whchen@mail.nsysu.edu.tw](mailto:whchen@mail.nsysu.edu.tw), [wilchen726@gmail.com](mailto:wilchen726@gmail.com) (W.-H. Chen).

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frequently detected in municipal and industrial wastewater discharged from domestic, commercial, and industrial activities. The main reason for VOCs in the environment to be of concern is their detrimental effects on the environment and human health. Various VOCs generate ozone, a major component of photochemical smog (Liu et al., 2014; USEPA, 2016a). While many VOCs are potential or probable human carcinogens (e.g., methylene chloride and perchloroethylene used as paint stripper and dry cleaning fluid, respectively), their potentials to adversely affect human health via the exposure of inhalation have been reported (Guo et al., 2004; Yang et al., 2012; Chen et al., 2016; USEPA, 2016a,b).

Among anthropogenic activities releasing VOCs into the environment, wastewater treatment plants (WWTPs) have become an increasingly important source with respect to their health impacts on local workers and residents living nearby the sites (Lehtinen and Veijanen, 2011; Chen et al., 2013, 2014; Yang et al., 2014). While wastewater undergoes up to three levels of treatment before its discharge, VOCs in the wastewater are emitted into the atmosphere via volatilization during treatment. One example is equalization in which the VOC concentrations are expected to be relatively higher than those in subsequent treatment processes. Studies have been performed to investigate the VOC emissions at different stages of wastewater treatment (Yang et al., 2012; Chen et al., 2014; Yang et al., 2014). A study focusing on organic sulfur compounds revealed appreciable dimethylsulfide emission during equalization in a WWTP in Turkey by using two different methods, direct flux measurement under a floating chamber (28.6 mg/m<sup>3</sup>) and calculation from direct ambient measurement (12.4 mg/m<sup>2</sup>-h) (Muezzinoglu, 2003). Yang et al. (2012) estimated the VOC emission rates in different treatment processes of a municipal WWTP in China, indicating strong emissions and high health risks in the primary sedimentation basins, which is one of the initial treatment steps in the WWTP. Research effort has also been made to estimate the fugitive emissions of VOCs early in the design phase of process development (Ng et al., 2017).

Two major approaches were used in previous studies that analyzed the VOC emissions in different stages of wastewater treatment. The method that employs a chamber device is one common approach that directly measures the VOC emissions in different environmental scenarios including WWTPs. The Taiwan Environmental Protection Agency (TWEPA) employs this approach as one standard method for VOC sampling and analysis in WWTPs. The application of this method has been observed in a number of studies that quantified the emissions of volatile pollutants in WWTPs (Jeon et al., 2009) and other cases such as unsaturated sub-surfaces (Tillman et al., 2003; Tillman and Smith, 2004) and static water environments (Leyris et al., 2005). Without considering the water-phase concentration, this method simulates the effects of advection and diffusion and directly measures the emission flux of a compound into the atmosphere. An alternative approach is to measure the compound's concentrations in the air and water phases and to utilize the concept of mass-transfer kinetics for estimating the associated transfer flux between two phases (Ramaswami et al., 2005; Yang et al., 2012). The theory behind this approach is well established; however, situations in the field such as aeration or turbulent flows in treatment processes could affect the accuracy of the result.

The main objective of this study was to investigate the VOC emissions during equalization, one of the typical initial steps to treat wastewater, and to determine whether the amounts of VOCs emitted

in this step dominate the VOC removals in the subsequent treatment processes. Besides, two approaches including the flux-chamber and mass-transfer methods were simultaneously carried out to compare the consistency between two approaches. Three WWTPs in southern Taiwan, which treat chemical industry wastewater and are notoriously known for the atmospheric release of their odorous compounds, were selected as the sites of interest in this study. As equalization is typically the initial treatment step and is expected to affect the VOC removals in WWTPs, the impact of VOC emissions during equalization needs to be clearly quantified to avoid over-estimating the true removal efficiencies through treatment technologies. Water quality and operational factors that possibly affected the VOC releases during equalization were also discussed. The novelty of this study is to determine whether the observed VOC emission during equalization could change if different approaches such as the flux-chamber standard method or the theoretical mass-transfer approach were used, further investigating its impact on predicted wastewater treatment performances and the important influential factors.

## 2. Methodologies

### 2.1. Study sites

Three full-scale WWTPs, which are located in the suburban regions of Tainan City in southern Taiwan, were selected for investigation. The influent wastewaters of three WWTPs are produced from three different chemical industrial manufacturers that use similar compounds as their materials. It provides a great opportunity to compare the fates of these VOCs in different full-scale treatment scenarios. The compounds include benzene, toluene, ethylbenzene, xylenes, styrene, and chloroform. After equalization as the 1st treatment step, the major treatment processes in the 1st WWTP (denoted as WWTP1) comprise pH adjustment, anaerobic fluidized bed reactor, biological contact oxidation reactor, and pH adjustment before the discharge, as listed in Table 1. In the 2nd and 3rd WWTPs (denoted as WWTP2 and WWTP3, respectively), with equalization being the initial treatment process, the major treatment processes consist of pH adjustment, coagulation, sedimentation, and filtration, as well as coagulation, pH adjustment, sedimentation, coagulation, and sedimentation, respectively (Table 1). Table 1 also lists the plant-view areas and hydraulic retention times (HRT) of the equalization tanks in three WWTPs, as their potential effects on the VOC emission during equalization were investigated in the following discussion.

During the sampling period, the total daily flow capacities of WWTP1, WWTP2, and WWTP3 were 85.0, 11.8, and 15.3 cubic meters per day, respectively (Table 1). The chemical oxygen demands (CODs) of the influents in three WWTPs were 574, 528, and 17,000 mg/L, respectively. Additional influent wastewater quality information of three WWTPs including the temperature, pH, conductivity, biological oxygen demand

**Table 1 – Flow rate, air–water interfacial area, and hydraulic retention time during equalization and the treatment technologies in three WWTPs.**

	Flow rate (CMD) <sup>a</sup>	Equalization tank		Treatment scheme
		Area (m <sup>2</sup> )	HRT <sup>a</sup> (h)	
WWTP1	85.0	44.1	171.5	pH adjustment; anaerobic fluidized bed reactor; biological contact oxidation reactor; pH adjustment
WWTP2	11.8	14.4	41.5	pH adjustment; coagulation; sedimentation; filtration
WWTP3	15.3	16.2	82.5	Coagulation; pH adjustment; sedimentation; coagulation; sedimentation

<sup>a</sup> CMD and HRT denote the cubic meter per day and hydraulic retention time, respectively.

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