

A preliminary investigation of occurrence of pharmaceuticals and personal care products in total suspended particulate matter in Ha Noi, Viet Nam

Nguyen Hai Doan¹, Kiwao Kadokami², Vu Le Minh³, Hanh Thi Duong^{3,*}

¹Graduate School of Global Environmental Studies, Sophia University, Tokyo, Japan

²Institute of Environmental Science and Technology, The University of Kitakyushu,
1-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka, 808-0135, Japan

³Institute of Science and Technology for Energy and Environment, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Ha Noi, Viet Nam

*Email: dthanh.iet@gmail.com

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Abstract. Air pollution has become a serious environmental issue in Viet Nam, particularly in large cities. There is little information regarding the presence of pharmaceuticals and personal care products (PPCPs) in suspended particulate matter in Ha Noi, Viet Nam. The present study screened 163 PPCPs from 12 total suspended particulate matter (TSP) samples collected in Ha Noi using a novel analytical method, the liquid chromatography-mass spectrometry-quadrupole time of flight-Sequential Window Acquisition of All Theoretical Fragment Ion Spectra method (LC-QTOF-MS-SWATH). We identified and quantified 6 of the 163 PPCPs. All of the 6 PPCPs were detected for the first time in TSP. The total concentration ranged from 37.3 to 401.0 $\mu\text{g m}^{-3}$ (median: 143 $\mu\text{g m}^{-3}$). The number of PPCPs detected per sample ranged from 1 to 5 (median: 3), and their figure found was higher in the nighttime than that of the daytime.

Keywords: Target screening analysis, LC-QTOF-MS-SWATH, PPCP, air particle.

Classification numbers: 3.2.1, 3.4.5.

1. INTRODUCTION

Although clean air is regarded as a fundamental demand, air pollution continues to pose a significant threat to human health and well-being. According to a report by the World Health Organization (WHO), more than two million premature deaths per year can be attributed to the effect of air pollution. More than half of this burden falls on people in developing countries, particularly in urban areas [1]. In recent years, the pollution of the ambient air in large cities in Viet Nam has become a major concern, especially in Ha Noi and Ho Chi Minh City. During these years, Ha Noi has been witnessing a significant increase in the pollution level of total suspended particulate matter (TSP) in the atmosphere, which is often higher than the recommended concentration suggested by WHO and the limit concentration by the Vietnamese

national standard for ambient air quality [2]. Thus, it has been listed in the list of the world's most polluted cities [2].

Currently, more than 350 thousands chemicals and mixtures of chemicals are in use, and the amounts and categories of chemicals being produced have been rapidly increasing throughout the world [3], and a considerable amount has been discharged into the environment. Up to the present, in Viet Nam certain studies on the pollution status of organic micropollutants in atmospheric particles have been conducted, mainly focusing on polycyclic aromatic hydrocarbons [4, 5], persistent organic pollutants [6, 7], brominated flame retardants [8], siloxanes [9], and pesticides [10]. With the continuously increasing contamination of pharmaceuticals and personal care products (PPCPs) in the atmosphere in most parts of the world, the pollution of environments caused by PPCPs has become a major issue of social concern. PPCPs are characterized by high toxicity and strong bioaccumulation in the environment for a long time [11]. Even concentrations of just $\mu\text{g L}^{-1}$ or ng L^{-1} will have serious effects on human health and the ecological environment [12]. However, investigation on the occurrence and distribution of these contaminants in TSP in Ha Noi, Viet Nam is limited. Only a few studies have been carried out showing evidence of the presence of these emerging contaminants in the atmosphere. One of them indicated that in the Hanoi TSP, concentration of aspirin in urban house was up to 240 ng m^{-3} [5], while the outdoor concentration of diethyltoluamide was up to 32 ng m^{-3} [10].

Several analytical methods for determining PPCPs in air have been developed in the last decade [13 - 15]. Gas chromatography-mass spectrometry (GC-MS) is the usual instrumental technique for determining organic compounds from low to moderate polarity in TSP [16, 17]. However, GC-MS measurement is unsuitable for chemical compounds featuring highly polar functional groups alongside thermally decomposable or low vapor pressure properties [18]. To solve these limitations, numerous liquid chromatography-mass spectrometry (LC-MS) methodologies were used for the analysis of organic pollutants classes such as PPCPs, pesticides, and persistent organic pollutants [19]. Recently, a method called LC-TOF (time of flight)-MS method has been enhanced through the incorporation of Sequential Window Acquisition of All Theoretical Fragment Ion Spectra Acquisition (SWATH), significantly enhanced its capability to analyse target compounds [18, 20]. In this trend, LC-TOF-MS-SWATH stands out as potentially one of the most suitable methods presently available for simultaneously measuring a wide range of polar PPCPs.

To our knowledge the present study would be one of the earliest reports that used the comprehensive measurement method of LC-QTOF-MS-SWATH to investigate the occurrence of PPCPs in TSP from 12 samples collected in Ha Noi, Viet Nam.

2. MATERIALS AND METHODS

2.1. Reagents and equipment

LC-MS-grade methanol was manufactured by Kanto Chemical. The internal standards (IS) including methamidophos-d6, methomyl-d3, carbendazim-d4, pirimicarb-d6, imazalil-d5, etofenprox-d5 and surrogates such as sulfadimethoxine-d6, diflubenzuron-d4, sulfamethoxazole-d4, carbofuran-d3, carbaryl-d7 were obtained from Kanto Chemical and Hayashi Pure Chemical (Osaka, Japan). The HPLC-grade ammonium acetate (CAS No. 631-61-8, 1 mol L^{-1}) was manufactured by Wako Pure Chemical Industries. Quartz fiber filters (QR-100; $203 \times 254 \times 0.38 \text{ mm}$) were purchased from Advantec Toyo (Tokyo, Japan). Millex-LG syringe filters (0.2

µm pore size, Ø4 mm) were received from Merck Millipore (Darmstadt, Germany). A high-volume air sampler (Model-120H) was produced by Kimoto Electric (Osaka, Japan). LC-QTOF System (AB Sciex, Tokyo, Japan) was applied. All glassware and plastic ware were cleaned with detergent and water, washed in an ultrasonic cleaner, dried and rinsed with methanol before use.

2.2. Sample collection

TSP samples were collected according to the method by Duong *et al.* [10]. Briefly, at the site (AP) on the 8 m-height roof of a building (21°2'31.94" N and 105°46'53.00E) in a densely populated residential area (Phu Do, Tu Liem District), 12 air particle samples were deployed. Samples were collected during the day and night for 6 successive days in April 2017. Daytime samples were taken from around 8:00 to 18:00, and nighttime samples were performed from around 18:00 to 23:00 to avoid making noise to citizens, the time to take each daytime and nighttime sample was about 10 and 5 hours, respectively. Samples were collected by a high-volume air sampler and the sampling rate of 400 L/min was operated. Blank analysis was carried out to control the contamination during sampling and analysis. Field blank samples were daily taken along with TSP samples and laboratory blank samples were examined (one for every batch of 4 samples). The blank samples were analysed using the same analytical method as that used to examine the TSP samples. The average annual rainfall in April in Ha Noi is 75 mm (NCHMF, 2020), and the temperature ranged from 22.4 - 31.6 °C.

The quartz fiber filters utilized in the air sampler were preconditioned in a desiccator at room temperature for 48 hours. Subsequently, upon removal from the air sampler, each filter was individually enveloped in aluminum foil and stored at -20 °C until extraction.

2.3. Chemical analysis

Table 1. LC-QTOF-MS conditions.

Instrument	Sciex X500R QTOF system			
Column	GL Science ODS-4 HP (150 mm, 2.1 mm, 3 µm)			
Column temp.	40 °C			
Flow rate	0.3 mL min ⁻¹			
Mobile phase	A: 5 mM CH ₃ COONH ₄ in H ₂ O B: 5 mM CH ₃ COONH ₄ in CH ₃ OH			
Gradient profile	Time, min	0	30 - 40	40.01 - 50
	B, %	5	95	5
Injection Volume	2 mL			
Ion source	TurbolonSpray			
Ionization	ESI-positive			
Measurement mode	Swath			
TOF-MS (scan range)	50 - 1000 Da, 0.1s			
TOF MS/MS	50 - 1000 Da, 22 ranges, 0.07 s each			
Collision energy ramp	20 – 50 V			
Mass resolution	30000			
Total cycle time	1.768 s			

To extract efficiently mixtures of PPCPs from TSP, various solvents such as methanol, acetonitrile, ethyl acetate, hexane, and dichloromethane were previously tested, and consequently methanol with high recovery extraction was the most suitable for extracting PPCPs from TSP in this study. Sample preparation was performed according to Doan *et al.* [21]. In short, a filter from the high-volume air sampler was cut into small pieces, these pieces were spiked with 50 μL of a mixture of surrogate compounds ($4 \mu\text{g mL}^{-1}$ each), then PPCPs were sonication-extracted (at 35 kHz) with 20 mL of methanol, and were centrifuged at 2000 rpm for 20 min, and the extraction solution was transferred to a 50-mL pear-shaped evaporation flask. This extraction process was repeated twice with 15 mL of methanol. After mixing the extracts, the extract was concentrated by rotary evaporation to approximately 2-3 mL, shifted to a vial and further evaporated to 0.2 mL using a gentle stream of high-purity nitrogen. Next, a mixed internal standard (50 μL , $4 \mu\text{g mL}^{-1}$ each) was added, then the volume was adjusted to 0.5 mL with methanol. The final concentrate was filtered with a syringe filter prior to LC-QTOF-MS-SWATH analysis. The instrument conditions are listed in Table 1.

2.4. Quality assurance and quality control

To validate the analysis process, several quality control measures were implemented, including the analysis of field blank and laboratory blank samples, sample duplication, and surrogate recovery assessment. Laboratory blank samples underwent scrutiny (one for every four samples per batch) using the identical procedure employed for the actual samples. The concentrations of target compounds were determined by subtracting the average blank value. Duplicate analyses were carried out on two samples, one during the daytime and another during the nighttime; the relative standard deviations of the target compounds were below 20 %.

The fitness of the extraction process was checked using surrogate compounds. Prior to extraction, one sample within the batch (typically 3 samples per batch) was spiked with surrogate compounds. The good average recovery rates of the surrogates ranged from 63.5 % to 87.1 %, with the exception of sulfamethoxazole-d4 (48.7 %), potentially attributed to the matrix effect [18]; however, these results did not affect the quantification, owing to the compensatory effect of utilizing internal standards [18]. The relative standard deviation ranged from 8.4 % to 34.1 %, indicating the suitability of the sample analyses. The favorable recovery rates obtained demonstrated that the method is satisfactory for measuring PPCPs in TSP.

The method detection limits (MDLs) and the level of quantitation (LOQ) of each target were determined according to the relationship between the instrument detection limit (IDL) and the MDL and the LOQ (IDL: MDL: LOQ = 1:4:10) (SMEWW, 2017). For the target analytes, the MDLs were from 0.30 pg m^{-3} for acetaminophen to 15.0 pg m^{-3} for sulfamethoxazole.

2.5. Statistical analysis

Microsoft Excel 2010 (Microsoft Japan, Tokyo, Japan) were used to calculate the statistical analyses. To determine differences of concentrations among daytime and nighttime, single factor ANOVA was used.

3. RESULTS AND DISCUSSION

3.1. Overall contamination status

Six out of the 163 PPCPs were detected at least once in the TSP samples. All these PPCPs including acetaminophen, butyl methoxydibenzoylmethane (BMDM), clarithromycin, flumequine, sulfamethoxazole, benzophenone-3 (BP-3) are reported for the first time in TSP in Ha Noi, Viet Nam. Previous studies have included these PPCPs in analyses of TSP, but resulted in no detection, even samples were collected at the same set of location [5, 10], because they are the polar and low or non-volatile compounds, therefore easily detected by LC-QTOF-MS-SWATH. Numerous PPCPs are present in TSP perhaps due to the sorption of PPCPs on the air particles after their application, then distribution to the atmosphere.

The detection frequency of PPCPs in all samples collected was in the order: Acetaminophen (100 %) > BP-3 (67 %) > BMDM (50 %) > clarithromycin (25 %) > sulfamethoxazole (17 %) > flumequine (8 %). The total concentration of the detected PPCPs varied from 37.3 to 401 pg m⁻³ (median, 143 pg m⁻³). The number of PPCPs detected per sample ranged from 1 to 5 (median, 3), and their figure found in the nighttime was higher than that of the daytime.

A Single Factor mode of ANOVA demonstrated that differences in the average concentrations of each PPCP in the atmosphere between the daytime and nighttime were not found ($p = 2.05 > 0.05$). This could be illuminated by the fact that the concentration of a PPCP in the atmosphere depends not only on temporal variations but also on its chemo-physical properties, consumption demand, sampling sites, and the seasonal variations.

3.2. Acetaminophen

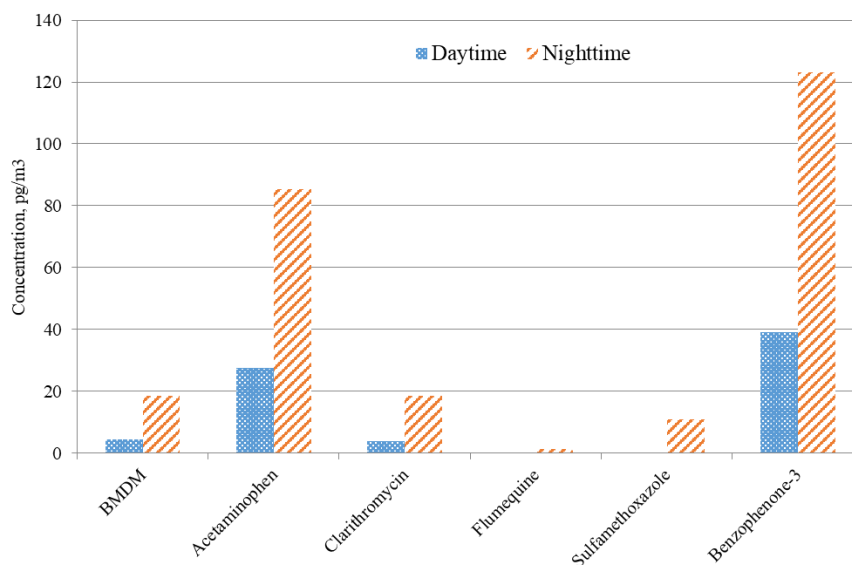


Figure 1. Average concentration of each PPCP in the daytime and nighttime.

N-acetyl-p-aminophenol (APAP, also commonly known as acetaminophen or paracetamol) is one of the most widely used analgesic and antipyretic agents. WHO lists it as an indispensable drug, and clinical guidelines in many countries. Its action is focused on hypothalamic centre, where APAP regulates the temperature. In addition, APAP inhibits the synthesis of prostaglandin in the central nervous system, blocking the generation of painful impulse at the peripheral level [22]. In the current study, average APAP concentration was lower in the

daytime than in the nighttime (Figure 1). This chemical was present in all survey samples, with the highest concentration recorded at 124 pg m^{-3} . This pharmaceutical is generally one of the most frequently detected drugs in rivers and estuaries with high concentrations ranging from 0.03 to 9822 ng L^{-1} [23 - 25].

3.3. Benzophenone-3

Benzophenone-3 (BP-3), also known as 2-hydroxy-4-methoxy-benzophenone or oxybenzophenone, is widely used in a variety of cosmetic products as a sunscreen agent that absorbs and dissipates ultraviolet (UV) radiation [26]. BP-3 has also been approved by the US Food and Drug Administration for use as a UV stabilizer in plastic surface coatings for food packaging to prevent polymer or food photodegradation [27]. As was the common trend of mode, BP-3 concentration in the nighttime was 3 times higher than those in the daytime (Figure 1). The BP-3 concentration varied from 0 to 270 pg m^{-3} . Its detection frequency was relatively high, which proved that the primary source of BP-3 exposure in the general population from personal care products containing UV filters such as sunscreens, lotions, and cosmetics is comparatively popular in Ha Noi, Viet Nam. BP-3 is consistently reported to occur in freshwater systems, with concentrations as high as $\mu\text{g L}^{-1}$ [28, 29].

3.4. Butyl methoxydibenzoylmethane

Butyl methoxydibenzoylmethane (BMDM) is the most effective and widely used for UV-A filtering in sunscreen preparations as well as in the photoprotection of cosmetic products [30, 31]. It is included in the list of authorized sunscreen agents in Europe, USA, Japan and Australia [31]. In our study, its level in the nighttime was 4 times higher than that recorded in the daytime (Figure 1), because BMDM experienced marked photodegradation and produced free radicals under solar UV irradiation [30, 32, 33]. BMDM was frequently detected in sewage treatment plants at the level of hundreds of ng L^{-1} [34].

3.5. Other PPCPs

Three other substances were detected from 8 to 25 % of the samples. These substances also corresponded to the families of PPCPs most sold in Viet Nam for use as antibiotics (clarithromycin), antimicrobial agents (flumequine), and antibacterial agents (sulfamethoxazole). These PPCPs also followed the significantly common trends of temporal variations.

4. CONCLUSIONS

This study is the first in the world to use LC-QTOF-MS-SWATH to monitor PPCPs in TSP. We quantified 6 of 163 PPCPs in at least one sample collected in the metropolitan area of Ha Noi, Viet Nam during April 2017. All quantified substances were (to our knowledge) detected for the first time in TSP in Viet Nam. The total PPCPs concentration ranged from 37.3 to 401 pg m^{-3} (median, 143 pg m^{-3}), and the number of PPCPs detected per sample ranged from 1 to 5 (median, 3), and their figure found in the nighttime was higher than that of the daytime.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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