Occurrence of trimethyl phosphate and triethyl phosphate in a municipal wastewater treatment plant and human urine

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\textbf{ABSTRACT}

Trimethyl phosphate (TMP) and triethyl phosphate (TEP) are extensively used as flame retardants, but their analytical methods are scarce. In this study, a robust method for both TMP and TEP in environmental water and human urine was developed by coupling of solid phase extraction (SPE) with liquid chromatography-tandem mass spectrometry (LC-MS/MS). For both TMP and TEP, the method showed good recoveries (>81%) and precisions (RSD < 5%), as well as a limit of quantification of 3 ng/L for water and 40 ng/L for urine samples, respectively. Through this method, the occurrence of TMP and TEP in municipal wastewater treatment plant (WWTP) were profiled and the anoxic step was found as the key role for their removal. Furthermore, TEP (110-2470 ng/L) was detected in all urine samples with generally higher concentration than TMP (70-2330 ng/L), which agreed with their occurrence profiles in the influent and effluent of the WWTP.

\textbf{1 Introduction}

Organophosphate esters (OPEs) are widely used as flame retardants, plasticizers and antifoaming agents in plastic, electronic equipment and furniture [1]. With the gradually restricted usage of brominated diphenyl ethers as flame retardants worldwide, the consumption of OPEs has boomed sharply in recent years [2–4]. Currently, dozens of OPEs have been applied as flame retardants, including nonhalogenated and halogenated alkyl esters, as well as aromatic derivatives [5].

Among all the widely used OPE flame retardants, trimethyl phosphate (TMP) and triethyl phosphate (TEP) are the most polar and volatile ones (Table 1). TMP has been widely used in various industrial processes, including as solvent and methylating agent for chemical reaction, as color inhibitor for fiber, and as intermediate or catalyst for pesticide or pharmaceuticals [6,7]. The primary applications of TEP were as a flame retardant in the plastics and vehicle industry, as a hydrolysed compound in ketone synthesis, and as a solvent or intermediate for the preparation of pharmaceuticals, pesticides and lacquers [8]. TMP and TEP have also been extensively studied as stimulants of organophosphorous warfare agents [9].

The extensive use of TMP and TEP will inevitably give rise to their release into the environment and therefore uptake to organisms, as both TMP and TEP were believed to be persistent in neutral, acidic, and alkaline water, soil or gas phase [10]. Therefore, it is of great importance to understand the environmental processes and toxic effects of these compounds. Although studies on the occurrence [5,11–15], transportation [16–19] and degradation [20–22] in ecosystem, as well as accumulation [23–25] and toxicology toward human health [26] of OPEs have been reported, data on the occurrence, fate and toxicity of TMP and TEP are relatively limited. Although they can be ingested through drinking water, inhalation and skin contact are considered to be the two main exposure routes for TMP and TEP into the human body. The LD\textsubscript{50} of TMP and TEP were relatively high (Table 1) for rat [2,27]. TMP was demonstrated to be genotoxic in a micronucleus test in vivo [27]. Besides, the repeated exposure of TMP at low dose could induce substantial change in hematology, injury of kidney, loss of body weight, as well as the heritable genetic damage to human germ cell [28,29]. TEP showed a narcotic effect and certain neurotoxic properties at high doses, as well as a potential mutagenic effect [30].

The lack of information on the environmental occurrence of TMP and TEP is mainly attributed to the lack of proper methods for their analysis in environmental and biological samples. Currently available methods for the analysis of OPEs are mainly based on solid-phase extraction (SPE) coupled with gas chromatography-mass...
spectrumtrometer (GC-MS) [12,16,31,32] or liquid chromatography–tandem mass spectrometry (LC-MS/MS) [5,18]. Due to the high polarity and volatility of TMP, however, the SPE of TMP usually suffered from low recoveries that did not meet the requirement for quantification by GC-MS or LC-MS/MS [5,13,33,34]. Although direct analysis in real-time by triple quadrupole mass spectrometer (DART-MS/MS) [35] and headspace solid-phase microextraction [36] were proposed for determination of TMP, they are unsuitable for analysis of TEP and other OPEs. Consequently, it remains a great challenge to determine TMP and TEP in environmental and biological samples to study the occurrence and fate of TMP and TEP in the environment.

The purpose of this study is to develop a highly sensitive and accurate method for the analysis of TMP and TEP in environmental water and human urine, and to further study the occurrences of these two compounds in some typical environmental media. Given their various advantages, SPE and LC-MS/MS were adopted in this developed method. An SPE cartridge with relatively high recovery for these two compounds was selected after screening a number of commercially available SPE cartridges. In addition, commercially available isotopically labeled TMP and TEP were used as internal standards (IS) to enhance the method accuracy. With this developed method, the concentration of the TMP and TEP in environmental and biological samples was determined, and the wide occurrence of TMP and TEP in municipal wastewater and human urine was demonstrated.

### Table 1. The structure and some properties of Trimethyl Phosphate (TMP) and Triethyl Phosphate (TEP).

| Structure | TMP | TEP |
|-----------|-----|-----|
| [H3CO]_2POCH_3 | [C_2H_5OC]_2POCH_3 |
| logKow | −0.65 | 0.80 |
| Melting point (°C) | −6 | 39 |
| Vapor pressure (Pa) | 0.74 (25°C) | 56 |
| LD50 (mg/kg) | 840 | 1131 |

* *cited from ref [27].
* *cited from ref [30].

TMP and TEP were determined by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The UPLC system (ACQUITY UPLC, Waters, USA), consisting of a degasser, a sample manager and a binary solvent manager, was interfaced to a TSQ Quantum Access triple quadrupole mass spectrometer (MS/MS, Thermo Scientific, US) equipped with an electrospray ionization (ESI) system. Nitrogen served as sheath gas and aux gas was generated from liquid nitrogen tank. Argon (99.999%) was used as a collision gas. The UPLC-MS/MS system was manipulated with LCquan system (Thermo Scientific, US). Detailed information on the instrument parameters and analytic performance was described in our previous study [34]. The retention time and selected reaction monitoring (SRM) transitions of the target compounds and the ISs are listed in Table 2. For comparison, the concentration of TCEP, TCPP and TnBP in water samples was also determined by our previously developed method [34].

### 2 Materials and methods

#### 2.1 Reagents and materials

TMP, TEP, tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP) and tri-n-propyl phosphate (TnBP) standards were purchased from Dr. Ehrenstorfer GmbH (Germany). The isotopically labeled TMP (trimethyl-d_2-phosphate, TMP-d_2) and TEP (triethyl-d_2-phosphate, TEP-d_2) were obtained from C/D/N ISOTOPES INC. (Quebec, Canada). The isotopically labeled TnBP (tributyl-d_27-phosphate, TnBP-d_27) was obtained from Cambridge Isotope Laboratories (UK). Formic acid was bought from Sigma-Aldrich (Germany). Acetonitrile (ACN, Optima grade) was purchased from Fisher Scientific (USA). Ultra-pure water (18.3 MΩ) produced with a Milli-Q Gradient system (Millipore, Bedford, USA) was used throughout.

Individual stock solutions of TMP and TEP (2000 mg/L) were prepared by dissolving the reference materials in ACN. A mixed stock solution containing 10 mg/L each of TMP and TEP was prepared by dilution of the stock solutions with ACN. All of the stock solutions were kept in a 4°C refrigerator.

ODS-C18 SPE cartridge (3 mL, 200 mg) was obtained from Agilent (Santa Clara, USA). Oasis HLB (3 mL, 60 mg) and VAC-C18 (3 mL, 200 mg) SPE cartridge were purchased from Waters (Milford, USA). LC-18 (3 mL, 500 mg), ENV1-18 (3 mL, 500 mg), and ENV1-Carb (3 mL, 500 mg) SPE cartridges were obtained from Supelco (Bellefonte, USA).

#### 2.2 LC-MS/MS analysis

TMP and TEP were determined by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The UPLC system (ACQUITY UPLC, Waters, USA), consisting of a degasser, a sample manager and a binary solvent manager, was interfaced to a TSQ Quantum Access triple quadrupole mass spectrometer (MS/MS, Thermo Scientific, US) equipped with an electrospray ionization (ESI) system. Nitrogen served as sheath gas and aux gas was generated from liquid nitrogen tank. Argon (99.999%) was used as a collision gas. The UPLC-MS/MS system was manipulated with LCquan system (Thermo Scientific, US). Detailed information on the instrument parameters and analytic performance was described in our previous study [34]. The retention time and selected reaction monitoring (SRM) transitions of the target compounds and the ISs are listed in Table 2. For comparison, the concentration of TCEP, TCPP and TnBP in water samples was also determined by our previously developed method [34].
2.3 Sample collection and pretreatment

Water samples were collected from each processing stage of a major municipal wastewater treatment plant (WWTP) in Beijing, China. This WWTP has two activated sludge treatment processes running in parallel, the anaerobic-anoxic-aerobic (AAO) and anoxic-anaerobic-aerobic (interval AAO) processes. Figure 1 shows the nine specific sampling sites in these two processes. Human urine samples were collected from five workers at a plastic packaging plant in Inner Mongolia, five students from a research institute in Beijing, and three members of a family in Beijing. All samples were preserved at 4°C and pretreated within 48 h after sampling.

Table 2. The LC-ESI+-MS/MS parameters for the target compounds and ISs.

| Compound              | Retention Time (min) | Transitions (collision energy, ev) | Transition Ratio (%)** |
|-----------------------|----------------------|------------------------------------|------------------------|
| Trimethyl phosphate   | 0.90                 | 141.0 → 79.3                       | 17.26                  |
|                       |                      | 141.0 → 109.1                      | (17)                   |
| Trimethyl-δ14-phosphate| 0.90                 | 150.0 → 83.3                       | 14.31                  |
|                       |                      | 150.0 → 115.2                      | (18)                   |
| Triethyl phosphate    | 1.28                 | 183.0 → 81.3                       | 36.44                  |
|                       |                      | 183.0 → 99.2                       | (18)                   |
| Triethyl-δ15-phosphate| 1.28                 | 198.2 → 102.2                      | 49.16                  |
|                       |                      | 198.2 → 166.2                      | (10)                   |

* Quantification transition
** Transition ratio between the qualitative transition and the quantification transition

3 Results and discussions

3.1 Development of analytical method

Five kinds of commercial SPE cartridges were tested for the recovery of TMP and TEP in water samples, which were prepared by spiking into 200 mL reagent water with 20 μL of a standard solution containing 10 mg/L each of TMP and TEP, and 10 μL ISs (1 mg/L). The performance of these SPE cartridges was evaluated using the absolute recovery of TMP and TEP, as well as the recovery of TMP and TEP calibrated with their corresponding ISs. As shown in Figure 2, the HLB, LC-18, ODS-C18 and VAC-C18 cartridges exhibited very

Figure 1. Schematic map of sampling site and concentration (ng/L) of TMP and TEP in a municipal WWTP.
low recoveries for TMP (<23%), and thus high relative standard deviations (RSD) up to 87%. Among the tested cartridges, the HLB cartridge showed the lowest recovery for TMP that agreed with the literature [2], whereas the ENVI-18 cartridge had the highest recovery (~50%) and thus the lowest RSD (<3%) for TMP. This relatively high absolute recovery of TMP ensured a high recovery (~100%) after corrected by their ISs. For the TEP, though all the tested cartridges showed acceptable recovery in relation to the IS, ENVI-
18 cartridge exhibited the highest recovery. Therefore, ENVI-18 cartridge is the choice for extracting TMP and TEP from environmental waters and was selected in this study.

The elution volume and loading capacity of the ENVI-18 cartridge were tested using samples prepared by spiking 1 μg/L each of TMP and TEP, as well as 10 ng each of the ISs in reagent water. Results showed that 3 mL ACN was enough for complete elution of the target compounds (Figure 3), and the ENVI-18 cartridge provided sufficiently high recoveries toward TMP and TEP for water samples no more than 500 mL (Figure 4). Therefore, 200 mL was chosen as a conserved volume to ensure satisfactory recoveries for trace TMP and TEP in water samples.

Four SPE cartridges, including HLB, VAC-C18, ENVI-18 and ENVI-Carb, were tested for extracting TMP and TEP from human urine samples, which were prepared by spiking 100 ng each of TMP and TEP, as well as 10 ng each of the ISs into 10 mL of blank urine. Using the same SPE procedure as that for water samples, it was demonstrated that the ENVI-Carb cartridge displayed no recovery toward both target compounds and their ISs, which may be attributed to the high polarities of the target compounds and thus the strong adsorption to the SPE sorbent that prohibited their elution by ACN. Among the other three SPE cartridges, HLB showed low absolute and IS-calibrated recovery for TMP in urine. This is because HLB is more suitable for the extraction of target compounds with higher hydrophobicity than the higher polar compounds like TMP [37], making it difficult to extract TMP and the IS counterpart. This further gives rise to large deviation and inaccurate recovery. As with that in SPE of water samples, ENVI-18 also presented the highest recovery among the other three cartridges (Figure 2), and 3 mL ACN was enough for the complete elution of the target analytes (Figure 3).

Under the above optimized SPE procedure and LC-MS/MS conditions optimized in our previous study [34], the calibration curves for TMP and TEP were measured using 10 standard solutions with concentrations ranging from 0.1 to 1000 μg/L. This proposed methods have good linearity ($R^2 > 0.999$) and precision (RSD < 5%, $n = 5$) for both water and urine samples. The limit of quantification (LOQ, S/N ≥ 10 for the quantification transition) obtained by SPE of 200 mL water samples was 3 ng/L for both TMP and TEP, while that by SPE of 10 mL urine samples was 40 ng/L for both TMP and TEP.

Water samples spiked with 0, 5, 10 and 50 ng/L each of TMP and TEP, and 10 ng each of ISs, and human urine samples spiked with 0, 100, 250, and 500 ng/L each of TMP and TEP and 10 ng each of ISs were adopted to test the recovery of the proposed method. Results showed that the recoveries are satisfactory with values in the range of 81.6–99.9% (Table 3). This demonstrated that the recovery of TMP can be improved by using appropriate SPE cartridges and isotope labeled internal standard of TMP, and the low recovery of TMP in previous

**Table 3. Recoveries of TMP and TEP (mean ± s, n = 3) from water and urine samples at various spiked levels.**

| Spiked (ng/L) | TMP (%) | TEP (%) |
|--------------|---------|---------|
| Water        |         |         |
| 5            | 98.3 ± 1.5 | 94.6 ± 5.0 |
| 10           | 99.6 ± 0.3 | 97.7 ± 1.9 |
| 50           | 99.9 ± 1.7 | 99.4 ± 0.5 |
| Urine        |         |         |
| 100          | 81.6 ± 4.4 | 82.1 ± 4.5 |
| 250          | 85.8 ± 4.3 | 88.3 ± 3.8 |
| 500          | 94.4 ± 4.8 | 97.6 ± 5.1 |

![Figure 4](image-url). Optimization of the water sample loading volume for the recovery of TMP and TEP. (a) TMP; (b) IS of TMP; (c) TEP; (d) IS of TEP.
3.2 Occurrence of TMP and TEP in wastewater samples

Although most of the OPEs other than TMP were determined in the influent, effluent and wastewaters of the various treatment stages of a WWTP [2,38], the occurrence of TMP in these samples is not reported due to the lack of analytical techniques. Using the above developed method, we studied the occurrence of TMP and TEP in the wastewater samples collected from each stage of a municipal WWTP, which runs the AAO and interval AAO activated sludge treatment processes in parallel. As shown in Figure 1, both TMP and TEP were detected in all the samples. In both processes, the highest concentration of the TMP occurred after the anaerobic stage, which were 70.1 ng/L in the interval AAO and 69.0 ng/L in AAO, respectively, and were significantly higher than that of the influent. This result suggested that TMP can be released from the bacteria in the anaerobic process of the active sludge treatment process. Figure 1 also indicates that the anoxic was the most efficient step for the removal of TMP, though the aerobic step also contributed to the reduction of TMP concentration. It is noteworthy that the AAO process is much more efficient than the interval AAO for the removal of TMP. For the same influent with 60.2 ng/L TMP, the concentration of the effluent reduced to 16.1 and 37.4 ng/L after the AAO and the interval AAO processes, respectively. This difference was mainly attributed to the different sequences of the anoxic and the anaerobic steps, which then resulted in the difference in removal efficiency between the two processes. In the AAO process, the TMP released in the anaerobic step can be efficiently uptaken by the following anoxic and aerobic steps. In the interval AAO, however, the most efficient removal process of anoxic was performed ahead of the anaerobic step, giving rise to enhanced release of TMP from the anaerobic step due to the reduced TMP content after anoxic process, and the reduced removal of TMP released from the anaerobic step.

Unlike in the case of TMP, the TEP concentration was in the range of 91.3–169.1 ng/L in each stage of the two processes (Figure 1). For both treatment processes, the TEP concentration in the effluents was higher than that in the influent, suggesting that the TEP cannot be used by bacteria as phosphate during the active sludge treatment process, and the possible formation of TEP from the degradation of other OPEs or release from the equipment used in the treatment process.

Table 4 also shows the concentrations of three other typical OPEs including TCEP, TCPP and TnP, which were lower in comparison to that reported in the literature (90–52,000 ng/L) [12,18]. As that for TMP and TEP, the AAO process is more efficient than the interval AAO process in removal of TCEP, TCPP and TnP. It is noteworthy that the TCEP concentration in the effluent was twice of that in the influent, suggesting the input of TCEP from some unknown source during this process.

3.3 Occurrence of TMP and TEP in human urine

OPEs had been detected in human milk [25], indicating that OPEs can accumulate in the human body and affect human health [26]. There were no relevant reports concerning the occurrence of TMP and TEP in human body, though researches focus on the detection of OPEs metabolites in human urine has been conducted [39–42].

TMP and TEP in human urine samples collected from five workers of a plastic packaging plant in Inner Mongolia (IM1-IM5), five students from a research institute in Beijing (BJ1-BJ5), and three members of a family in Beijing (BJ6-BJ8) were determined with this developed method. Results (Table 5) showed that TMP was detected in 11 of the 13 samples, and TEP was detected in all the 13 samples. Both the highest (2330 ng/L) and the lowest (below the detection limit) TMP occurred in persons living in Inner Mongolia, where the environment is regarded as less polluted than that in Beijing. However, the highest (2470 ng/L) and the lowest (110 ng/L) TEP occurred in persons living in Beijing. For the five students (BJ1-BJ5), their TMP concentrations in urine were all around 100 ng/L, but the TEP concentrations are quite different even though they work in the

| Table 4. Concentrations of TMP, TEP and three other OPEs (ng/L, mean ± s, n = 3) in samples from two activated sludge treatment processes of a municipal WWTP. |
|--------------------------------------------------|
| TMP | TEP | TCEP | TCPP | TnP |
| influent | 60.2 ± 0.6 | 103.7 ± 2.8 | 76.8 ± 1.8 | 189.3 ± 5.5 | 113.8 ± 2.3 |
| interval AAO process | | | | | |
| IA1 | 41.2 ± 5.1 | 91.3 ± 3.2 | 194.4 ± 4.8 | 281.3 ± 38.9 | 191.1 ± 36.0 |
| IA2 | 70.1 ± 1.4 | 127.9 ± 13.2 | 202.9 ± 11.2 | 252.6 ± 9.3 | 80.2 ± 2.7 |
| IA3 | 57.1 ± 3.3 | 125.1 ± 1.3 | 113.6 ± 18.3 | 167.6 ± 6.5 | 54.2 ± 0.5 |
| IA4 | 37.4 ± 4.3 | 133.6 ± 8.9 | 153.5 ± 16.5 | 186.0 ± 15.5 | 43.2 ± 3.5 |
| AAO process | | | | | |
| A1 | 69.0 ± 0.9 | 106.2 ± 4.4 | 143.6 ± 3.2 | 165.8 ± 1.0 | 52.5 ± 3.4 |
| A2 | 35.2 ± 6.1 | 120.6 ± 2.1 | 35.4 ± 2.3 | 123.5 ± 3.8 | 84.8 ± 2.5 |
| A3 | 14.4 ± 4.9 | 138.5 ± 4.6 | 45.8 ± 5.1 | 111.5 ± 2.5 | 132.5 ± 4.5 |
| A4 | 16.1 ± 4.9 | 169.1 ± 10.9 | 65.2 ± 4.1 | 82.5 ± 18.2 | 48.4 ± 1.7 |
Table 5. Concentration of TMP and TEP (mean ± s, n = 3) in urine samples from workers of a plastic packaging plant and students of a research institute.

| Sample | Gender | Age | Job     | TMP (ng/L) | TEP (ng/L) |
|--------|--------|-----|---------|------------|------------|
| Inner Mongolia | IM1 | female | 33 | officer | 310 ± 40 | 990 ± 120 |
|          | IM2 | female | 28 | worker | 2330 ± 100 | 1390 ± 100 |
|          | IM3 | male | 20 | worker | ND * | 430 ± 40 |
|          | IM4 | male | 22 | worker | ND | 1120 ± 200 |
|          | IM5 | male | 47 | concierge | 130 ± 20 | 1070 ± 110 |
| Beijing | BJ1 | female | 25 | student | 85 ± 10 | 2470 ± 190 |
|          | BJ2 | female | 25 | student | 70 ± 4 | 850 ± 60 |
|          | BJ3 | male | 24 | student | 90 ± 10 | 2100 ± 120 |
|          | BJ4 | male | 27 | student | 110 ± 10 | 110 ± 30 |
|          | BJ5 | male | 28 | student | 90 ± 10 | 1900 ± 110 |
|          | BJ6 | female | 51 | retiree | 85 ± 15 | 280 ± 15 |
|          | BJ7 | female | 28 | account | 70 ± 3 | 200 ± 15 |
|          | BJ8 | male | 27 | researcher | 120 ± 5 | 530 ± 25 |

*ND = not detected.

same laboratory and drink the same source of water. Also, for samples BJ6-BJ8 that come from the same family, the TMP concentrations were very close, but the TEP concentrations were quite different.

Although the total number of analyzed samples was not large enough to get statistic results, it seems that the TMP and TEP concentrations in human urine are person dependent rather than place dependent. Further study is needed to evaluate the general TMP and TEP levels in human urine, and to identify the exposure methods and factors influencing the concentration level in human urine.

4 Conclusions

In summary, analytical methods for quantification of TMP in water samples of municipal WWTP and human urine are developed. The removal efficiency for TMP in the AAO process reached 73%, which was much higher than that in the interval AAO process (38%) of a WWTP, whereas this difference was not observed for TEP. Except for one urine sample that had higher concentration of TMP, the TEP concentrations in urine were remarkably higher than that of TMP, which agreed with the occurrence profile of TMP and TEP in the influent and effluent of a WWTP. Further investigations regarding source identification, temporal trend and regional/global monitoring of TMP and TEP are needed to understand their occurrences, fates and risks.

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