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FIRST ASSESSMENT OF TRICLOSAN, TRICLOCARBAN AND PARABEN MASS LOADS AT A VERY LARGE REGIONAL SCALE: CASE OF PARIS CONURBATION (FRANCE)

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Abstract

The objective of this study was to examine the occurrence of parabens (5 congeners), triclosan (TCS) and triclocarban (TCC) at the scale of the Parisian sewer network and to provide representative knowledge on these compounds in France for a large area. For this purpose and in collaboration with the Parisian public sanitation service (SIAAP) in charge of the collect and treatment of the Parisian wastewater, this study focused on seven main sewer trunks of the Paris conurbation, accounting for 1 900 000 m³ d⁻¹, i.e., about 8 million inhabitants. Concentrations lying in the 2 000 - 20 000 ng l⁻¹ ranges were found in wastewater, confirming the ubiquity of parabens, TCS and TCC in our environment and household products. Parabens (> 97%) and to a lesser extent TCS (68% in median) were mainly associated to the dissolved fraction, as demonstrated by low K_D and K_{OC} values. For the first time, this study also evaluated the pollutant mass loads per population equivalent (PE) of parabens, TCS and TCC at the large and representative scale of the Parisian conurbation. Hence, the median mass loads varied from 176 to 3 040 µg PE⁻¹ d⁻¹ for parabens and from 26 to 762 µg PE⁻¹ d⁻¹ for TCS and TCC. Based on these results and according to the assumptions done, the extrapolation of the mass loads at the national scale pointed out an annual mass loads between 51.8 and 100.7 t y⁻¹ for methyl paraben (MeP) and between 11.2 and 23.5 t y⁻¹ for TCS. Mass loads per equivalent habitant and national mass loads are both extremely relevant and innovative data. Contrary to other countries, such data are nowadays rather difficult to gain in France and no enquiry nor database provide access to information on the use and production of these chemicals. Since cosmetic industries are voluntarily and fully engaged in the substitution of parabens, triclosan and triclocarban in personal care product, this study could constitute a “time reference status” which could be used as a basis for future monitoring.

Keywords

Parabens, triclosan, triclocarban, wastewater, loads, population equivalent

1. Introduction

As a result of human activities and consumption of a large array of chemicals, numerous contaminants including pharmaceuticals and personal care products (PPCPs), flame retardants, endocrine disruptors and priority pollutants as defined by the European water framework Directive are present in wastewater (Berge et al., 2013; Gasperi et al., 2008a; Kolpin et al., 2002; Lee et al., 2005; Paxeus, 1996). Among them, PPCPs are of increasing concerns owing to their ubiquities in environmental compartments, their persistent inputs, and their potential threat to environment and human health (Halling-Sorensen et al., 1998; Lee et al., 2005; Liu and Wong, 2013; Onesios et al., 2009). Among the most concerned PPCPs, preservative agents such as parabens (esters of p-hydroxybenzoic acid), triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy) and triclocarban (TCC, 3,4,4'-trichlorocarbanilide) are commonly employed in food, cosmetic (soaps, shampoos, detergents, toothpastes, etc.) and pharmaceutical products. These compounds are antiseptic, bactericidal and fungicidal agents. The esters of p-hydroxybenzoic acids with alkyl and aryl substituents including methyl- (MeP), ethyl- (EtP), propyl- (PrP), isobutyl- (IsoBuP), butyl- (BuP) and benzyl-paraben (BzP) are mostly used in personal care products. Short chain parabens (methyl-, ethyl- and propyl-) are mainly used in liquid personal care products (liquid soap, etc.), while long chain congeners (butyl- and isobutyl-) are mostly employed in creams (Eriksson et al. 2009). According to an enquiry led by Tavares *et al.* (2009) in Spain on 215 personal care products, 99% of creams and 77% of cleansing lotions and make-up removers contained parabens. In France in 2009, about 7 000 personal care products or formulations containing MeP were marketed against 3 000 – 5 000 products containing the remaining paraben esters (Mintel database, Global Market Research and Market Insight (Mintel, 2013)). Similarly, 860 products containing TCS were listed against only 4 containing TCC. Data on their mass loads are nevertheless not available.

For parabens, the maximum allowable concentrations is 1% (w/w) (Tavares et al., 2009). According to EC Scientific Committee on Consumer Safety (SCCS) updated opinion in 2013 (SCCS, 2013), ethyl- and methyl-parabens are considered safe at a maximum concentration of 0.4% w/w for single and 0.8% w/w for mixtures of esters. Following the recent debate on the safety of the use of parabens as preservatives in cosmetics in 2013, and based on the last SCCS opinion, the European Commission (EC) decided to ban benzyl-, pentyl-, isopropyl-, isobutyl- and phenyl-parabens. The combined use of butyl- and propyl-parabens is to be limited to 0.19% w/w (as esters).

Similarly to parabens, TCS is used in a large array of products including soaps, deodorants, toothpastes and can be also used as additives for plastics or food packaging and textiles whereas TCC has a more restricted use (soaps or body washes). The main application of TCS is in PPCPs (85% of total production) against 10% for textile or food packaging (Bedoux et al., 2012). Recently in 2010, the use of TCS as additive in food plastic packaging was banned by the EC 2010/169/EU. For TCS and TCC, up to 0.3% (w/w) and 5% (w/w) are respectively added to a variety of consumer products in the US (Halden and Paull, 2005).

For these compounds, a particular attention have been paid to their fate within wastewater treatment plants (WWTP) in different areas (Gracia-Lor et al., 2012; Kasprzyk-Hordern et al., 2009; Miege et al., 2009; Sim et al., 2010). However, today, data on their production and consumption are confidential and thus rather difficult to obtain. As an alternative way, some experimental studies estimated the mass loads of triclosan and parabens in wastewater at different scales (houses, neighborhood or catchments) (Eriksson et al., 2009; Lindstrom et al., 2002; Palmquist and Hanæus, 2005; Wind et al., 2004). For parabens, only Eriksson *et al.* (2009) in Denmark evaluated individual paraben mass loads in greywater between 30 and 275 $\mu\text{g inhab}^{-1} \text{d}^{-1}$ at the scale of 120 resident buildings. In Sweden, Palmquist and Hanaeus (2005) evaluated the load of triclosan at 200 μg per population equivalent and per

day ($\mu\text{g PE}^{-1} \text{ d}^{-1}$) in greywater and $100 \mu\text{g PE}^{-1} \text{ d}^{-1}$ in blackwater for a block of 47 small one-family houses consisting of 169 persons. At a larger scale, Lindström *et al.* (2002) reported in Switzerland triclosan mass loads at $412 \mu\text{g inhab}^{-1} \text{ d}^{-1}$ ($190\text{-}750 \mu\text{g inhab}^{-1} \text{ d}^{-1}$) in influents from WWTPs serving populations between 4 500 and 19 000 persons. In spite of these significant experimental inputs, knowledge on the occurrence and mass loads of these chemicals are deeply needed since data are rather limited for both compound families and concerned quite small areas. Due to high short-term variation in flow and pollutant concentrations, working at a too small scale can lead to potential bias to get a representative mass load evaluation. In addition, and due to the emerging concerns and the media coverage of parabens and triclosan as potential endocrine disruptors, a consumption decrease of personal care products containing parabens, TCS and TCC is expected. To date, no data show this trend and no study fixed an initial state.

In this context, this study was therefore launched as part of the OPUR (Observatory of Urban Pollutants in Paris) research program, with the objective of examining the occurrence of parabens, TCS and TCC at the scale of the Parisian sewer network and to provide representative data on these compounds in France at the scale of the Parisian conurbation. For this purpose and in collaboration with the Parisian public sanitation service (SIAAP) in charge of the collect and treatment of the Parisian wastewater, this study focused on the main seven sewer trunks of the Paris conurbation (Figure 1). The total flow was estimated at $1\,900\,000 \text{ m}^3 \text{ d}^{-1}$, corresponding to about 8 million inhabitants, i.e., 13% of the national population. At this scale, the objectives of the present study are i) to assess the occurrence and the concentration ranges of parabens, TCS and TCC in the Parisian wastewater, ii) to examine their partitioning between the dissolved and particulate phases, iii) to evaluate pollutant mass loads per population equivalent (PE) at a large scale area and finally iv) to extrapolate mass loads at a national scale.

By investigating the occurrence and mass loads of these chemicals at the Parisian and then at the national scales, this study delivers new and original data on the actual consumption

of these chemicals in developed countries such as France. This study also provides a reference status which could be used as a basis for future monitoring and for setting sustainable policies.

2. Materials and methods

2.1 Site description and sampling strategy

The main seven Parisian sewer trunks were considered; the 5 deservings the Seine Aval wastewater treatment plant (WWTP): Saint-Denis Achères (SDA), Clichy Achères Argenteuil (CAA), Clichy Achères Bezons (CAB), Sèvres Achères Nanterre (SN), Sèvres Achères Rueil (SR), and those deservings the Seine Amont (SAM) and Marne Aval (MAV) WWTPs. The Parisian sewer network is combined and all campaigns were performed during dry weather periods. The main characteristics of these sewer trunks are given in Table 1. Depending on the sewer trunks, the daily average wastewater flows range from 49 500 to 458 000 m³ d⁻¹. At a daily scale, the total volume is about 1 900 000 ± 79 400 m³ corresponding to 9 485 000 ± 581 900 PE. The Seine Aval WWTP is one of the greatest in Europe collecting about 1 452 000 ± 54 800 m³ d⁻¹, i.e., 6 800 000 ± 389 000 PE. The other two WWTPs respectively collect 49 500 ± 4 600 and 398 000 ± 48 500 m³ d⁻¹. Four sampling campaigns were carried out in April, May, and December (n=2, 1st and 2th December) 2010. Systematically, 24h-flow weight average samples were considered. Samples were collected using automatic and refrigerated samplers from SIAAP, equipped with Teflon® pipe.

2.2 Analytical procedure

Wastewater quality parameters

For each sample, wastewater quality parameters, such as total suspended solids (TSS), chemical and biochemical oxygen demands (COD and BOD₅), ammonium (NH₄⁺), total Kjeldahl nitrogen (TKN), total phosphorous (P_{tot}) and orthophosphates (PO₄³⁻), were analyzed by the internal SIAAP laboratory, a laboratory certified by the French Ministry of the Environment, i.e., COFRAC (French Accreditation Committee). Analyses were then performed

according to the French (AFNOR) or International (ISO) standard methods (Supporting Table 1). Additionally, dissolved (DOC) and particulate organic (POC) carbons were respectively analyzed in duplicate via a Shimadzu TOC-Vws and rapid cube system (Elementar Analysen system GmbH). Wastewater quality parameters were measured in order (i) to determine the representativeness of our sampling campaigns by comparing our results to those of the annual database of SIAAP, (ii) to evaluate population equivalent (with respect to TKN levels) and (iii) to establish whether it exists a relationship between wastewater quality parameters and pollutant concentrations. Those results are provided in Supporting Table 2.

Parabens, triclosan and triclocarban analysis

Height compounds were monitored, including 6 parabens (MeP, EtP, PrP, BzP, BuP and BuP), TCS and TCC. The protocol is here briefly described but more analytical details can be found elsewhere (Geara-Matta, 2012; Geara-Matta et al., 2011) and also in Supporting Table 3.

After homogenization of samples and filtration on glass fiber filters (GF/D 2.7 μm and GF/F 0.7 μm), 100 ml of the dissolved phase were acidified to pH 2-3 with sulfuric acid 98 % (40 μl for 100 ml) and spiked with two surrogate standards (PrP-d4 and TCS-d3, CDN isotopes). Triclosan, triclocarban and parabens were isolated from wastewater by solid phase extraction using Oasis HLB® cartridges (6 ml, 200 mg, Waters). The cartridges were preconditioned with 10 ml of methanol and 10 ml of ultra-pure water. After sample loading at a flow rate of 1 ml min⁻¹, cartridges were washed with 2 ml of ultra-pure water and 200 μL of methanol, dried under vacuum and eluted with 10 ml of methanol. Finally, the eluates were spiked with internal standards (TCC-d4 and MeP-d4, CDN isotopes), dried under a gentle stream of N₂, and finally reconstituted in 1 ml of mobile phase.

For solids, the particles (about 100 mg) were first microwave extracted (Multiwave 3000®, Anton Paar) with 20 ml of dichloromethane/methanol (90:10, v/v) and spiked with similar surrogate standards over a 30 min cycle. Two successive extractions were performed.

After N₂ drying, each aliquot (300 µl of heptane) was purified on Oasis HLB® cartridges (6 ml, 200 mg, Waters).

Parabens, triclosan and triclocarban were analyzed by UPLC-MS/MS in negative mode using an Acquity UPLC system (Waters), coupled to a triple quadrupole TQD (Waters). An Acquity UPLC BEH C18® column (1.7 µm x 2.1 mm x 100 mm) maintained at 40°C, fitted with a guard column (4 mm x 2.0 mm C18, Phenomenex), was used to achieve the chromatographic separation. The injected volume was 10 µL. The mobile phases A and B consisted, respectively in ultra-pure water (5 mM NH₄OAc) and methanol (5 mM NH₄OAc). The quantification was assessed by internal calibration: MeP-d4 for MeP, PrP-d4 for EtP, PrP, BuP, IsoBuP and BzP, TCC-d4 for TCC and TCS-d3 for TCS. Recoveries of surrogate and internal standards, as well as those of the targeted compounds for the dissolved phase are given in Supporting Table 3.

According to this analytical procedure, the limits of quantification (LOQ) ranged between 46 and 56 ng l⁻¹ for parabens, and were respectively equal to 220 and 58 ng l⁻¹ for TCS and TCC for dissolved phase (100 ml). For particles (100 mg), LOQs were evaluated at 0.02 mg kg⁻¹ for parabens, 0.15 and 0.02 mg kg⁻¹ for TCS and TCC.

2.3 Load calculation

Load calculation per equivalent inhabitant

To establish loads of parabens, TCS and TCC per PE and per day, the population equivalent had to be determined. The population equivalent or unit per capita loading was determined by using TKN levels rather than BOD₅ ones (biological oxygen demand, 1 population equivalent equals 60 g BOD₅ d⁻¹). Indeed, TKN in wastewater exclusively results from physiological emissions (Vienneras, 2001) and 80% of TKN is present in dissolved form (Thoburn, 1984). As a consequence, this parameter can be taken into consideration for an improved evaluation of PE. Therefore one PE was defined as the load of 12 g.inhab⁻¹ of

dissolved TKN per day (Gasperi et al., 2008b). For each campaign (j), mass loads (Loads_i^j) were then calculated for each compound (i) as follows:

$$\text{Loads}_i^j (\mu\text{g PE}^{-1} \text{ d}^{-1}) = 12 (\text{g TKN per inhabitant per d}) \times \frac{[X_i] (\mu\text{g m}^{-3})}{[\text{TKN}_j] (\text{g TKN m}^{-3})} \quad \text{Equation 1}$$

Where $[X_i]$ was the concentration of the given compound (i) in $\mu\text{g m}^{-3}$ and $[\text{TKN}_j]$ the concentration of dissolved TKN for the considered campaign (j) in g TKN m^{-3} .

Load calculation at the national scale

The mass loads of parabens, TCS and TCC were also estimated at the national scale. Therefore, two methods were applied. The first method considered that one population equivalent, as defined in this paper, is equal to 1 inhabitant and thus evaluated national loads on the basis of the French population (65 450 000 inhabitants in 2012). For this method, the d10 and d90 percentiles, as well the median mass loads per equivalent habitant were considered (n=28), leading to d10-d90 and median national loads. The second method assessed the total pollutant loads (g d^{-1}) discharged in the Parisian sewer for 8 million inhabitants for the four campaigns and the national loads were then proportionally evaluated. Since only four campaigns were performed, minimal and maximal values along with the average mass loads at the national scale were given.

3. Results and discussion

3.1 Concentrations of parabens, triclosan and triclocarban in wastewater

The total concentrations of parabens, TCS and TCC in wastewater are illustrated in Figure 2. Mean concentrations \pm standards deviations (SD) on the basis of the four campaigns performed are shown for each sewer trunk. Numeric results are available in Supporting Table 4. Out of the eight compounds monitored, benzyl-paraben was never detected in both dissolved and particulate phases ($< 52 \text{ ng l}^{-1}$ for dissolved and $< 0.02 \text{ mg kg}^{-1}$ for particulate phases) whereas the remaining compounds were systematically detected in dissolved phase and

to a lesser extent in particulate phase (60% of occurrence for EtP and PrP, 40% for BuP). This is in accordance with results reported by Eriksson *et al.* (2009) for greywater, indicating that short chain parabens (MeP, PrP and EtP) are detected in 83-97% of samples whereas long chain parabens (BuP and IsoBuP) were found less frequently.

Wastewaters were featured by the predominance of MeP, with total concentrations ranging from 10 300 to 20 100 ng l⁻¹ (first and last percentiles, d10-d90, n=28), followed by EtP (2 670 – 4 670 ng l⁻¹), PrP (2 440 – 3 980 ng l⁻¹) and TCS (2 140 - 5 260 ng l⁻¹). BuP showed an intermediate behavior with concentrations lying in the 450 - 1 280 ng l⁻¹ range while IsoBuP and TCC concentrations were far lower (98 - 230 ng l⁻¹ for IsoBuP and 97 - 140 ng l⁻¹ for TCC). MeP accounted for 66% of total parabens against 15% for PrP and EtP and less than 4% for BuP and IsoBuP. These results were in accordance with both the common paraben patterns reported in literature and paraben uses in personal care products. Indeed, MeP, EtP and PrP are the most commonly used congeners owing to their solubility in comparison to long chain congeners. In France in 2009, about 7 000 personal care products or formulations containing MeP were marketed against 3 000 – 5 000 products containing the remaining paraben esters (Mintel database). Similarly, and as demonstrated by the ratio TCS / TCC evaluated in median at 29 (19-52, d10-d90), TCS is much more used than TCC. The production of each product in ton per year at the national scale is unfortunately not available.

Interestingly, MeP, EtP, PrP and BuP were correlated (Spearman test, $\alpha=0.05$, Supporting Table 5). This correlation could suggest i) these compounds are used in mixture in personal care products, or ii) the personal care products containing these pollutants are used at the same extent at the scale of the Parisian conurbation. No correlation was found between TCS and TCC or between this group and parabens probably reflecting different sources and consumption practices. Today, data are nevertheless too limited to draw a clear conclusion and further investigations are required. MeP and TCS are also significantly correlated to DOC, TKN

and NH_4^+ (Spearman test, $\alpha=0.05$), establishing a link between these pollutants and the human activities.

Table 2 provides a short review of concentrations found in wastewater for these chemicals (Andersen *et al.*, 2007; Chen *et al.*, 2012; Eriksson *et al.*, 2009; Gonzalez-Marino *et al.*, 2009; Halden and Paull, 2004; Jonkers *et al.*, 2009; Kasprzyk-Hordern *et al.*, 2008; Kumar *et al.*, 2008; Kumar *et al.*, 2010; Lozano *et al.*, 2013; Wu *et al.*, 2007; Yu *et al.*, 2011). Globally and despite some methodological differences concerning the phases studied, the MeP and EtP concentrations found in this study lay in the upper range of concentrations reported in the literature while PrP, BuP and IsoBuP ranges lay in the middle and middle low region of the literature interval. In spite of the dilution of Parisian wastewater by parasite waters (street-cleaning water, infiltration and leakage from the drinking water network as reported by Gasperi *et al.*, 2008b), the concentrations found are far higher than those reported in greywater (Eriksson *et al.*, 2009), in Switzerland (Jonkers *et al.*, 2009), in Canada (Lee *et al.*, 2005) or more recently in US (Yu *et al.*, 2011), but are slightly higher than levels quoted by Kasprzyk-Hordern *et al.* (2009) in UK and by Andersen *et al.* (2007) in Denmark. Extremely low concentrations are reported in China (Chen *et al.*, 2012). Except for Yu *et al.* (2011), Kasprzyk-Hordern *et al.* (2009) and Chen *et al.* (2012) who analyzed both dissolved and particulate phases, it should be mentioned that the other studies only consider the dissolved fraction (Table 3).

For TCS, a similar trend is also observed with concentrations lying in the middle-upper range of concentration reported in literature. Hence, TCS concentrations were globally similar to those reported by Halden and Paull (2005), Kumar *et al.* (2010) or Lozano *et al.* (2013) in US but far higher than those reported in Germany, UK or Spain (Table 2). In a review, TCS concentration range in influent from municipal WWTP varied from 220 to 7 000 ng l^{-1} , median value being 1 900 ng l^{-1} (Verlicchi *et al.*, 2012). Kumar *et al.* (2010) is the sole study reporting a similar TCS/TCC ratio than for Parisian wastewater.

Whatever the compound under consideration, this short comparison with the literature data highlighted both geographic disparities and some potential difference of awareness in different countries as regard personal care products. This involves and confirms the need of monitoring program for these compounds at the French national scale.

Whatever the sewer trunk under consideration, concentrations slightly vary from campaign to campaign. The relative standard deviation (RSD), for all campaigns and sites, do not exceed 25%. This weak variability is mainly related to the scale considered. Actually, our approach at a large scale allows a smoothing or buffering of the quality of wastewater.

As regards the spatial variability, the quality of wastewater is quite homogenous among sewer trunks for parabens. Some slight but no significant differences appear for SAN and SAR trunks, indeed both sites presented lower concentrations (-20% in comparison to mean value), and SDA trunk with higher levels (+27%). These differences could be linked to a more or less dilution of wastewater by parasite waters depending on the catchment considered. The dilution of the Parisian wastewater is actually known as demonstrated by Gasperi *et al.* (2008) and can vary depending on the sewer trunk considered. To confirm this hypothesis, the concentrations were normalized to TKN, considered as a tracer of human emission (Figure 2). Since for normalized concentrations, the differences are less marked among the sewer trunks, this confirms that the initial observed differences for concentrations are partially due to the wastewater dilution. The higher normalized concentrations of parabens for SDA trunk could be probably due to higher inputs. For TCS, higher concentrations are observed in MAV and SAM trunks. Such trend is not observed for TCC.

3.2 Partitioning of pollutants between dissolved and particulate phase

Table 3 summarizes the pollutant contents (in mg kg⁻¹), as well as the distribution coefficients (K_D , l kg⁻¹) and the organic carbon-water partitioning coefficients (K_{OC}) for all sewer trunks and field campaigns (n=28). Median values as well as first and last percentiles are

provided. TCC was only detected in particulate phase and its partitioning was hence not evaluated. Few studies reported the partitioning of such chemicals in wastewater, and to our knowledge no study provides K_D and K_{OC} values for these compounds in wastewater. Interestingly and in spite of the octanol-water coefficient range ($1.96 < \log K_{ow} < 3.57$), parabens are mainly associated to the dissolved fraction ($> 97\%$). This low affinity for particles leads to i) low contents (0.20 mg kg^{-1} for MeP $0.01 - 0.04 \text{ mg kg}^{-1}$ for the others parabens in median) and ii) low $\log K_D$ ($0.78 - 2.09 \text{ l kg}^{-1}$) and $\log K_{OC}$ values ($1.19 - 2.42$). TCS revealed a stronger affinity for particles as demonstrated by the higher contents (10.44 mg kg^{-1} , Table 3) and higher $\log K_D$ (3.99 l kg^{-1} in median) and $\log K_{OC}$ (4.35) values. In spite of the matrix difference, the $\log K_D$ for primary ($3.2-3.3 \text{ l kg}^{-1}$) and secondary ($2.7-3.2 \text{ l kg}^{-1}$) sludges estimated in municipal WWTP in Greece (Stasinakis et al., 2013) were close. For TCS, dissolved phase account for $68 \pm 13\%$. This is in accordance with the partitioning quoted by Kumar *et al.* (2010) or results reported in Greek wastewater (Stasinakis et al., 2008). In US, Kumar et al. (2010) also indicated that the dissolved phase account between 32.8 and 86.9% for TCS. The contents of TCS are in good accordance with those reported in Greece ($1.1 - 37 \text{ mg kg}^{-1}$) (Gatidou et al., 2007) or in US ($1.4 - 48 \text{ mg kg}^{-1}$) (Kumar et al., 2010). No study reports contents for parabens.

3.3 Loads per population equivalent

Paraben, triclosan and triclocarban mass loads per PE and per day are reported in Figure 3. Based on all campaigns ($n=28$), median mass loads were respectively estimated about 760 and $26 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$ for TCS and TCC and median mass loads vary between 30 and $3\,040 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$ for parabens, i.e., MeP ($3\,040 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$), EtP ($750 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$), PrP ($710 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$), IsoBuP ($30 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$) and BuP ($180 \text{ } \mu\text{g PE}^{-1} \text{ d}^{-1}$).

For parabens, TCS and TCC, the comparison with French studies is not possible since no data are available. Based on an accounting of products containing parabens with industries,

Masset (2007) estimated the French paraben use reach about 4 000 t y⁻¹, corresponding to a daily consumption about 144 000 µg inhab⁻¹ d⁻¹ for the main parabens (MeP, EtP and PrP, (Masset, 2007)). This assumption is far higher than the experimental results (3 800 - 6 500 µg PE⁻¹ d⁻¹) found in this study, demonstrating the difficulties to gain reliable data on the consumption of parabens and/or on the link between the paraben uses and the quality of wastewater.

To date, only Eriksson *et al.* (2009) provided paraben mass loads for greywater based on experiments on 120-resident building. These mass loads were respectively estimated at 275, 130, 140, 30 and 65 µg inhab⁻¹ d⁻¹ for MeP, EtP, PrP, IsoBuP and BuP; they are far lower than those calculated in our study. Two hypotheses could explain these differences. First, alone greywater (showers and hand wash basins) were considered by Eriksson *et al.* (2009), i.e., 43 l inhab⁻¹ d⁻¹ while raw wastewater were considered in this study. For reference, at the Parisian sewer scale, water consumption was estimated about 160 l.inhab⁻¹ d⁻¹ according to the local water utility *Compagnie des eaux de Paris* (Gasperi *et al.*, 2008b) and showers and hand wash basins account for 20-30% of the daily volume, i.e., 32-48 l.inhab⁻¹ d⁻¹. This suggests that blackwater could be also contaminated by parabens. This contamination can be linked to the human emission via urine (Ye *et al.*, 2006), sanitary cleaning products or other discharges into water closet (emptying a scouring pail, other cleaning products, etc.). The differences could also result from different practices and/or a higher concern of these chemicals leading to a lower consumption of personal care products containing paraben in Denmark in comparison to France. Besides, on 2011, Denmark introduced a national ban on parabens in cosmetic products intended for children under 3 years.

For TCS, some studies reported mass loads in Europe or in US. Wind (2004) in Germany estimated TCS mass loads about 1 370 µg inhab⁻¹ d⁻¹, on the basis of annual national consumption. This load is twice higher than the ones established in this study. The difference

could reflect both i) the difficulties to estimate the real consumption at a national scale and ii) the consumption decrease of products containing triclosan between 2004 and 2010 because of the awareness of the hazards such compound may represent. This evolution could also explain the significant differences between the mass loads in this study and those reported by Halden and Paull (2004) in US, i.e., 3 096 and 2 822 $\mu\text{g inhab}^{-1} \text{ d}^{-1}$ for TCS and TCC. Median mass load for TCS ($762 \mu\text{g PE}^{-1} \text{ d}^{-1}$) is also far higher than those reported in Switzerland or in Sweden, even if these studies were carried out earlier (Lindstrom et al., 2002; Palmquist and Hanaeus, 2005). In Switzerland, Lindström *et al.* (2002) quoted TCS mass loads at $412 \mu\text{g inhab}^{-1} \text{ d}^{-1}$ ($190\text{-}750 \mu\text{g inhab}^{-1} \text{ d}^{-1}$). In Sweden, Palmquist and Hanaeus (2005) evaluated about $200 \mu\text{g PE}^{-1} \text{ d}^{-1}$ in greywater and $100 \mu\text{g PE}^{-1} \text{ d}^{-1}$ in blackwater. As for parabens, this may reflect geographical differences of consumption and practices as regards personal care products.

3.4 Extrapolation at the national scale

Based on the previous results, the national mass loads of parabens, TCS and TCC are provided in Table 4 according to calculation methods previously described. Globally, both methods gave mass loads in the same order of magnitude. For MeP, the annual national mass loads were in the $51.8 - 98.1 \text{ t yr}^{-1}$ (d10-d90, method 1, based on the daily mass load per PE, $n=28$) or $78.2 - 100.6 \text{ t yr}^{-1}$ (min-max, method 2, based on 4 campaigns) ranges. For TCS, median mass loads were respectively estimated at 18.2 and 19.9 t yr^{-1} using methods 1 and 2. To compare, Singer *et al.* (2002) estimated that about 350 t of TCS are annually produced for commercial applications (Singer et al., 2002), while in USA, more than 300 t yr^{-1} of TCS are estimated to be disposed into wastewater (Halden and Paull, 2005). At the national scale, such data are extremely relevant and innovative since this study is one of the first to report national mass loads for these chemicals. Nevertheless, no data on the paraben, TCS and TCC market or production are to date available to compare and to consolidate our results.

4. Conclusions

This study was launched with the objectives of examining the occurrence and concentration ranges of parabens, TCS and TCC in wastewater at the scale of the Parisian sewer network and for providing representative knowledge on these compounds in developed countries such as France and for a large area. In this context, this innovative approach delivers some interesting findings.

For the first time, this study evaluated the pollutant mass loads per population equivalent of parabens, TCS and TCC at the large and representative scale of the Parisian sewer network. Hence, the median mass loads vary from 176 to 3 039 $\mu\text{g PE}^{-1} \text{ d}^{-1}$ for parabens and from 26 to 762 for TCS and TCC (minimum and maximum median mass loads, depending on the compound). Based on these results and according to the assumption done, the extrapolation of the mass loads at the national scale points out an annual mass loads between 51.8 and 100.7 t y^{-1} for MeP and between 11.2 and 23.5 t y^{-1} for TCS (extreme values according both methods). Mass loads per equivalent habitant and national mass loads are both extremely relevant and innovative data. At a national scale, geographic disparities between Paris and others regions in France are expected to be weak. Nevertheless, the question of the representativeness of French consumption to other developed countries raise. Contrary to other countries, such data are nowadays rather difficult to gain in France and no enquiry or database provides access to all of the information on the use and production of these chemicals. Since cosmetic industries are voluntarily and fully engaged in the substitution of parabens in personal care product, this study could constitute a “time reference status” which could be used as a basis for future monitoring. Hence, changes in practice could be studied.

In pursuit of this work, the amount of personal care products could be estimated at the Parisian or French scales according to different chemical composition assumptions or established regulation. Hence, mass loads of other pollutants contained in personal care

products such as musk, fragrance, emulsifying agents, other types of preservatives or additives or nanoparticles could be hence evaluated. Based on the reviews quoting the WWTP efficiencies for these chemicals, mass loads of parabens, TCS and TCC discharged in the receiving water could be also assessed in order to better determine the potential risk of these chemicals on aquatic organisms.

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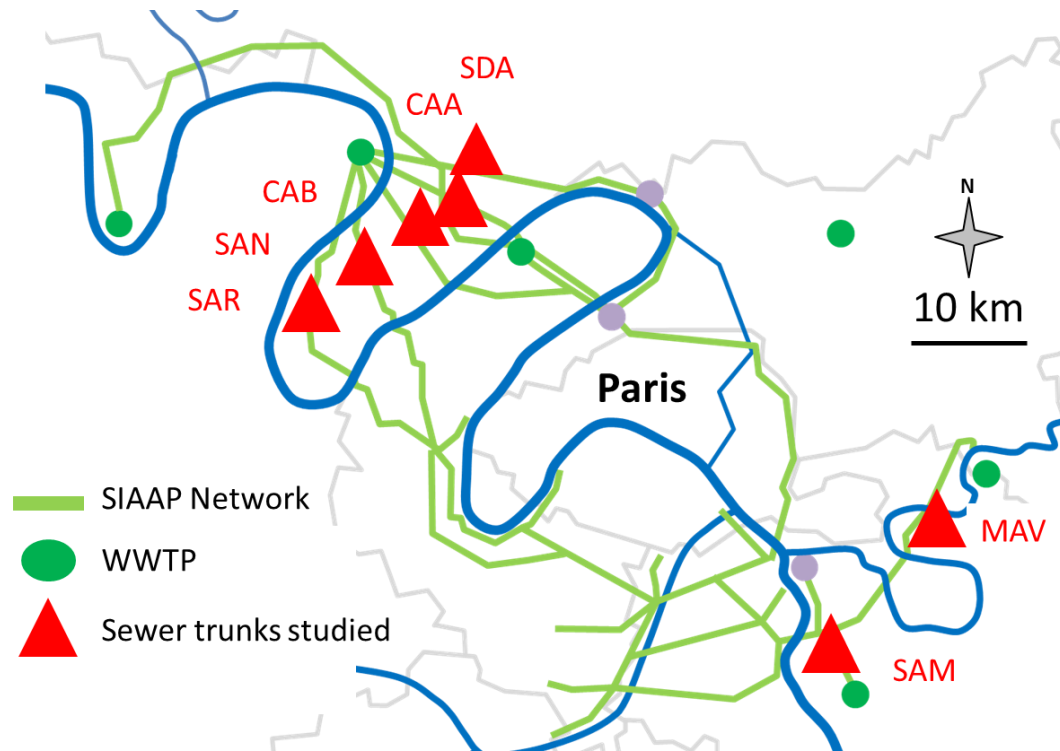
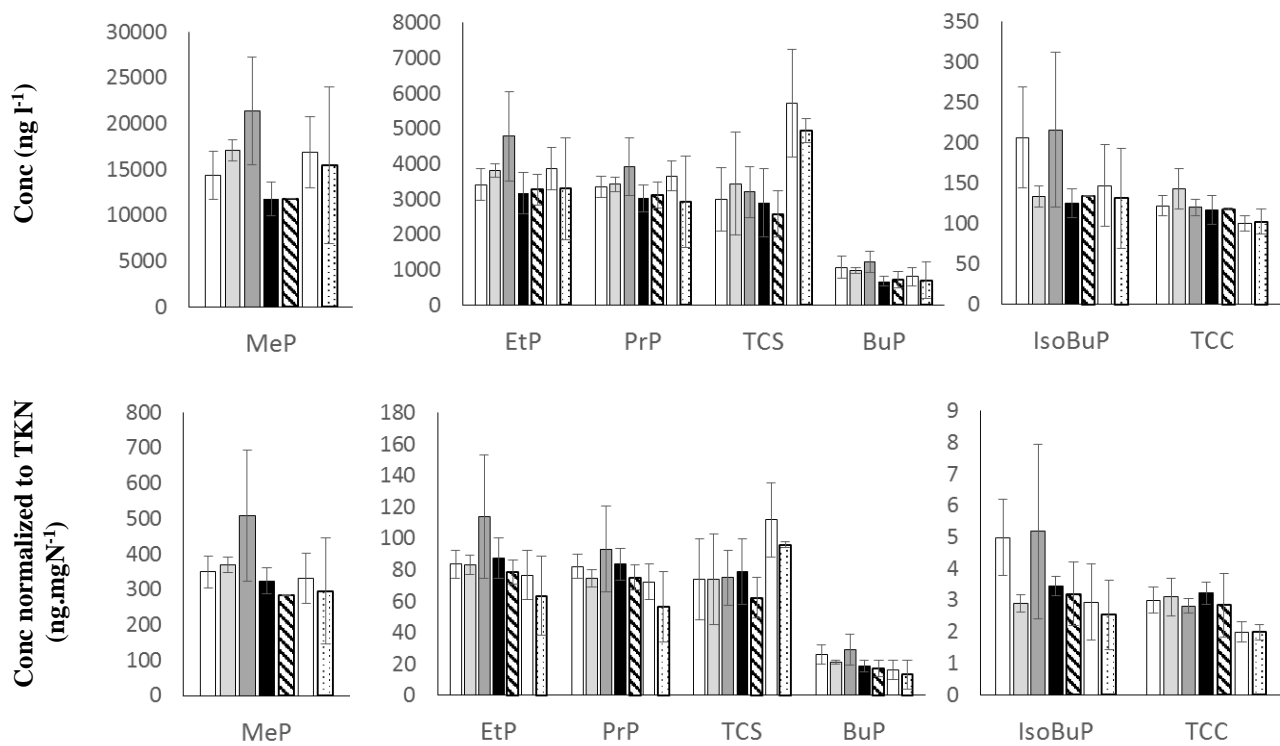
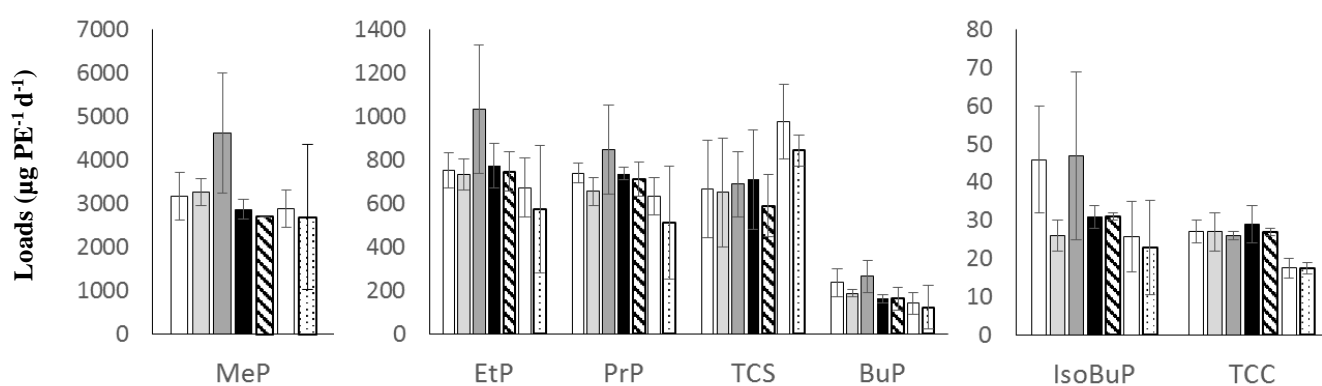


Figure 1: Map of the Parisian sewer network and location of the sewer trunks studied



From left to right: 1) CAB, 2) CAA, 3) SDA, 4) SAN, 5) SAR, 6) MAV and 7) SAM

Figure 2: Total concentrations (mean \pm SD, including dissolved + particulate phases) of parabens, TCC and TCS in wastewater



From left to right: 1) CAB, 2) CAA, 3) SDA, 4) SAN, 5) SAR, 6) MAV and 7) SAM

Figure 3: Loads per population equivalent ($\mu\text{g PE}^{-1} \text{d}^{-1}$, mean \pm SD) of parabens, TCC and TCS in wastewater

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2

Table 1: Sewer trunks studied and connected WWTPs (mean \pm SD)

Trunks	WWTP	Flow (m ³ d ⁻¹)	PE*	TSS (mg.l ⁻¹)	DOC (mgC.l ⁻¹)	TKN (mgN.l ⁻¹)
Saint-Denis Achères (SDA)	Seine Aval	249 000 \pm 110 000	1 173 200 \pm 575 000	219 \pm 68	38 \pm 7	56 \pm 3
Clichy Achères Argenteuil (CAA)	Seine Aval	458 000 \pm 39 300	2 390 000 \pm 172 000	239 \pm 98	58 \pm 10	63 \pm 3
Clichy Achères Bezons (CAB)	Seine Aval	274 000 \pm 48 900	1 234 400 \pm 210 000	189 \pm 85	43 \pm 3	54 \pm 2
Sèvres Achères Nanterre (SAN)	Seine Aval	53 000 \pm 42 000	225 900 \pm 207 000	178 \pm 35	27 \pm 5	49 \pm 7
Sèvres Achères Rueil (SAR)	Seine Aval	418 000 \pm 12 800	1 830 000 \pm 27 450	214 \pm 67	30 \pm 3	53 \pm 1
Marne Aval (MAV)	Marne Aval	49 500 \pm 4 600	290 000 \pm 37 200	392 \pm 34	51 \pm 5	70 \pm 8
Seine Amont (SAM)	Seine Amont	398 000 \pm 48 500	2 350 000 \pm 375 000	368 \pm 43	45 \pm 7	70 \pm 5
Total**		1 900 000 \pm 79 400	9 485 000 \pm 581 900			

3 * PE = population equivalent calculated according to dissolved TKN nitrogen, ** Total = total volume flowing in a day along the 7 selected trucks and the total PE

4

1

2

Table 2: Concentrations of parabens, TCS and TCC reported in the literature (ng l⁻¹)

Reference	Country	Phase*	MeP	EtP	PrP	IsoBuP	BuP	TCS	TCC
This study* (d10-d90) Median	France	D+P	10 300-20 100 15 000	2 670-4 670 3 610	2 440-3 980 3 340	98-230 130	450-1 280 870	2 140-5 260 3 450	97-140 110
Halden and Paull (2005)**	US	D+P						6 100 ± 1600	6 700 ± 100
Lee <i>et al.</i> (2005)	Canada	D	100-1 470	20-270	200-2 430	-	20-260	870-1 830	
Wu <i>et al.</i> (2007)	Germany	T						142-214	
Andersen <i>et al.</i> (2007)	Denmark	D	7 600-17 600	3 250-3 950	7 900-10 700	770-1 050	1300-1900		
Kumar <i>et al.</i> (2008)	US	D						6 178-38 255	157-1 372
Kasprzyk-Hordern <i>et al.</i> (2009)	UK	D+P	661-15646	192-1948	<2-1703	<2-114		33-463	
Jonkers <i>et al.</i> (2009)	Switzerland	D	65-9880	2.2-719	43-1540	-	9.7-864		
Eriksson <i>et al.</i> (2009)	Denmark	D	100-3700	<100-4 100	<100-2 100	100-8 000	200-1700		
Gonzalez-Marino <i>et al.</i> (2009)	Spain	D	1 926-5 138	452-549	1 147-1 302	83-86	150-181	< LOQ-936	< LOQ
Yu <i>et al.</i> (2011)	US	D+P	1 002-1 194					712-2 301	1 217-2 354
Chen <i>et al.</i> (2012)	China	D+P	347-397	42.5-50.3	63.1-75.3		4.6-5.4	104-122	249-285
Stasinakis <i>et al.</i> (2008)	Greece	D+P						170-23 900	
Lozano <i>et al.</i> (2013)	US	D+P						7 580-8 520	920-5 920

3 *Phase studied: D = dissolved, P = particulate, T = Total*4 ** this study = first and last percentiles (d10 and d90), median value, ** Halden and Paull (2005) = mean ± standard deviation*5 *For other references, min and max values are provided.*

1 **Table 3: Contents of particles (mg kg⁻¹), log (K_d) and log (K_{oc}) for parabens, TCS and**
2 **TCC**

		MeP	PrP	EtP	IsoBuP	BuP	TCS	TCC
Log K _{ow}		1.96	3.04	2.47	3.27	3.57	4.76	4.90
Contents	d10-d90	0.14-0.29	0.02-0.06	0.02-0.12	0.01-0.02	0.02-0.06	8.11-12.93	0.12-0.28
	median	0.20	0.02	0.04	0.01	0.03	10.44	0.17
Log K _d	d10-d90	0.88-1.32	0.67-1.30	0.79-1.56	1.81-2.18	1.27-2.03	3.74-4.18	
	median	1.14	0.78	1.14	2.09	1.50	3.99	
Log K _{oc}	d10-d90	1.22-1.69	0.99-1.64	1.13-1.89	2.14-2.52	1.64-2.36	4.10-4.52	
	median	1.50	1.19	1.46	2.42	1.83	4.35	

3 *d10 = first percentile, d90 = last percentile*
4

5

¹ **Table 4: Evaluation of the national mass loads of parabens, TCS and TCC (t y⁻¹)**

	MeP	EtP	PrP	IsoBuP	BuP	TCS	TCC
Method 1*							
d10-d90	51.8-98.1	11.7-22.7	11.7-19.8	0.5-1.2	2.2-6.3	11.2-23.5	0.4-0.7
median	72.4	18.0	17.0	0.7	4.2	18.2	0.6
Method 2**							
Min-max	78.2-100.6	18.7- 23.4	17.2-20.3	0.7-1.0	3.9-6.0	18.8-22.0	0.6-0.8
mean	86.8	20.3	18.5	0.9	5.0	19.9	0.7

² Method 1*: median and d10-d90 values are provided since results are compiled (n=28)

³ Method 2**: the total mass loads were evaluated for the four campaigns carried out and then extrapolated to

⁴ the entire population: mean, min and max values are provided.