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Estimation of chemical emissions from down-the-drain consumer products using consumer survey data at a country and wastewater treatment plant level

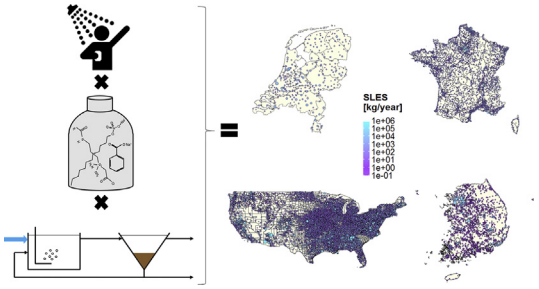
Mélanie Douziech [a, *], Rosalie van Zelm [a], Rik Oldenkamp [a], Antonio Franco [b], A. Jan Hendriks [a], Henry King [b], Mark A.J. Huijbregts [a]

[a] Department of Environmental Science, Institute for Water and Wetland Research, Radboud University Nijmegen, P.O. Box 9010, 6500 GL, Nijmegen, The Netherlands
[b] Safety and Environmental Assurance Centre, Unilever, Colworth Science Park, Bedfordshire, MK44 1LQ, United Kingdom

HIGHLIGHTS

- Chemical emission loads from the use of personal care products were quantified.
- Consumer use surveys from four countries were used.
- Point source emissions differed up to two orders of magnitude between countries.
- Emission uncertainty (95% confidence interval) was up to 5 times the mean value.
- This approach does not rely on confidential or commercial tonnage data.

GRAPHICAL ABSTRACT



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ABSTRACT

Deriving reliable estimates of chemical emissions to the environment is a key challenge for impact and risk assessment methods and typically the associated uncertainty is not characterised. We have developed an approach to spatially quantify annual chemical emission loads to the aquatic environment together with their associated uncertainty using consumer survey data and publicly accessible and non-confidential data sources. The approach is applicable for chemicals widely used across a product sector. Product usage data from consumer survey studies in France, the Netherlands, South Korea and the USA were combined with information on typical product formulations, wastewater removal rates, and the spatial distribution of populations and wastewater treatment plants (WWTPs) in the four countries. Results are presented for three chemicals common to three types of personal care products (shampoo, conditioner, and bodywash) at WWTP and national levels. Uncertainty in WWTP-specific emission estimates was characterised with a 95% confidence interval and ranged up to a factor of 4.8 around the mean, mainly due to uncertainty associated with removal efficiency. Estimates of whole country product usage were comparable to total market estimates derived from sectorial market sales data with differences ranging from a factor 0.8 (for the Netherlands) to 5 (for the USA). The proposed approach is

* Corresponding author.
E-mail address: m.douziech@science.ru.nl (M. Douziech).

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suitable where measured data on chemical emissions is missing and is applicable for use in risk assessments and chemical footprinting methods when applied to specific product categories.
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1. Introduction

Many of our everyday actions, like household cleaning or taking a shower, involve the use of consumer products (CPs). After use, such products are often released with household wastewater and their constituent chemicals or ingredients may end up in the environment after passing through the sewerage and wastewater treatment system. To assess potential environmental impacts and safe use of the chemicals, techniques such as risk assessment and chemical footprinting methods are employed (e.g. Bjorn et al. (2014); Salvito et al. (2001)). These methods require a reliable quantification of the amount of chemicals used and subsequently released into the various environmental compartments, such as freshwater. Concentrations measured analytically would best reflect the chemical's inflow into a specific catchment (Earnshaw et al., 2014; Kasprzyk-Hordern et al., 2008; Lindim and Cousins, 2015; Whelan et al., 2012). Unfortunately, monitoring data for many chemicals is poor or not available with the exception of certain classes or problematic chemicals. Furthermore, where monitoring data exists, it is often temporally and spatially limited (Petrie et al., 2015). New modelling approaches are therefore required to provide more reliable and realistic estimates of chemical emissions associated with consumer products.

When deriving chemical emission estimates, a measure of their uncertainty is desirable (Ascough et al., 2008; van der Sluijs, 2002) even more since this has been identified as a deficiency in the application of risk assessment and chemical footprinting methods (Bjorn et al., 2014; Chevre et al., 2013; Harbers et al., 2006). For example, in their work on the risk assessment of chemicals from wastewater, Escher et al. (2011) only used a worst-case scenario approach to quantify emissions of pharmaceuticals in wastewater from hospital usage data. In contrast, Oldenkamp et al. (2016) determined the uncertainty in spatially-explicit pharmaceutical emission estimates resulting from substance characteristics and consumption volumes. However, this work did not consider the variability induced by different consumption habits and assumed one absolute per-capita consumption value per pharmaceutical considered. In their top-down approaches where sales data of personal care products at a global level are used to derive smaller scale chemical emissions, Hodges et al. (2014); Price et al. (2010); Whelan et al. (2012) acknowledged the uncertainty of their estimates, but without quantifying it.

Chemical emissions from CPs can be estimated from product use amounts and product formulations. Two approaches exist to derive product use amounts: total market or sales based (top-down) and individual consumption-based (bottom-up). Total market consumption data may be collected directly from manufacturers (Salvito et al., 2001) or derived by commercial market research organisation (e.g. Euromonitor) (Hodges et al., 2014; Keller et al., 2007; Price et al., 2010). However, access to such data is often restricted to commercial companies and the confidentiality of the data and methods used to generate them limits their transparency and reproducibility by others. Although the average consumption approach is described in the OECD Emission Scenario Documents (ECHA, 2000), worst-case default values are generally used to risk assess chemicals. An exception is for pharmaceuticals where consumer usage data were readily used to estimate emissions into wastewater (Escher et al. (2011), Chevre et al. (2013), and Oldenkamp et al. (2016)). However, to our knowledge, bottom-up approaches have not yet been used for larger scale estimates of more mass market products, such as personal care products, which are typically associated with a wide range of habits and common set of widely used chemicals.

The goal of this paper was to develop a consumer use-based approach to estimate the annual chemical emission loads from the use of personal care products at the country and the WWTP level. We explored how a bottom-up approach starting with easily accessible consumption data derived from consumer surveys can be used to estimate product related chemical emission loads. To illustrate the potential of this approach, three personal care product types were used, namely shampoo, conditioner, and bodywash. These products were chosen because of available consumer survey reports and because they are expected to be almost completely washed off down the drain after use. The study focussed on common chemicals used across the product categories namely three surfactants: sodium lauryl ether sulfate (SLES), cocamidopropyl betaine (CAPB), and cetearyl alcohol (CA) and two preservatives: sodium benzoate (SB) and dimethyloldimethyl hydantoin (DMDMH). As the consumer surveys also report consumer characteristics, variability in consumer behaviour was studied by considering different user category groups, based on age and gender. In addition, the uncertainty in consumer behaviour due to the limited size of the assessed consumer groups was quantified. Combined with uncertainties inherent to chemical inclusion levels in products and to removal efficiencies from wastewater, uncertainty estimates of chemical emissions from WWTPs were quantified.

2. Materials and methods

2.1. Framework

Chemical emissions from the use of CPs were estimated for each country as well as for every single WWTP using Equation (1). Population data was hereby taken from census data.

$$M_{X,i} = 365 \cdot \sum_{P=1}^{m} F_{mass,X,P} \cdot F_{X,P} \cdot (1 - E_X) \left(\sum_{c=1}^{n} A_{P,c} \cdot F_{PU,P,c} \cdot N_{c,i} \right) \quad (1)$$

$M_{X,i}$ Emission from WWTP i of chemical X [g/year]
m Number of product classes considered: shampoo, bodywash, and conditioner
n Number of categories c of persons considered, men and women when possible differentiated by age
P Product class
C Consumer category
$A_{P,c}$ Amount of product P used per person of category c per day [g/person/day]

$F_{PU,P,c}$ Prevalence of use, fraction of persons of category c using product P [dimensionless]
$N_{c,i}$ Number of persons belonging to category c connected to the WWTP i [persons]
$F_{mass,X,P}$ Mass fraction of chemical X in product P [dimensionless]
$F_{X,P}$ Fraction of products P where chemical X is present [dimensionless]
E_X Removal efficiency of the chemical X by wastewater treatment plants [dimensionless]

The different terms of Equation (1) are described in Section 2.2 ($A_{P,c}$ and $F_{PU,P,c}$), Section 2.3 ($F_{mass,X,P}$ and $F_{X,P}$), and Section 2.4 ($N_{c,i}$ and E_X). The parameter uncertainty in $A_{P,c}$, $F_{mass,X,P}$ and E_X is propagated into $M_{X,i}$ using Monte Carlo simulations (Section 2.5).

2.2. Use of consumer products

2.2.1. Consumer data collection and treatment

The amount of CP used per person was derived from consumer habits studies reported in scientific literature. To retrieve this information, a literature search was performed using Web of Science, combining the keywords “consumer”, “population”, “use”, “habit”, “amount”, “personal care product”, and “exposure”. The search was limited to articles in English. Articles were selected if they provided information on either the amount of product used per day and the frequency of use, and/or the amount used per application. Studies aggregating the results over the entire EU or considering only one specific consumer group (e.g. pregnant women) were not selected. As a result, the analysis focused on four countries: the USA (Loretz et al., 2006, 2008), the Netherlands (Biesterbos et al., 2013), France (Ficheux et al. 2015, 2016), and South Korea (Park et al., 2015). Table 1 summarizes the consumer categories considered in each study. A more extensive description of the single studies can be found in the supporting information (SI, section S1).

Each study reported the amount of product P used per person per day ($A_{P,c}$) and the prevalence of use of one product across a consumer category ($F_{PU,P,c}$) differently. Some differentiated the values according to both age and gender, while others only did so for one of the two categories. This required a differentiated approach further explained in the supporting information (SI, S2).

2.2.2. Total market estimates

Our final chemical emission load estimates cannot be validated by measurements, since they represent the emissions resulting from the use of only three CPs. A sense-check of our approach is however possible by comparing the estimated country-level product consumption from consumer survey data with total market estimates. Product use data from 2011 were obtained from the market research company Euromonitor. Euromonitor analysts use a combination of various sources of information (e.g. desk research, trade surveys, store checks and global and local company analysis) to derive sale volumes (Euromonitor, 2015). Data for specific product types were grouped as shampoo (standard shampoo, salon hair care and men's hair care), bodywash (men's bath and shower and body wash shower gel), and conditioner (single type). This method is referred to as “Euromonitor estimate”.

2.3. Chemical ingredient content estimation

The inclusion level, meaning the amount of a chemical X contained in a given product P, $F_{mass,X,P}$, as well as the fraction of products where chemical X is present, $F_{X,P}$, are reported in Table 2, per product included, for the three surfactants and two preservatives considered. The $F_{X,P}$ values were taken from Escamilla et al. (2012) and assumed to be certain, because of the large number of products investigated (20,362 liquid soaps, 13,188 shampoos, 5327 hair conditioners). The geometric means of $F_{mass,X,P}$ were computed from both publicly available data, like patents and standard product formulations (Escamilla et al., 2012), and product formulations from Unilever. Since the three chosen products have similar inclusion levels for preservatives, the same $F_{mass,X,P}$ was used for both preservatives across all products. Geometric standard deviations are reported in Table 2 as well. More details on the sources used to derive $F_{mass,X,P}$ are provided in the SI, S3.

2.4. Wastewater treatment

2.4.1. Location

We expressed the reported capacity of each WWTP as the number of persons served. 100% of the emissions from the use of CPs were therefore assumed to be directed to WWTPs. The possibilities that the considered chemicals would reach on-site treatment, such as septic tanks, or that they would be released directly to the environment were not further investigated. Potential degradation of the chemicals in the sewage system was also not considered. The treated wastewater was then assumed to be emitted to surface water. Information on the location and size of WWTPs was collected for each country to estimate point source emissions.

2.4.1.1. United States of America. The latest Clean Watershed Needs Survey (CWNS) of 2012 reports the wastewater collection and treatment facilities found in the USA (US EPA, 2016). The coordinates, type of treatment, and served population of the recorded WWTPs are provided.

2.4.1.2. France and The Netherlands. The Urban Waste Water Treatment Directive (UWWTD) asks European Countries to report on the status of their wastewater treatment (European Commission, 2016). The database resulting from this regulation is available online (European Environmental Agency, 2016). It includes, among others, information on the location of every WWTP, the type of WWTP, and the incoming load in population equivalent (p.e.). This value was assumed to represent the number of persons connected to the WWTPs.

2.4.1.3. South Korea. Information on the location (Korean address) and capacity of the wastewater treatment plants were provided by

Table 1
Summary of the information provided in each of the selected studies. Pdf stands for probability distribution function. n.p. stands for not provided.

Country	Consumer categories
France (Ficheux et al., 2015)	2713 adult women, 251 adult pregnant women, 535 girls, 2693 adult men, 544 boys, 199 baby girls, 196 baby boys
France (Ficheux et al., 2016)	564 women, 209 men, 70 children or babies
South Korea (Park et al., 2015)	Households from 15 metropolitan areas and provinces including rural areas, Total of 3333 persons
The Netherlands (Biesterbos et al., 2013)	302 Adult women, 210 adult men
The USA (Loretz et al., 2006; Loretz et al., 2008)	Adult women: 340 for shampoo and bodywash, 297 for hair conditioner.

Table 2
Prevalence in product ($F_{X,P}$), geometric mean of the inclusion level (Geom. M $F_{mass,X,P}$), and geometric standard deviation of the inclusion level (Geom. SD $F_{mass,X,P}$) of the chosen chemicals sodium lauryl ether sulfate (SLES), cocamidopropyl betaine (CAPB), cetearyl alcohol (CA), sodium benzoate (SB) and dimethyloldimethyl hydantoin (DMDMH) for the three products shampoo, bodywash, and conditioner prior to 2016.

	Shampoo			Bodywash			Conditioner		
	$F_{X,P}$	Geom. M $F_{mass,X,P}$	Geom. SD $F_{mass,X,P}$	$F_{X,P}$	Geom. M $F_{mass,X,P}$	Geom. SD $F_{mass,X,P}$	$F_{X,P}$	Geom. M $F_{mass,X,P}$	Geom. SD $F_{mass,X,P}$
	[%]	[%]	[−]	[%]	[%]	[−]	[%]	[%]	[−]
Surfactants									
SLES	15.9	9.9	1.4	18.4	7.7	1.7	n.c.		
CAPB	13.0	1.9	1.6	18.7	2.4	2.2	n.c.		
CetearylAlcohol	n.c.			n.c.			19.7	3.2	1.6
Preservatives									
SodiumBenzoate	15.1	$3.1\cdot10^{-1}$	3.3	17.8	$3.1\cdot10^{-1}$	3.3	4.5	$3.1\cdot10^{-1}$	3.3
DMDMH	7.9	$1.3\cdot10^{-1}$	1.8	3.9	$1.3\cdot10^{-1}$	1.8	3.3	$1.3\cdot10^{-1}$	1.8

n.c. stands for not contained in formulations analysed.

the Ministry of Environment in South Korea (Park, 2016). The capacity in kg Biological Oxygen Demand (BOD)/d was used to derive the corresponding population equivalent using a mean value of 60gBOD/p/d (Gujer, 2006). For most WWTPs, geocoding queries allowed to derive their coordinates. For the larger plants not identified with this procedure, a visual check on Google Maps was necessary to determine their coordinates. Still, 222 plants could not be identified clearly. As they served only 1% of the reported population, we decided not to take them into account.

2.4.2. Removal efficiency E_X

WWTP removal efficiencies for the chosen compounds (E_X) were derived using the wastewater treatment model SimpleTreat 4.0 for activated sludge WWTPs (Struijs et al., 2016). Only removal efficiencies for WWTPs from both primary and secondary treatment were considered. This was justified as neither France nor the Netherlands reported WWTPs with primary treatment alone. In addition, less than 1% of the centralised US WWTPs considered, as well as of the Korean sewage treatment infrastructure, implemented primary treatment only (KOSIS, 2014; US EPA, 2016)

SimpleTreat 4.0 requires chemical-specific physicochemical and biodegradation properties as input (SI, S4), as well as WWTP specific parameters. For the latter, the available specified mean values of Franco et al. (2013) were preferred over the default values of SimpleTreat as they represent more up-to-date design characteristics for WWTPs in Europe. Differences in the size of the WWTPs was accounted for only by adapting the inflowing chemical amount.

All chemicals analysed were readily biodegradable, meaning that a rapid and complete degradation can be expected in WWTPs (DOFO Chemicals, 2005). They were assigned a lognormal distribution with median biodegradation rate equal to 3 hr^{-1} and geometric standard deviation 1.42 (Jager et al., 1997).

2.5. Uncertainty analysis

2.5.1. Monte Carlo

A Monte Carlo analysis with 10,000 iterations was performed on the parameters $A_{P,C}$, $F_{mass,X,P}$, and E_X to quantify the total uncertainty in the emissions. Each parameter was assumed to be independent from another. For the product usage and the chemical loads in WWTP effluents, the results of the 10,000 Monte Carlo simulations were summarised using the geometric mean and geometric standard deviation. Further, the contribution of each parameter to the overall uncertainty in the chemical emissions was quantified using Spearman's rank correlation coefficients, a nonparametric rank statistic which shows the strength of an association between two variables. Sections 2.5.2 and 2.5.3 describe how the uncertainty distributions were derived for $A_{P,C}$, $F_{mass,X,P}$, and E_X.

2.5.2. Uncertainty distribution of the mean amount of product used and mean chemical inclusion level

Differences in use between men and women were reported for South Korea, France, and the Netherlands. In addition, differences in use habits between age groups were considered in France and the Netherlands. The study from the USA only reported differences in use among female age groups. This variability was communicated as standard deviations, ranges, percentiles, or probability distribution functions. However, when extrapolating the amounts used to a larger spatial scale, e.g. at the level of individual countries or at the WWTP level, consumer variability is expected to average out. What requires attention then, is the uncertainty of the reported mean values. The daily use of CPs in the Netherlands, the only study for which the raw data were available (Biesterbos et al., 2013), was found to be skewed towards higher uses. Therefore, the log-transformed data were assumed to be normally distributed. The same distribution type was used to describe the uncertainty in the other consumer studies.

The log-transformed chemical inclusion levels reported were also assumed to be normally distributed. This allowed to describe the distribution of the mean $A_{P,C}$ and $F_{mass,X,P}$ with a Student's-*t*-distribution (Van Zelm et al., 2007). Detailed explanation on the procedure applied can be found in the SI, S5.

Overall, 10,000 mean $A_{P,C}$ and $F_{mass,X,P}$ were sampled from the corresponding Student's-*t*-distribution. These values were back-transformed to the normal scale (geometric means) and fed into Equation (1).

2.5.3. Uncertainty distributions for the removal efficiency

The Crystal Ball software (Oracle Corporation, 2016) was used to derive a set of 10,000 E_X by assigning uncertainty distribution to the operational and chemical-specific input parameters of the SimpleTreat 4.0 model. Operational parameter distributions were characterised according to Franco et al. (2013). Characterisation of chemical-specific parameter distributions was based on the available data (SI, S4). When only one value for a parameter was available, the uncertainty characterisation was based on the recommendations of Jager et al. (1997). When no literature data was available, the estimation accuracy of the methods from EPIweb and of the ones implemented in SimpleTreat (Sablijc et al., 1995) were used. Details on the uncertainties assigned to each physicochemical property are provided in the SI, S4.

The presented results were derived using the program R version 3.3.2 (R Core Team, 2016) and additional packages: *ggplot2*, and

tmap to derive the different figures and maps; *ggmap*, *rgdal*, *rgeos* and *maptools* to conduct spatial operations; *dplyr* and *tidyr* to handle data frames.

3. Results

3.1. Chemical emission estimates

Fig. 1 illustrates the spatial distribution of the geometric mean effluent emissions of DMDMH and Fig. 2 of SLES resulting from the use of shampoo, bodywash, and conditioner in the Netherlands, France, the USA and South Korea. The maps for the three other ingredients are in the SI, S6.

Figs. 1 and 2 reveal the location of large chemical point sources, representing WWTP with large treatment capacity. Both figures further depict clear differences in the ranges of chemical emissions across countries: In the USA, the largest emissions of SLES from WWTPs can be as much as two orders of magnitude larger than in the Netherlands. The same holds for DMDMH. The uncertainty in the chemical emissions is nearly constant across all locations in all four countries and for all chemicals (95% confidence interval spreading around 3.6 times around the mean), except for the chemical CA, which has a larger uncertainty (95% confidence interval spreading around 4.9 times around the mean).

The representation of chemical emission loads from WWTPs is one way of applying our methodology to generate spatial estimates of chemical emission loads. In the SI, S6 we also present an alternative with chemical emission loads aggregated at the county level for the USA, the NUTS 2 level for France and the Netherlands, and the municipality level for South Korea.

3.2. Product use and chemical emission estimates

The use of bodywash, conditioner, and shampoo vary between countries and products (Fig. 3). Numerical results can be found in the SI, S7.

Conditioner is the product used the least in all countries. In France, the Netherlands, and the USA, bodywash is the product used the most over all three categories considered. For South Korea, in contrast, it is shampoo.

Fig. 3 further highlights the differences between consumer survey and total market estimates obtained from Euromonitor. In most cases, consumer survey estimates are in fair agreement with total market estimates. The best agreement is seen in the

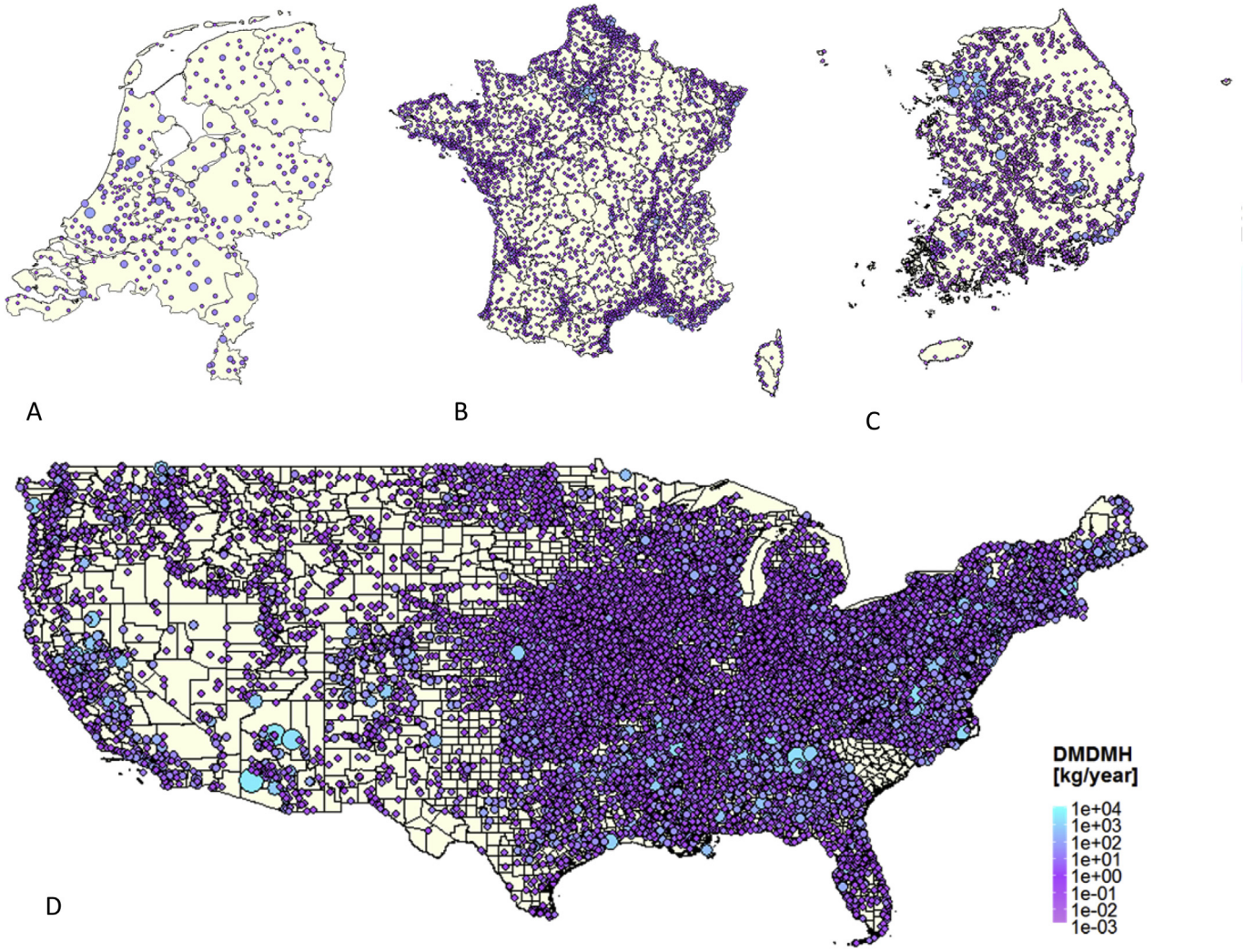


Fig. 1. Geometric mean effluent emission estimates of dimethyloldimethyl hydantoin (DMDMH) in the Netherlands (A), France (B), South Korea (C), and the USA (D) resulting from the use of conditioner, bodywash, and shampoo. The size and the color of the dots represent the geometric mean of the emission loads at each WWTP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

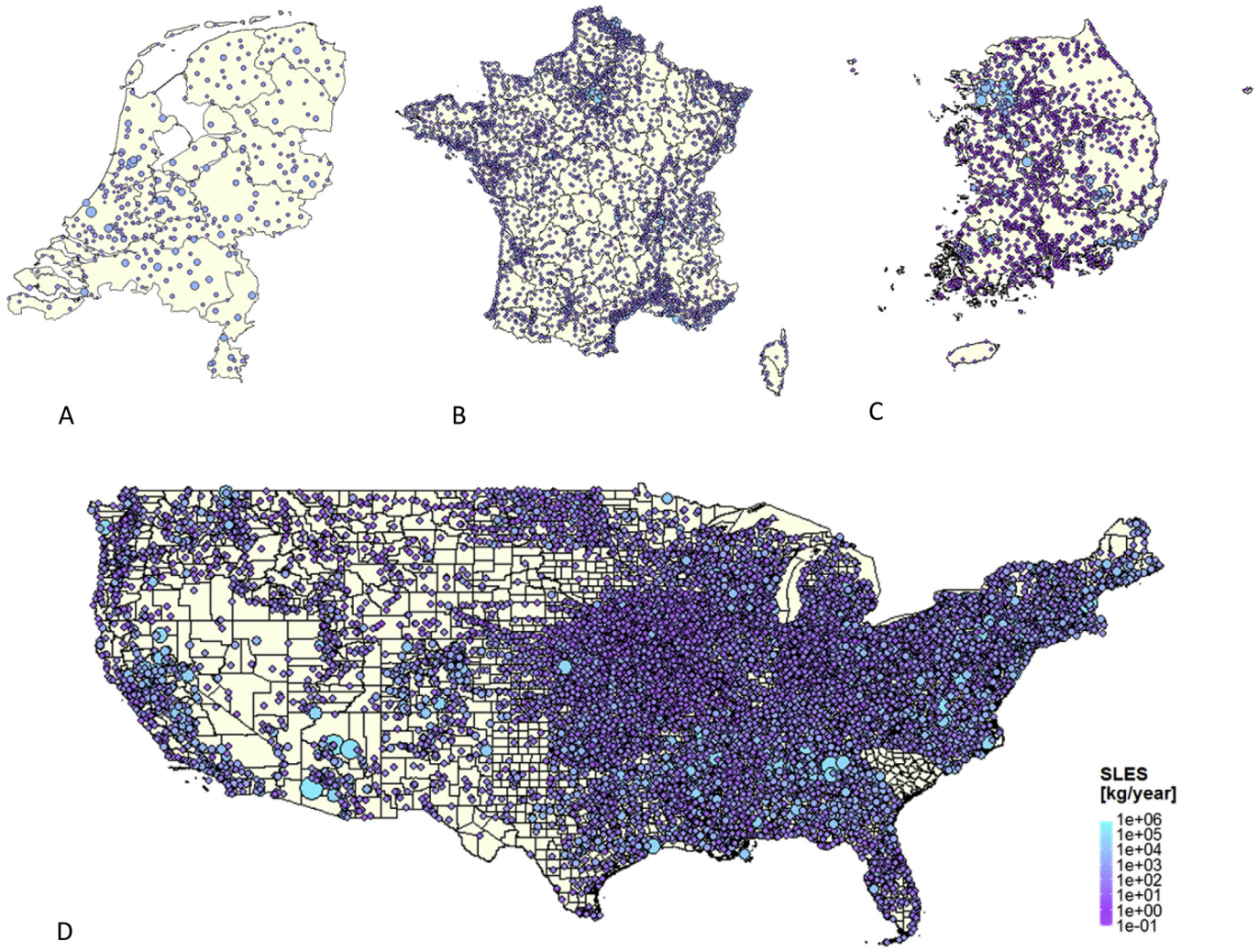


Fig. 2. Geometric mean effluent emission estimates of sodium lauryl ether sulfate (SLES) in the Netherlands (A), France (B), South Korea (C), and the USA (D) resulting from the use of conditioner, bodywash, and shampoo. The size and the color of the dots represent the geometric mean of the emission loads at each WWTP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

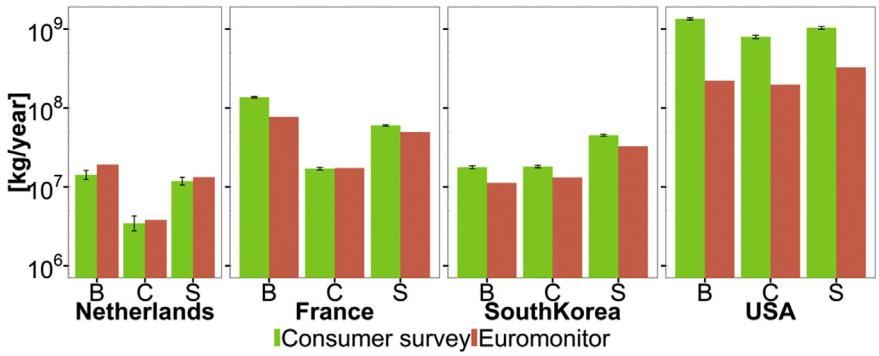


Fig. 3. Total product use estimates [kg/year] for the four countries considered (green bar) compared to estimates from the total market approaches Euromonitor (red bar). B: Bodywash, C: Conditioner, S: Shampoo. The error bars represent the 95% confidence interval of the Monte Carlo results. The results are presented on a logarithmic scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Netherlands, where our approach leads to slightly lower values than the Euromonitor estimates (on average 20% lower). On the contrary, the use volumes derived with our approach led to higher estimates in the USA, on average nearly 4-folds higher compared to Euromonitor. For France and South Korea, our values were roughly 1.5 times larger than Euromonitor. The differences in estimates are comparable across all product types within a country. Finally, Fig. 3 shows that the estimated uncertainty in the use of products does not explain differences between the two estimation techniques. The 95% confidence interval (95P-CI) is largest around the

estimated use volumes of conditioner in the Netherlands and spreads up to 1.24 times around the mean value. This spread only reaches 1.04 of the mean use of conditioner in France.

Chemical emission loads from WWTP effluents per country are shown in Fig. 4. The numerical results can be found in the SI, S8. These estimated loads are only representative for the use of shampoo, conditioner, and bodywash in the four countries chosen. A per capita use of 75.5 g/year/person for SLES is reported for Denmark (Product Registries of Sweden Norway Denmark and Finland. Substances in Preparations in Nordic Countries (Spin), 2013), while we derived values of 2.8 for the Netherlands, 5.2 for France, 2.1 for South Korea and 10.0 for the USA.

For all countries, the emissions of DMDMH are around two orders of magnitude lower than the emissions of SLES. Further, we can observe that SB is released in higher amounts than CA in the Netherlands and France, while it is the opposite in South Korea and the USA. Fig. 4 also displays the uncertainty of the total chemical emission estimates. The largest uncertainty, displayed as the 95% confidence interval of the Monte Carlo results, appears for CA. Exemplarily, for the Netherlands the mean emission of SLES was 24,068 tonnes/year (95P-CI: 6840 - 84,690 tonnes/year). The mean emission of CA was 479 tonnes/year (95P-CI: 97 - 2363 tonnes/year). This was the case for the other countries as well, where the spreads of the 95% confidence intervals were comparable.

3.3. Uncertainty importance

The uncertain parameters in the estimation of chemical emissions are the amount of product reaching WWTPs ($A_{P,C}$), the inclusion level of a chemical in a product ($F_{mass,X,P}$), and the fraction of chemical going through WWTPs (E_X). From those three parameters, $A_{P,C}$ has the smallest relative Spearman importance (below 1%, except for the use of conditioner in the Netherlands where it is 3%), and therefore the smallest influence on the uncertainty of the chemical emission estimates. $F_{mass,X,P}$ has a higher relative Spearman importance ranging from approximately 1% (for SLES, CAPB, DMDMH and CA) to up to 7% (for SB). Finally, E_X explains most of the uncertainty in the chemical emission estimates (relative Spearman importance ranging from 68% for SB in France and around 78% for the other countries to up to around 98% for CA). Detailed results can be found in the SI, S9.

Fig. 5 shows which SimpleTreat parameters influence the estimated removal efficiencies of SLES and CA the most. Negative values represent parameters that are negatively correlated to the removal efficiency. The sludge loading rate and the biodegradation rate are the two parameters with the highest correlation to the removal efficiency for SLES. This is also the case for SB, CAPB, and DMDMH (SI, S10). The influence of the design properties apparently varies according to the environmental behaviour of the chemical. Hence for the highly hydrophobic CA, the concentration of suspended solids in the second clarifier contributes most to the uncertainty of the removal efficiency, while it is the sludge loading rate for the other chemicals. Experimental values for chemical properties were assumed to be more reliable than estimated values, leading to a smaller contribution to the overall uncertainty. Because no experimental value was found for the organic carbon-water partitioning coefficient (K_{OC}) of CA the uncertainty importance analysis showed an increased contribution of K_{OC} and K_{OW} for this chemical. This also explains the larger overall uncertainty of CA emissions compared to the other chemicals.

4. Discussion

With the methodology developed in our study, we estimated the total annual use of shampoo, conditioner, and bodywash in France, the Netherlands, South Korea, and the USA including their associated uncertainty. Furthermore, spatially enabled annual emission loads from WWTPs resulting from the use of these CPs were estimated for three surfactants and two preservatives. Our methodology represents a transparent and reproducible way to estimate chemical emission loads resulting from the use of personal care and similar products with common sets of chemicals. The estimated product use volumes highlighted differences in product usage across countries, which were also reflected in the estimated chemical emission loads. They were further compared to use volumes derived from a top-down approach with restricted access. Validation of our product -related chemical load estimates was not possible because few monitoring data exist for the specific chemicals considered and, where monitoring data exists, it is indicative of the total commercial use of the 5 chemicals. Nevertheless, this method should be applicable for other product types and chemicals as discussed in Section 4.3 and importantly provides a measure of the associated uncertainty. Below, we discuss the data requirements and methodological choices of our study in more

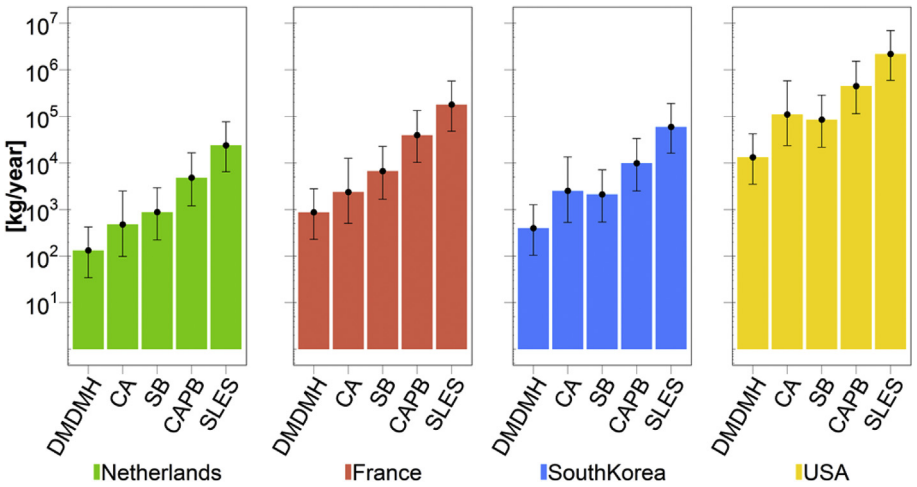


Fig. 4. Chemical emissions in the effluents of WWTPs resulting from the use of shampoo, bodywash and conditioner in the four analysed countries. SLES: sodium lauryl ether sulfate, CAPB: cocamidopropyl betaine, CA: cetearyl alcohol, SB: sodium benzoate, DMDMH: dimethyloldimethyl hydantoin. The error bars represent the 95% confidence Interval of the Monte Carlo results.

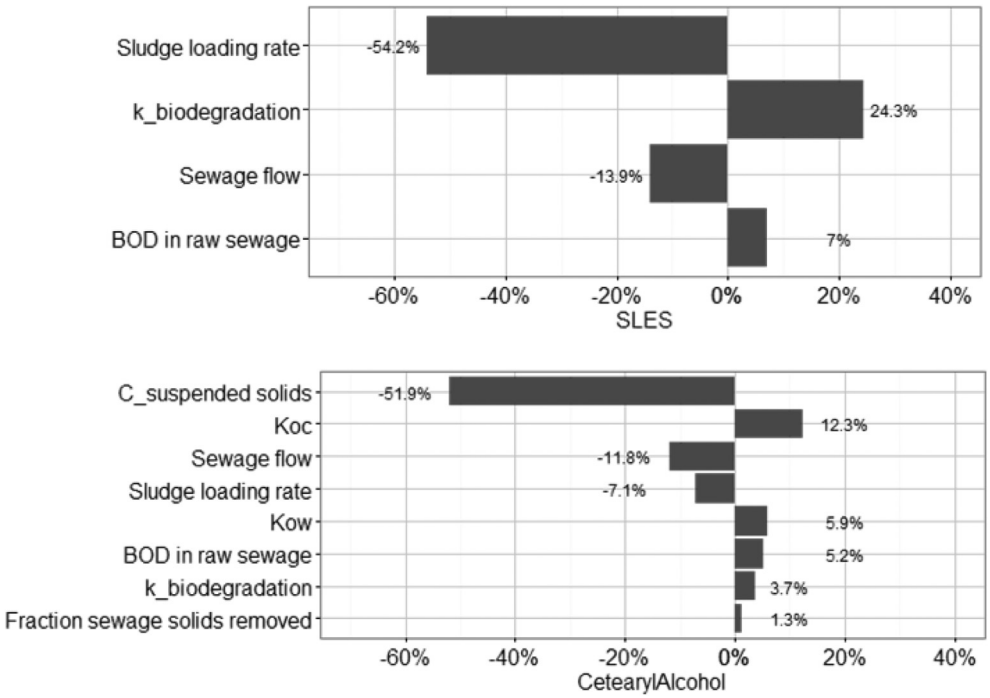


Fig. 5. Relative correlation of the uncertain parameters (with an absolute relative contribution > 1%) used to derive the removal efficiencies of sodium lauryl ether sulfate (SLES, top) and cetearyl alcohol (bottom) from wastewater coupling the SimpleTreat model to a Monte Carlo analysis.

detail.

4.1. Data requirements

One of the main challenges of our bottom-up approach is variability in the survey's methodologies. The four consumer use surveys included all applied different interviewing techniques which restricts the interpretation of the small quantifiable uncertainty in total use volume estimates derived from them. In addition, the derived uncertainty does not allow to explain the observed differences to total market estimates thus potentially pointing to a higher level of (non-quantifiable) uncertainty related to our approach. The representativeness of the interviewed consumer panel might here be an example of a non-quantified uncertainty source. In the French study (Ficheux et al., 2015), where children as well as elderly people were considered, the country's product use is probably closer to reality than the one extrapolated from the US study where only women were included (Loretz et al., 2006). Also, Loretz et al. (2006); (2008) only considered frequent users in their study, which might influence the mean value derived. In addition, different forms of interviewing techniques were used across the studies included. Biesterbos et al. (2013) used a web-questionnaire, while Loretz et al. (2006) assessed real-life uses of CPs. Other differences in study design concern the time-period over which the use of CPs was assessed which ranged from two weeks (Loretz et al., 2006) to 12 months (Ficheux et al., 2015).

Secondly, data on inclusion levels of chemicals in products is required to apply the approach and a single mean value was derived by using internal company data and literature searches. It was assumed that all products considered contributed equally to the mean inclusion level of the chemical in the product, thus their importance on the market was not taken into account. This assumption likely has limited influence on the results, because, on the one hand, the products assessed by Unilever are representative of the products sold. On the other hand, literature data comprised mostly patents, which are also expected to represent actual products well. We therefore expect no bias towards Unilever products composition.

Thirdly, the information on wastewater treatment systems we collected might not be available for every country. Instead of presenting chemical emission loads at WWTP effluents, one could use agglomeration census data to derive estimates at this level. This could be a way to handle missing WWTP location information.

Finally, measured values of the removal efficiencies of the chemicals should ideally have been used but instead removal efficiencies were modelled and this represents the largest source of uncertainty in the estimated chemical loads.

4.2. Methodological choices

Apart from the data requirements, our approach incorporated some methodological choices and assumptions, which we discuss below.

First, the high dependency on the availability, quality, and representativeness of consumer surveys data may limit its application in other countries. Only a few extensive consumer studies were found, and all published different levels of details. This made it difficult to formulate a single consistent methodology across geographies.

Second, we assumed that 100% of the consumed CPs ended up in WWTPs for the four countries considered. This assumption is considered justified, as nearly 100% of the rural and urban US population is connected to a wastewater treatment system (Sanitation, 2015). However, on average 20% of the US population uses septic tanks, as was reported in 2007 by the American Groundwatertrust (2014). In states with high connectivity to septic tanks, like Vermont with 55% connectivity (US EPA, 2017), our approach could overestimate the emissions via WWTPs to freshwater. In fact, septic tanks treat wastewater directly thus retaining 60–70% of the solids, oil, and grease. The septage, meaning the

material pumped from the tank, can then either be further treated in WWTPs or disposed on land (US EPA, 1999). Furthermore, only 2% of the French households were reported not to have their wastewaters treated in the year 2008 (Comissariat général au Développement durable, 2013). In the Netherlands the fraction of the population not connected to wastewater treatment was only 0.3% (DELTARES and TNO, 2015). Finally, the KOSIS (2014) reported that 5% of the South Korean population was connected to septic tanks and only 3% was not connected to any form of treatment in 2013. In addition, we estimated emissions from activated sludge WWTPs using the SimpleTreat model, thus neglecting potential tertiary treatment. While this model is used widely in risk assessment, SimpleTreat does not fully reflect all WWTP designs and operational conditions which are known to influence the removal efficiency of chemicals (Clara et al., 2005; Luo et al., 2014; Suarez et al., 2010). Our approach could therefore be extended to take WWTP specificities better into account (e.g. tertiary treatment type). Finally, if our approach was to be extended to countries where WWTPs are not widely implemented yet, it would need to be adapted to account for direct emissions to overflow.

Third, for France and the Netherlands, the number of persons connected to WWTPs was estimated from the reported person equivalents (p.e.). However, since p.e. also include industry effluents, this assumption led to an overestimation of the French total population by 8.5%, and by around 3% for the Dutch population. Similarly, deriving the South Korean population served by a WWTP from the BOD overestimated the total population by around 5%. These assumptions potentially led to an overestimation of the chemical emissions to surface water.

Fourth, the estimated total chemical emissions for CPs presented in this study are not representative of total use volumes of these chemicals at the country level. The chemicals we analysed can namely be found in other products. In fact, of the CPs in the Household Products Database (National Institutes of Health and Health and Human Services, 2015) that contain the chemicals studied here, shampoo, conditioner, and bodywash make up approximately 50% (EWG, 2015).

Finally, our approach specifically considers emissions of chemicals from CPs to freshwater. For a complete risk assessment of hydrophobic substances (i.e. with $\log(K_{OW})$ values greater than 3.5, like CA) their concentration in sludge should be assessed. In fact, Clara et al. (2007) measured that up to 70% of the removal of quaternary ammonia compounds, a class of cationic surfactants used in CPs, was due to adsorption to sludge. This would be especially important for countries like France, the USA, or South Korea, where treated sludge is used for agricultural purposes (Eurostat, 2015; Rezek, 2017; Spinosa, 2011).

4.3. Application

Common CPs' chemicals are found over a wide range of product types. This limits the applicability of our method for total market risk assessment of a chemical. Nevertheless, the method we propose can still be applied in different contexts. A first example is to define the overall environmental impact of certain product classes or sectors within a country. The chemical footprinting methodologies proposed by Zijp et al. (2014) and Bjorn et al. (2014) could in fact implement our emission estimation technique to compute a national chemical footprint of the personal care product sector for example. Further, our approach could be a valuable addition in regionalized life cycle assessment as it allows for emissions to be estimated at various geographical scales.

A second example is to apply our methodology to help identify important point sources within a country and direct mitigation efforts. In risk assessments, environmental risk is quantified as the ratio of the environmental concentration and the chemical concentration at which no effect on the ecosystem is observed. The emission loads estimated by our approach should therefore be corrected for dilution in the receiving water body to estimate chemical concentrations at the point of WWTP discharge. Correction for dilution helps to account for the fact that larger WWTPs often release emission loads in larger water bodies, thus reducing their environmental risk.

5. Conclusion

This work proves the feasibility of a bottom-up method to estimate country-wide product uses and point source chemical load emissions from WWTPs and their uncertainties from consumption data of specific products, namely shampoo, conditioner, and bodywash, quantified using consumer surveys. Our work stresses the need for measured WWTP removal efficiencies for a more reality-driven assessment of this uncertainty. Further, the need for uncertainty quantification methods to account for differences in consumer use survey designs and actual consumer habits is also highlighted by our results. While the presented results are limited to three CPs, estimating chemical loads for more CPs might be of interest to better understand the overall impact of their use. This approach can also be used in combination with fate models to provide realistic freshwater chemical emission estimates resulting from the use of CPs. An extension of the approach to the quantification of chemical emissions in sludge is also possible.

Ultimately, the developed method would benefit greatly from new knowledge in the field of consumer behaviour. The representativeness of the population sampled and any potential source of bias introduced in the survey are very important. In addition, a combination of different surveying techniques (face-to-face interviews, questionnaires, or sensoring techniques) might increase the reliability of the use estimates provided by these surveys.

Still, this work with its quantification of the uncertainty in chemical emission estimates from the use of consumer products aligns with current efforts made to improve the reliability of product environmental footprints. It proposes an alternative to costly chemical emission monitoring campaigns and top-down estimation techniques that are difficult to replicate.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.11.009.

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