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Biozide Wirkstoffe im Haushalt – Anwendungsmuster und Einträge in das Abwasser

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Zusammenfassung

Biozide Wirkstoffe sind Chemikalien, die zum Schutz der menschlichen oder tierischen Gesundheit oder zum Schutz von Materialien vor Schädlingen eingesetzt werden. Da diese Stoffe eine beabsichtigte Wirkung auf Organismen haben, besteht das Risiko, dass auch ungewollte Auswirkungen auf Nicht-Zielorganismen auftreten. Monitoringergebnisse lassen vermuten, dass diese Wirkstoffe auch häufig im Innenraum von Haushalten eingesetzt werden und von dort vor allem über Abwasserleitungen und Kläranlagen in die Umwelt gelangen, wenn sie in Kläranlagen nicht eliminiert werden. Die Produkte, aus denen die Wirkstoffe aus Haushalten in das Abwasser gelangen, sind bislang jedoch nicht identifiziert worden. Aus diesem Grund konnten die daraus resultierenden Umweltbelastungen nicht eingeschätzt und keine entsprechenden Emissionsminderungsmaßnahmen umgesetzt werden. In dieser Arbeit wurde deshalb untersucht, in welchen Haushaltsprodukten biozide Wirkstoffe eingesetzt werden und in das Abwasser gelangen. Zudem sollte erforscht werden, was die Haushaltsmitglieder über Biozidprodukte wissen und wie sie mit ihnen umgehen. Ziel war es, die Anwendungen von bioziden Wirkstoffen in Haushalten zu identifizieren, von denen die höchsten Umweltbelastungen zu erwarten sind, und geeignete Emissionsminderungsmaßnahmen abzuleiten.

Um die Anwendung biozider Wirkstoffe in Haushalten zu untersuchen, wurde zunächst durch eine Befragung in Haushalten eines dörflichen Wohngebietes ermittelt, was die Haushaltsmitglieder über Biozidprodukte wissen und wie sie die damit verbundenen Risiken im Vergleich zu anderen Haushaltsprodukten einschätzen. Zudem wurde für jeden der teilnehmenden Haushalte ein Inventar der vorhandenen Produkte erstellt. Dabei wurden neben den Biozidprodukten auch Wasch- und Reinigungsmittel und Körperpflegeprodukte untersucht. Ähnliche Erhebungen fanden zusätzlich in Haushalten in urbanen Gebieten statt. Die aufgrund der inventarisierten Produkte zu erwartenden Stoffe wurden im Laufe eines Jahres durch ein speziell abgestimmtes Monitoringprogramm im Abwasser des dörflichen Wohngebietes in Tages- und Stundenmischproben untersucht. Alle Proben wurden nach der Probenahme aufgearbeitet und mittels Flüssigchromatographie gekoppelt mit einem Triple-Quad-Massenspektrometer analysiert. Dabei wurden die Konzentrationen von 14 Wirkstoffen gemessen: 1,2-Benzisothiazol-3(2H)-on (BIT), C_{12}-Benzalkoniumchlorid, Carbendazim, 5-Chlor-2-methyl-2H-isothiazol-3-on (CMIT), Dichloroctylisothiazolinon (DCOIT), N,N-Diethyl-meta-toluamid (DEET), Diuron, Icaridin, 2-Octyl-2H-isothiazol-3-on (OIT), Piperonylbutoxid (PBO), Triclosan, Tebuconazol, Terbutryn und Tetramethrin.

Vielen Befragten war nicht bewusst, dass sie Biozidprodukte nutzen. Der Begriff „Biozid“ war oft nicht bekannt und wurde inhaltlich häufig falsch verstanden. Oft brachten die Befragten damit „ökologische Schädlingsbekämpfung“ in Verbindung oder sie hatten keine Vorstellung, was der Begriff bedeuten könnte. Die Auswertungen der inventarisierten Produkte und der darin enthaltenen bioziden Wirkstoffe zeigten, dass ein Großteil der Wirkstoffe nicht aus Biozidprodukten in das Abwasser gelangt, sondern aus Körperpflegeprodukten und Wasch- und Reinigungsmitteln. Insgesamt 64 % der

Anwendungen von bioziden Wirkstoffen in den inventarisierten Produkten wurden nicht unter der Umweltrisikobewertung der *Verordnung (EU) 528/2012 über die Bereitstellung auf dem Markt und die Verwendung von Biozidprodukten* berücksichtigt, was zu einer erheblichen Unterschätzung der Umweltrisiken führt.

Die Ergebnisse der Abwasseruntersuchungen deuten ebenfalls darauf hin, dass biozide Wirkstoffe aus Wasch- und Reinigungsmitteln, Körperpflegeprodukten und Biozidprodukten gleichermaßen in das Abwasser eingetragen werden. Die Messergebnisse können gut mit den Produktinventaren in Verbindung gebracht werden. Einige Wirkstoffe, wie die Repellentien gegen Mücken, DEET und Icaridin, oder das Desinfektionsmittel C_{12}-Benzalkoniumchlorid scheinen maßgeblich durch Biozidprodukte eingetragen zu werden. Auch Konservierungsmittel, wie beispielsweise Isothiazolinone, die vor allem in Wasch- und Reinigungsmitteln eingesetzt werden, wurden regelmäßig nachgewiesen. Für Triclosan hingegen ist gemäß den Inventaren Zahnpasta vermutlich die Produktgruppe, die in dem untersuchten Wohngebiet maßgeblich für den Eintrag ins Abwasser verantwortlich ist.

Diese Arbeit zeigt zum ersten Mal, welche Produkte im Haushalt eine wichtige Quelle für biozide Wirkstoffe im Abwasser sind. Sie müssen mit einbezogen werden, wenn Emissionen an der Quelle reduziert werden sollen. Die daraus resultierenden komplexen Eintragspfade und -quellen sind für die Haushaltsmitglieder schwer zu durchschauen. Die Anwendungen in Haushaltsprodukten fallen oft nicht unter die Umweltrisikobewertung der *Verordnung (EU) 528/2012 über die Bereitstellung auf dem Markt und die Verwendung von Biozidprodukten*. Dies kann zu einer Unterschätzung des Risikos im Rahmen der Umweltrisikobewertung führen. Aus diesem Grund sollten Maßnahmen ergriffen werden, die über die Produktzulassung von Biozidprodukten hinausgehen, um die Emissionen so gering wie möglich zu halten. Diese Maßnahmen sollten sich nicht darauf beschränken, die Bevölkerung über Biozidprodukte aufzuklären und zu sensibilisieren, da dies aufgrund der hier vorgelegten Ergebnisse nicht immer erfolgsversprechend scheint. Stattdessen sollten Maßnahmen früher in der Wertschöpfungskette ansetzen, wie zum Beispiel beim Design der Wirkstoffe oder der Formulierung der Produkte, um so Einträge biozider Wirkstoffe in die Umwelt zu verringern.

Abstract

Chemicals used to protect human or animal health or materials against harmful organisms are called biocidal active substances. As these substances are supposed to have an effect on organisms, it is possible that they affect non-target organisms as well. Monitoring results indicate that these substances are frequently used within households. From there, the substances are emitted into wastewater and enter the environment via sewage treatment plants if they are not eliminated there. The products used in households that are associated with these emissions have, however, yet to be identified. For this reason, the resulting environmental pollution cannot be assessed, and related measures to minimise the emissions cannot be implemented.

To address this problem, this thesis evaluated which household products contain biocidal active substances and which substances are emitted into municipal wastewater. It also assessed what consumers know about biocidal products and how those are used in households. It aimed to identify the applications in households responsible for the highest emissions and to propose appropriate measures to minimise these emissions.

To understand the use of biocidal active substances in households, the study focussed on a rural neighbourhood and analysed inhabitants' knowledge and risk perception of biocidal products compared to other household products. In addition, product inventories for all participating households were compiled. Besides biocidal products, washing and cleaning agents and personal care products were included in the inventories. Similar surveys took place in households in urban neighbourhoods. Based on the biocidal active substances contained in the products inventoried, a matching wastewater sampling campaign was conducted in the rural neighbourhood. Daily and hourly composite samples were analysed during the course of the year. The concentrations of 14 active substances were measured by liquid chromatography coupled with a triple quad-mass spectrometer: 1,2-benzisothiazol-3(2H)-one (BIT), C12-benzalkonium chloride, carbendazim, 5-chloro-2-methyl-2h-isothiazol-3-one (CMIT), dichlorooctylisothiazolinone (DCOIT), N,N-diethyl-meta-toluamide (DEET), diuron, icaridine, 2-octyl-2H-isothiazol-3-one (OIT), piperonyl butoxide (PBO), triclosan, tebuconazole, terbutryn and tetramethrin.

The results of interviews conducted with household members demonstrated that many interviewees were not aware of using biocidal products. The term "biocide" was often unfamiliar to them or misunderstood. In many cases, interviewees related organic pest control with this term or were not able to figure out its meaning at all. The evaluation of the products inventoried and the biocidal active substances contained in those products showed that the majority of the uses is not in biocidal products but in personal care products and washing and cleaning agents. Of those uses, 64 % do not fall under the *Regulation (EU) 528/2012 concerning the making available on the market and use of biocidal products*, which seems to underestimate the environmental risk of biocidal active substances.

The measured concentrations of the substances also showed that biocidal active substances are evenly emitted to wastewater by washing and cleaning agents, personal care products and biocidal products. The results matched the product inventories. Some active substances such as the mosquito repellents DEET and icaridine or the disinfectant C12-benzalkonium chloride were primarily emitted by biocidal products. Preservatives, such as isothiazolinones, which are used primarily in washing and cleaning agents, were detected frequently. For triclosan, a disinfectant, inventories showed that toothpaste probably was the product group mainly responsible for its emission into wastewater.

This thesis shows that household products are an important source for biocidal active substances in wastewater. They should not be neglected if emissions are to be reduced at the source. The resulting complex emission pathways and sources are hard to understand for consumers. The uses often do not fall under the environmental risk assessment of *Regulation (EU) 528/2012 concerning the making available on the market and use of biocidal products*. As a consequence, the environmental risk assessment under this regulation may underestimate the risk posed by biocidal active substances. For this reason, measures that minimise emissions to the minimum possible and that go beyond current product authorisation should be adopted. These measures should not be limited to information and awareness raising campaigns, as this does not seem promising due to the limited knowledge of consumers regarding biocidal products. Instead, measures should focus on stages early in the value chain, for example the design of the active substances or the formulation of the product, and thus minimise emissions of biocidal active substance into the environment.

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Abkürzungsverzeichnis

BBSR	Bundesinstitut für Bau-, Stadt- und Raumforschung
BIT	1,2-Benzisothiazol-3(2H)-on
BKC	C_{12}-Benzalkoniumchlorid
CAR	Carbendazim
CAS	Chemical Abstracts Service
CMIT	5-Chlor-2-methyl-2H-isothiazol-3-on
DCOIT	Dichloroctylisothiazolinone
DEET	N,N-Diethyl-meta-toluamid
DIU	Diuron
ECHA	Europäische Chemikalienagentur
ICA	Icaridin
LC-MS/MS	Flüssigchromatographie gekoppelt mit Triple-Quad-Massenspektrometer
OIT	2-Octyl-2H-isothiazol-3-on
PA	Produktart
PBO	Piperonylbutoxid
REACH	Verordnung (EG) Nr. 1907/2006 des europäischen Parlamentes und des Rates vom 18. Dezember 2006 zur Registrierung, Bewertung, Zulassung und Beschränkung chemischer Stoffe (REACH), zur Schaffung einer Europäischen Chemikalienagentur, zur Änderung der Richtlinie 1999/45/EG und zur Aufhebung der Verordnung (EWG) Nr. 793/93 des Rates, der Verordnung (EG) Nr. 1488/94 der Kommission, der Richtlinie 76/769/EWG des Rates sowie der Richtlinien 91/155/EWG, 93/67/EWG, 93/105/EG und 2000/21/EG der Kommission
SPE	Festphasenextraktion (solid phase extraction)
TCS	Triclosan
TEB	Tebuconazol
TER	Terbutryn
TET	Tetramethrin

1 Einleitung

Die Verschmutzung der Erde mit Chemikalien ist eine der menschengemachten Entwicklungen, die ein sicheres Leben auf der Erde bedrohen, sollte die Verschmutzung die Grenzen der planetaren Tragfähigkeit überschreiten (Rockström et al. 2009). Die Grenze der planetaren Tragfähigkeit für chemische Verschmutzungen ist jedoch schwer zu quantifizieren, da es sich um eine Vielzahl an Chemikalien und Anwendungen handelt, die gleichzeitig eine Fülle von Arten in unterschiedlichsten Ökosystemen bedrohen (Diamond et al. 2015). Die prospektive Risikobewertung von Chemikalien soll dabei helfen, Risiken für Ökosysteme oder die Menschen frühzeitig zu erkennen und zu vermeiden. Sie leistet damit einen wichtigen Beitrag zum Erreichen zweier Unterziele der „Sustainable Development Goals“ der Vereinten Nationen: Das Unterziel 6.3 zielt darauf ab, die Freisetzung von Chemikalien ins Wasser zu minimieren und Unterziel 12.4 fordert einen umweltverträglichen Umgang mit Chemikalien, um deren nachteiligen Auswirkungen auf die menschliche Gesundheit und die Umwelt auf ein Mindestmaß zu beschränken (United Nations 2017).

Um diese Ziele systematisch erreichen zu können, ist es wichtig zu wissen, aus welchen Quellen die Chemikalien stammen, die in die Umwelt gelangen. Nur dann können Emissionen zielgerichtet minimiert werden. In dieser Arbeit soll daher der Beitrag von Haushaltsprodukten, wie zum Beispiel Wasch- und Reinigungsmitteln, zum Eintrag biozider Wirkstoffe ins häusliche Abwasser betrachtet und Ansatzpunkte zur möglichen Minimierung dieser Einträge geliefert werden.

1.1 Rechtlicher Hintergrund von bioziden Wirkstoffen

Biozide Wirkstoffe sind Substanzen, die angewendet werden, um Menschen, Tiere und Materialien vor für sie schädlichen Organismen zu schützen. Sie leisten damit per definitionem einen wichtigen Beitrag zum Schutz der Gesundheit und von Materialien. Dabei wirken sie in der Regel aber nicht nur auf die Zielorganismen, sondern auch auf Menschen und andere Organismen, insbesondere wenn die Stoffe nach der Anwendung in die Umwelt gelangen. Biozide Wirkstoffe werden innerhalb der EU in der *Verordnung 528/2012 über die Bereitstellung auf dem Markt und die Verwendung von Biozidprodukten* (Biozid-Verordnung) geregelt. Als Biozidprodukte gelten darin Produkte, die dazu bestimmt sind, „auf andere Art als durch bloße physikalische oder mechanische Einwirkung Schadorganismen zu zerstören, abzuschrecken, unschädlich zu machen, ihre Wirkung zu verhindern oder sie in anderer Weise zu bekämpfen“ (European Union 2013b).

Da diese Definition ein weites Feld von Anwendungen umfasst, werden Biozidprodukte gemäß Anhang V der Biozid-Verordnung in 22 verschiedene Produktarten (PA) eingeteilt, die wiederum in 4 Hauptgruppen zusammengefasst werden. Diese sind Desinfektionsmittel, Schutzmittel, Schädlingsbekämpfungsmittel und sonstige Biozidprodukte. Aktuell listet die Europäische Chemikalienagentur (ECHA) 275 biozide Wirkstoffe, deren Risiken aktuell von den EU-Mitgliedstaaten bewertet werden oder bereits bewertet worden sind (European Chemicals Agency 2017a). Die Bewertung umfasst 739 Wirkstoff-PA-Kombinationen, da jede Wirkstoff-Verwendung in jeder PA einzeln bewertet werden muss, wenn ein entsprechender Antrag gestellt wird.

Doch nicht alle Verwendungen der Stoffe fallen unter den Anwendungsbereich der Biozid-Verordnung. So gelten die Wirkstoffe nur dann als biozide Wirkstoffe, wenn sie zum Zwecke der Abwehr von Schäd- oder Lästlingen eingesetzt werden. Werden sie zu einem anderen Zweck eingesetzt, beispielsweise als Duftstoff, so gelten sie nicht mehr als biozide Wirkstoffe und ihre Verwendung wird nicht im Rahmen der Risikobewertung der Biozid-Verordnung betrachtet. Zudem werden ganze Produktgruppen aus dem Geltungsbereich der Biozid-Verordnung ausgenommen. Dies sind zum Beispiel Pflanzenschutzmittel oder Tier- und Humanarzneimittel. Der Einsatz von Schutzmitteln für Produkte während der Lagerung (PA 6) in Wasch- und Reinigungsmitteln fällt unter die Biozid-Verordnung, der vergleichbare Einsatz von Konservierungsmitteln in Körperpflegeprodukten jedoch nicht. Diese Ausnahmen führen immer wieder zu Grenzfällen, in denen die eindeutige Zuordnung von Anwendungen zu Regelungsbereichen schwierig ist (Woutersen et al. 2015).

Die verschiedenen Regelungsbereiche für gleiche Wirkstoffe führen dazu, dass die einzelnen Emissionen der Stoffe in die Umwelt während der Umweltrisikobewertung nicht aggregiert, also aufsummiert, werden. Die Folge ist, dass die errechneten Umweltkonzentrationen innerhalb der jeweiligen Expositionsberechnungen geringer sein können als die tatsächlich theoretisch möglichen oder tatsächlich vorhandenen Konzentrationen. Dies führt dazu, dass Umweltrisiken unterschätzt werden können. Zudem muss im Rahmen der Produktzulassung lediglich belegt werden, dass die Nebeneffekte des Produktes auf Nichtzielorganismen auf einem akzeptablen Level sind. Diese Grundannahme der Umweltrisikobewertung bedeutet jedoch nicht, dass keine Effekte auftreten dürfen. Zusammen mit der zuvor diskutieren Unterschätzung der Exposition führt dies auch zu möglichen Umweltauswirkungen durch zugelassene Produkte, die nicht akzeptabel sind. Es ist jedoch bisher unklar, in welchem Ausmaß Umweltrisiken unterschätzt werden.

1.2 Biozide Wirkstoffe im kommunalen Abwasser

Biozide Wirkstoffe werden regelmäßig im Zu- oder Ablauf von Kläranlagen nachgewiesen. Der Wirkstoff DEET beispielsweise, der als Repellent gegen Mücken und Zecken eingesetzt wird, wurde in allen 90 untersuchten Kläranlagenabflüssen in ganz Europa nachgewiesen (Loos et al. 2013). Auch Diuron, das beispielsweise in Mauerschutzmitteln verwendet wird, wurde in 70 % dieser Proben gefunden, Triclosan, ein Desinfektionsmittel, das heutzutage fast ausschließlich noch in Körperpflegeprodukten eingesetzt wird, in 40 % (Loos et al. 2013). Da die bioziden Wirkstoffe in der Regel nicht vollständig in Kläranlagen abgebaut werden, sind sie auch in Flüssen, Meeren und Biota zu finden (Corcellas et al. 2015; Engelmann 2016; Lao et al. 2010; Singer et al. 2010; Terzopoulou et al. 2015; Tran et al. 2013; Weigel et al. 2002; Wick et al. 2010; Wittmer et al. 2010; Zhang et al. 2015). Um die Konzentrationen von Schadstoffen in der Umwelt zu minimieren, existieren zwei verschiedene Konzepte: die Aufrüstung der Kläranlagen oder die Reduktion der Emissionen an der Quelle (Kümmerer et al. 2015). Es wurde bereits vermutet, dass Quellen biozider Wirkstoffe in Haushalten vorhanden sind, bislang wurden jedoch vor allem Emissionen aus dem Außenbereich der Häuser untersucht (Bollmann et al. 2014b; Burkhardt et al. 2007). Untersuchungen zum Eintrag biozider Wirkstoffe ins Abwasser aus Innenraumanwendungen fehlen bisher (Bollmann et al. 2014a; Launay et al. 2016; Wittmer et al. 2011). Aus diesem Grund ist es schwierig, geeignete Reduktionsmaßnahmen für diese Quelle vorzuschlagen.

Zur Untersuchung der Einträge aus Haushalten ist bei der Entnahme von Abwasserproben zu beachten, dass die Proben die Abwasserbelastung realistisch abbilden. Einfache Stichproben sind dabei für biozide Wirkstoffe im Abwasser in der Regel nicht ausreichend, da es sich hier nicht um kontinuierliche, sondern um gepulste Einträge handelt (Ort et al. 2010a). Im Idealfall sollten derartige Proben kontinuierlich durchflussproportional genommen werden. Aufgrund der technischen Komplexität dieser Probenahmeart sind jedoch diskontinuierliche durchfluss- oder zeitproportionale Stichproben die Regel. Die Probenahmefrequenz sollte idealerweise entsprechend der erwarteten Pulsfrequenz der Analyten gewählt werden, bei unbekannten Pulsen jedoch nicht größer als 15 Minuten sein (Ort et al. 2010b). Bisherige Probenahmen zur Untersuchung von bioziden Wirkstoffen im Abwasser beschränken sich auf Proben aus Mischkanalisationen (Bollmann et al. 2014a; Launay et al. 2016; Wick et al. 2010). Dies ermöglicht jedoch keine Differenzierung zwischen den Einträgen aus Auswaschung durch Regenwasser und den Einträgen aus den Innenräumen von Haushalten. Zudem fehlen Messkampagnen, die die saisonalen und tageszeitabhängigen Konzentrationsunterschiede biozider Wirkstoffe im häuslichen Abwasser darstellen.

Es existieren bereits einige Methoden zur Aufarbeitung von Abwasserproben und für deren Analyse auf biozide Wirkstoffe. Dabei ist es wichtig, nicht nur die wässrige Phase der Probe zu untersuchen, sondern auch die Schwebstoffe aufzuarbeiten (Barco-Bonilla et al. 2010; Ort et al. 2010b). Die Aufreinigung und -konzentrierung erfolgt in der Regel mittels Festphasenextraktion (SPE). Für die Analyse der aufgearbeiteten Proben wird am häufigsten die Flüssigchromatographie in Kombination mit einem Triple-Quad-Massenspektrometer (LC-MS/MS) verwendet (Chen et al. 2012; Singer et al. 2010; Wick et al. 2010). Als Ionisationsmethode wird die Elektrosprayionisation bevorzugt, wenn ein großes Spektrum an verschiedenen Substanzen untersucht werden soll. In diesem Fall sollten interne Standards verwendet werden, um die verstärkte oder unterdrückte Ionisierung der Substanzen aufgrund der komplexen Matrix zu kompensieren (Wick et al. 2010). Oft wird bei der Auswahl der Stoffe, die durch die Methoden untersucht werden sollen, auf bereits bestehende Monitoringergebnisse zurückgegriffen. Dieses Vorgehen wird von Daughton (2014) kritisiert, da die Substanzauswahl besser auf den zu erwartenden Substanzen in den zu analysierenden Proben basieren sollte.

1.3 Biozide Wirkstoffe in Haushaltsprodukten

In Haushalten werden biozide Wirkstoffe in sehr unterschiedlicher Weise eingesetzt. Die Wirkstoffe können zum einen in Biozidprodukten enthalten sein, die direkt in den Haushalten eingesetzt werden. Dies können Desinfektionsmittel (PA 1, 2, 3, 5), Beschichtungsschutzmittel (PA 7), Holzschutzmittel (PA 8), Schutzmittel für Baumaterialien (PA 10), Rodentizide (PA 14), Insektizide (PA 18), Repellentien (PA 19), Anti-Fouling-Produkte (PA 21) und Flüssigkeiten für Einbalsamierung und Taxidermie (PA 22) sein (COWI 2009). Zum anderen spielen in Haushalten biozide Wirkstoffe eine Rolle, die nicht in Biozidprodukten angewendet werden. Dies sind Schutzmittel für Produkte während der Lagerung (PA 6), die zum Beispiel Wasch- und Reinigungsmitteln zugegeben werden, um diese im Gebinde vor mikrobieller Schädigung zu schützen. Auch Körperpflegeprodukten werden derartige Wirkstoffe als Konservierungsmittel zugegeben, diese fallen jedoch nicht unter die Umweltrisikobewertung der Biozid-Verordnung (siehe 1.1). Zusätzlich werden biozide Wirkstoffe Materialien zu deren Schutz zugesetzt. Diese „behandelten Waren“ gemäß Artikel 3(1) der Biozid-Verordnung können beispielsweise Küchenartikel oder Kleidung sein. Auch sind in Haushalten Farben, Putze, Bodenbeläge oder Silikon-Dichtungen verbaut, die biozide Wirkstoffe enthalten. Der Anteil dieser nicht offensichtlichen Anwendungen biozider Wirkstoffe in Haushalten ist jedoch nicht bekannt.

Es gibt verschiedene Möglichkeiten Daten zu Produkten in Haushalten zu erheben. Grundsätzlich ist die Verwendung von Verkaufs- oder Verbrauchszahlen am zeit- und kostengünstigsten, wie es beispielsweise für Humanarzneimittel bereits mehrmals gemacht wurde (Herrmann et al. 2015b; Kümmerer und Henninger 2003; Verlicchi et al. 2014). Diese stehen für biozide Wirkstoffe oder Biozidprodukte jedoch nicht zur Verfügung. Stattdessen kann man auf Produktinventare innerhalb von Haushalten zurückgreifen. Diese können mittels telefonischer, internet-basierter oder persönlicher Befragung erhoben werden, wobei jede Methode Vor- und Nachteile hat (Bennett et al. 2012; Hertz-Picciotto et al. 2010; Wu et al. 2010). Obwohl Besuche vor Ort sehr zeitintensiv sind und von den Befragten als aufdringlich empfunden werden können, werden mit dieser Methode die wohl detailliertesten Ergebnisse gewonnen. Diese Methode wurde bereits für verschiedene Produktkategorien angewendet (ANSES 2010; Bennett et al. 2012; Eriksson et al. 2003). Werden dabei Barcode-Scanner verwendet, kann die zur Inventarisierung benötigte Zeit auf ein Mindestmaß reduziert werden (Bennett et al. 2012). Studien zu Biozidprodukten in ihrer Gesamtheit wurden bisher noch nicht durchgeführt.

Neben den bioziden Wirkstoffen, die in Haushalten angewendet werden, sind auch die Einstellung und die Kenntnisse der Bevölkerung zu diesen Produkten weitgehend unerforscht. Gleichzeitig wird jedoch von der Bevölkerung erwartet, dass sie empfohlene Risikominderungsmaßnahmen befolgt, Biozidprodukte nur einsetzt, wenn sie notwendig sind, und dass sie angemessen informiert, aufmerksam und verständig handelt (Bruinen de Bruin et al. 2007; European Court of Justice 1998; European Union 2013a; Ternes et al. 2004). Studien über die allgemeine Einstellung der Befragten zu Chemikalien zeigen, dass sie generell wenig über die Produkte wissen, die sie zu Hause verwenden (Epp et al. 2010; European Commission 2016; 2011; Glegg und Richards 2007). Dies ist insbesondere deshalb problematisch, da viele Risiken (und auch Vorteile) von Chemikalien für Laien unsichtbar sind (vgl. Beck 2017). Zudem stehen sie professionellen Marketingfachleuten gegenüber, deren Aussagen sie kaum bewerten können (Howells 2005).

Vor dem Hintergrund dieser Informationsasymmetrie ist es wichtig zu erfassen, was die Bevölkerung über Biozidprodukte weiß und wie sie deren Risiken einschätzt. Dies kann über Befragungen geschehen, die auf unterschiedliche Art und Weise durchgeführt werden können. Die meisten Studien verwenden quantitative Erhebungen mittels standardisierter Fragebögen (Epp et al. 2010; European Commission 2016; 2011). Es wurden jedoch auch qualitative Studien durchgeführt (Midden et al. 2011).

2 Ziele und Aufbau der Arbeit

2.1 Ziele

Produkte in Haushalten stellen eine wichtige Eintragsquelle für biozide Wirkstoffe in das Abwasser dar. Obwohl ihr Beitrag zur Abwasserbelastung bereits in mehreren Studien vermutet wurde (Bollmann et al. 2014a; Launay et al. 2016; Wittmer et al. 2010), ist der Einsatz biozider Wirkstoffe innerhalb der Haushalte noch nicht genauer untersucht worden.

Das Ziel dieser Arbeit war es daher anhand eines ausgewählten Studiengebietes die Produkte zu identifizieren, die den größten Anteil an der Belastung häuslicher Abwässer durch biozide Wirkstoffe haben. Das Studiengebiet wurde deshalb nach Kriterien ausgewählt, die einen ausschließlichen Eintrag der Wirkstoffe aus Innenräumen von Haushalten vermuten ließen. Zusätzlich sollte untersucht werden, in welchem Umfang die Haushaltsmitglieder über Wissen zu Biozidprodukten verfügen und wie sie die Risiken dieser Produkte im Vergleich zu anderen Haushaltschemikalien wahrnehmen. Damit sollten Ansatzpunkte zur Minimierung der Emission biozider Wirkstoffe aus Haushalten aufgezeigt werden.

Im Rahmen der Arbeit wurden dafür die folgenden Hypothesen aufgestellt, die untersucht werden:

1. Produkte, die Schutzmittel für Produkte während der Lagerung enthalten, sind in allen untersuchten Haushalten vorhanden.
2. Biozidprodukte aus weiteren bioziden Produktarten in Haushalten, wie zum Beispiel Desinfektionsmittel oder Insektizide, sind in der Mehrheit der untersuchten Haushalte vorhanden.
3. Der Einsatz der bioziden Wirkstoffe in Haushaltsprodukten fällt unter die Umweltrisikobewertung der Biozid-Verordnung.
4. Die befragten Personen sind sich der Nutzung biozider Wirkstoffe bewusst.
5. Die eingesetzten Schutzmittel für Produkte während der Lagerung können durchgehend im Abwasser nachgewiesen werden.
6. Andere in den Produkten enthaltenen Wirkstoffe können im Abwasser der Haushalte ebenfalls entsprechend ihrer Anwendungsmuster analytisch nachgewiesen werden.

2.2 Aufbau

Die praktischen Arbeiten wurden von September 2014 bis August 2017 an der Leuphana Universität Lüneburg am Institut für Nachhaltige Chemie und Umweltchemie durchgeführt. Die daraus hervorgegangenen Ergebnisse wurden in vier Artikeln in internationalen wissenschaftlichen Zeitschriften mit Peer-Review-Verfahren veröffentlicht, die in den folgenden Kapiteln zusammengefasst und diskutiert werden.

Diese Artikel sind:

Artikel 1

Stefanie Wieck, Oliver Olsson, Klaus Kümmerer (2016). Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater. *Environment International* 94:695-705.
DOI: https://doi.org/10.1016/j.envint.2016.07.007.

Artikel 2

Stefanie Wieck, Oliver Olsson, Klaus Kümmerer (2018). Consumers' perceptions of biocidal products in households. *International Journal of Hygiene and Environmental Health* 221(2):260-268.
DOI: https://doi.org/10.1016/j.ijheh.2017.11.005.

Artikel 3

Stefanie Wieck, Oliver Olsson, Klaus Kümmerer (2018). Not only biocidal products: Washing and cleaning agents and personal care products can act as further sources of biocidal active substances in wastewater. *Environment International* 115:247-256.
DOI: https://doi.org/10.1016/j.envint.2018.03.040.

Artikel 4

Stefanie Wieck, Oliver Olsson, Klaus Kümmerer, Ursula Klaschka (2018). Fragrance allergens in household detergents. *Regulatory Toxicology and Pharmacology* 97:163-169.
DOI: 10.1016/j.yrtph.2018.06.015.

3 Methoden

3.1 Studiengebiete

Die Arbeiten wurden in drei verschiedenen Wohngebieten (Abbildung 1) in Norddeutschland durchgeführt, die für die drei verschiedenen Raumtypen stehen: überwiegend städtisch, teilweise städtisch und ländlich (BBSR 2009). Insgesamt wurden 133 Haushalte besucht.

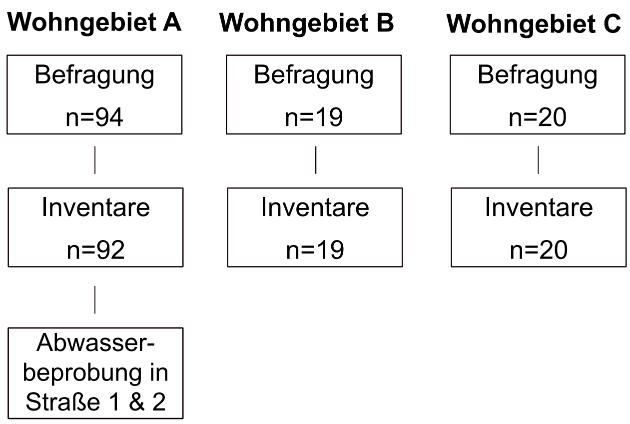

Abbildung 1: Übersicht über die durchgeführten Arbeiten in den Studiengebieten

Wohngebiet A repräsentiert die ländlich geprägten Regionen. Es gehört zu einem Gemeindeverbund mit einer Bevölkerungsdichte von 172 Einwohnern/km² (BBSR 2015). Während der Gesamtverbund als teilweise städtisch charakterisiert wird, kann das untersuchte Wohngebiet als ländlich definiert werden, da der Anteil urbaner Flächen hier bei nur 3,3 % liegt (persönliche Kommunikation mit BBSR, 12. Oktober 2015). Das Wohngebiet ist ein Neubaugebiet aus den 70er Jahren mit vorwiegend Einfamilienhäusern und liegt in einem Dorf mit ca. 3 000 Einwohnern. Das Wohngebiet ist in zwei Straßenzüge (Straße 1 und 2) unterteilt, die jeweils über einen eigenen Anschluss an die Hauptabwasserleitung verfügen. Insgesamt liegen in diesem Wohngebiet 145 Haushalte, von denen 132 Haushalte an die beiden beprobten Abwasserleitungen angeschlossen sind. Das Abwasser dieser Haushalte wird getrennt von den Regenwasserabflüssen geführt (Trennkanalisation).

Wohngebiet B steht für die teilweise städtischen Regionen. Das Wohngebiet liegt in einer Stadt mit 33 000 Einwohnern und hat eine Bevölkerungsdichte von 245 Einwohnern/km² (BBSR 2015), der Anteil urbaner Flächen liegt bei 36,6 % (persönliche Kommunikation mit BBSR, 12. Oktober 2015). In diesem Wohngebiet gibt es vor allem Mehrfamilienhäuser.

Wohngebiet C ist eine überwiegend städtische Region in einer Großstadt. Die Stadt hat 1,7 Mio. Einwohner und eine Bevölkerungsdichte von 2 296 Einwohnern/km² (BBSR 2015). In dem untersuchten Wohngebiet stehen vorwiegend Mehrfamilienhäuser mit einem hohen Anteil an Wohngemeinschaften.

Wie zu erwarten war, stehen die drei Wohngebiete für sehr unterschiedliche Wohnverhältnisse. Die durchschnittliche Wohnungsgröße ist dementsprechend sehr unterschiedlich (136 m^2 im Wohngebiet A gegen 65 und 67 m^2 in den Wohngebieten B und C). Im Wohngebiet A ist zudem der Anteil der Haushaltsmitglieder über 65 Jahre und das Nettohaushaltseinkommen höher. Weitere Informationen zu den Wohngebieten sind in Artikel 1 zu finden.

3.2 Fragebogen und Produktinventare

Zu Beginn der Untersuchungen wurden die Haushalte kontaktiert und pro teilnehmendem Haushalt ein Haushaltsmitglied befragt. Entsprechend der Empfehlungen des Statistischen Bundesamtes wurde ein Haushalt als eine wirtschaftliche Gemeinschaft definiert (Statistisches Bundesamt 2010). Im Wohngebiet A sollte eine Vollerhebung durchgeführt werden. Aus diesem Grund war keine Stichprobenziehung notwendig, es wurden alle 145 Haushalte kontaktiert. Mitglieder aus 94 Haushalten nahmen an der Befragung teil und 92 Haushaltsmitglieder stimmten einer Inventarisierung ihrer Produkte zu. In den Wohngebieten B und C wurde die Studie in den Haushalten durchgeführt, die sich dazu bereit erklärten teilzunehmen. Im Wohngebiet B beteiligten sich Mitglieder aus 19 Haushalten und im Wohngebiet C nahmen Mitglieder aus 20 Haushalten teil.

Wenn sich ein Haushaltsmitglied bereit erklärte, an der Befragung teilzunehmen, wurde diesem zunächst der Fragebogen Frage für Frage vorgelesen und die Antworten von der interviewenden Person notiert. Der standardisierte Fragebogen bestand aus offenen und geschlossenen Fragen. Die Fragen beschäftigten sich mit dem Verständnis des Begriffs „Biozid“, Informationsquellen zu Schädlingen im Haushalt, Vorgehen bei der Schädlingsbekämpfung, Risikowahrnehmung im Vergleich zu anderen Haushaltsprodukten und der Einstellung zu Emissionsminderungsmaßnahmen. Nach den Fragen zum Verständnis des Begriffes „Biozid“ wurde der Begriff erklärt, um nachfolgende Missverständnisse zu vermeiden. Am Ende des Fragbogens wurden Daten zu dem Haushalt und demographische Daten erhoben. Diese Fragen basierten auf den Empfehlungen des Statistischen Bundesamtes und können deshalb mit den Ergebnissen der deutschen Volkszählung verglichen werden (Statistisches Bundesamt 2010). Weitere Informationen zu dem Vorgehen bei der Befragung sind in Artikel 2 zu finden.

Im Anschluss an die Befragung wurden die in den Haushalten vorhandenen Produkte mithilfe eines Barcode-Scanners inventarisiert. Die Befragten konnten wählen, ob sie die Produkte zu der interviewenden Person bringen oder mit der Person durch das Haus gehen wollten. Dabei wurden folgende Produkte inventarisiert:

- alle Schädlingsbekämpfungsmittel (inkl. Biozidprodukten, Pflanzenschutzmitteln und Produkten gegen Flöhe und Läuse bei Mensch und Tier) mit relevanten Emissionen ins Abwasser;
- alle Wasch- und Reinigungsmittel;
- Körperpflegeprodukte mit relevanten Emissionen ins Abwasser: Shampoo, Duschgel, Badezusatz, Haarspülung/-kur, Flüssigseife, Zahnpasta, Mundspülung, Bodylotion, Handcreme, Haarstyling-Produkte, Haarfärbemittel und Abschminkprodukte.

Es wurden die Schädlingsbekämpfungsmittel inventarisiert, deren Anwendung wahrscheinlich zu einem Eintrag von bioziden Stoffen in das Abwasser führt (COWI 2009). Die Körperpflegeprodukte wurden nach dem theoretisch möglichen Eintrag von Konservierungsmitteln ins Abwasser ausgewählt, da diese vermutlich den größten Anteil der in Körperpflegeprodukten eingesetzten bioziden Wirkstoffe darstellen. Die Formeln zu dieser Berechnung sind in Artikel 1 zu finden.

Das Vorgehen wurde in Vortests (n=20) in zufällig ausgewählten Haushalten getestet. Eine öffentliche Datenbank (www.codecheck.info) wurde verwendet, um den inventarisierten Barcodes die entsprechenden Produkte und Inhaltsstoffe zuordnen zu können (Bennett et al. 2012). Wurde ein Produkt nicht in dieser Datenbank gefunden, wurde der Produktname zusätzlich mithilfe des Barcodes über eine Suchmaschine (www.google.de) gesucht. Waren in der Datenbank und mit Hilfe der Suchmaschine keine Inhaltsstoffe zu finden, wurden diese auf den Webseiten der Hersteller recherchiert. Die bioziden Wirkstoffe in den Produkten wurden durch einen Abgleich der CAS- und EC-Nummern mit der Liste der bioziden Wirkstoffe der Europäischen Chemikalienagentur identifiziert (Stand 14. Juni 2015, European Chemicals Agency 2015). Weiterführende Informationen zu dem Vorgehen bei der Inventarisierung sind in Artikel 1 zu finden.

Um die Anwendbarkeit der Methode auch bei andere Stoffgruppen zu testen, wurden die Inventare zusätzlich auf Duftstoffe in Wasch- und Reinigungsmitteln durchsucht. Dabei wurde die Listung von 26 allergenen Duftstoffe ausgewertet, die gemäß der *Verordnung (EG) Nr. 648/200 über Detergenzien* (Detergenzien-Verordnung) auf den Listen der Inhaltsstoffe angegeben werden müssen (European Union 2004). Das genaue Vorgehen ist in Artikel 4 zu finden.

3.3 Stoffauswahl

Aus den 74 bioziden Wirkstoffen, die laut der Rechercheergebnisse in den inventarisierten Produkten in Wohngebiet A enthalten waren, wurden 14 Stoffe ausgewählt, deren Abwasserkonzentrationen in Wohngebiet A überprüft werden sollten (Tabelle 1). Dabei wurden alle Stoffe ausgeschlossen, die z.B. in weniger als 10 Produkten inventarisiert wurden oder die leicht biologisch abbaubar sind. Zusätzlich wurden auch Stoffe ausgewählt, die nicht inventarisiert wurden. Auf diese Weise sollte überprüft werden, ob Produktinventare ausreichend sind, um alle Emissionen aus Haushalten zu erfassen. Zusätzlich mussten alle ausgewählten Stoffe mit einer Methode analysiert werden können, bei der Flüssigchromatographie gekoppelt mit einem Triple-Quad-Massenspektrometer (LC-MS/MS) zur Quantifizierung genutzt werden kann. Weitere Informationen zur Stoffauswahl sind in Artikel 3 zu finden.

Einige der Stoffe werden zusätzlich zu ihrem Einsatz als biozide Wirkstoffe auch in Produkten eingesetzt, die in andere Regelungsbereiche fallen. So wird BKC beispielsweise auch in Augentropfen verwendet, PBO in Mitteln gegen Kopfläuse und TCS in medizinischen Hautcremes (Tabelle 1).

Tabelle 1: Ausgewählte Substanzen und deren Anwendungen

Biozider Wirkstoff	Abkürzung	Anzahl Produkte	Anwendungen in: verbraucher-relevanten bioziden Produktarten (PA)[a]	Pflanzenschutz-mitteln[b]	Körperpflege-produkten[c]	REACH[d]	Humanarzneimitteln[e]
> 10 Produkte inventarisiert							
1,2-Benzisothiazol-3(2H)-on	BIT	261	2, 6, 9, 10	Nein	Nein	Nein	Nein
2-Octyl-2H-isothiazol-3-on	OIT	31	6, 7, 8, 9, 10	Nein	Nein	Nein	Nein
5-Chlor-2-methyl-2H-isothiazol-3-on	CMIT	102	2, 4, 6	Nein	Ja	Nein	Nein
C_{12}-Benzalkoniumchlorid	BKC	23	1, 2, 3, 4, 8, 10, 22	Nein	Ja	Ja	Ja[i]
Icaridin	ICA	15	19	Nein	Nein	Ja	Nein
Piperonylbutoxid	PBO	21	18	Ja[h]	Nein	Ja	Ja[i]
Tetramethrin	TET	12	18	Nein	Nein	Nein	Nein
< 10 Produkte inventarisiert, aber aufgenommen aufgrund regelmäßiger Funde im Abwasser							
Carbendazim	CAR	0	7, 9, 10	Nein	Nein	Nein	Nein
Dichloroctylisothiazolinon	DCOIT	0	7, 8, 9, 10	Nein	Nein	Nein	Nein
Diuron	DIU	0	7, 10	Ja[g]	Nein	Ja	Nein
Tebuconazol	TEB	0	7, 8, 10	Ja[i]	Nein	Nein	Nein
Terbutryn	TER	0	7, 9, 10	Nein	Nein	Nein	Nein
N,N-Diethyl-meta-toluamid	DEET	2	19	Nein	Nein	Nein	Nein
Triclosan	TCS	4	Verboten[f]	Nein	Ja	Ja	Ja[i]

[a]: European Chemicals Agency (2017a); PA 1-4 - Desinfektionsmittel, PA 6 - Schutzmittel für Produkte während der Lagerung, PA 7 – Beschichtungsschutzmittel, PA 8 – Holzschutzmittel, PA 9 - Schutzmittel für Fasern, Leder, Gummi und polymerisierte Materialien, PA 10 - Schutzmittel für Baumaterialien, PA 18 - Insektizide, Akarizide und Produkte gegen andere Arthropoden, PA 19 - Repellentien und Lockmittel, PA 22 - Flüssigkeiten für Einbalsamierung

[b]: European Commission (2017)

[c]: als Konservierungsmittel, European Union (2009), Anhang V

[d]: European Chemicals Agency (2017b)

[e]: Medizinische Medien Informations GmbH (2017)

[f]: Während der Inventarisierung erlaubt in PA 1 (European Chemicals Agency 2017a)

[g]: Keine Produkt in Deutschland erlaubt

[h]: Synergist (European Commission 2017)

[i]: Produkte in Deutschland erlaubt

3.4 Probenahme

Für die Probenahme wurden im Wohngebiet A zwei Probenahmestellen gewählt (Abbildung 2). Die erste Probenahmestelle befand sich kurz vor dem Auslass der Schmutzwasserleitung von Straße 1. Die zweite Probenahmestelle befand sich am Ende der Straße 2, ebenfalls kurz bevor die dortige Schmutzwasserleitung auf den Hauptabwasserkanal trifft. Die Proben wurden automatisiert mit einem Teledyne Isco 6712 Portable Sampler (Teledyne Isco, Lincoln, USA) genommen.

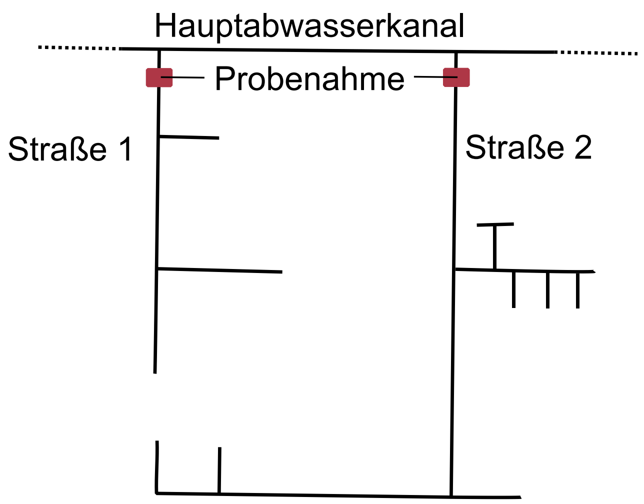

Abbildung 2: Probenahmestellen in Straße 1 und Straße 2 in Wohngebiet A

Die Probenahme erfolgte einmal pro Jahreszeit für jeweils ungefähr eine Woche. Dabei wurden 44 Tagesmischproben (14h-Mischproben) von 6 bis 20 Uhr mit einem Probenahmeintervall von 15 Minuten genommen. Zusätzlich wurden für morgens (6 bis 7 Uhr), mittags (12 bis 13 Uhr) und abends (19 bis 20 Uhr) jeweils eine Stundenprobe genommen, die ebenfalls mit einem Probenahmeintervall von 15 Minuten gezogen wurden (1h-Mischproben). Dies wurde an 12 Tagen durchgeführt. Weiterführende Informationen zu dem Vorgehen bei den Probenahmen sind im Artikel 3 zu finden.

3.5 Probenaufarbeitung und Analytik

Die Proben wurden in einer Kühltasche bei ca. 4°C transportiert und anschließend im Kühlschrank bei 4°C gelagert. Sie wurden nach der Probenahme in der Regel innerhalb eines Tages filtriert und das Filtrat und der Filterrückstand anschließend bei -20 °C gelagert. Vor der Analyse wurden die Filtrate mit einer Festphasenextraktion aufbereitet, die Filterrückstände wurden durch Ultraschall in einem mehrstufigen Extraktionsverfahren extrahiert. Die quantitative Bestimmung der Analyten erfolgte mit Hilfe interner Standards und LC-MS/MS. Weiterführende Informationen zu der verwendeten analytischen Methode sind in Artikel 3 zu finden.

4 Ergebnisse

4.1 Einsatz biozider Wirkstoffe in Haushaltsprodukten

In Artikel 1 werden die Ergebnisse der Produktinventarisierung im Detail diskutiert. Im Rahmen der Studie wurden in den Wohngebieten insgesamt 2 963 Produkte in 131 Haushalten gescannt. Für 93,4 % dieser Produkte konnten die Inhaltstoffe im Internet recherchiert werden. Wasch- und Reinigungsmittel (48 %) und Körperpflegeprodukte (43 %) stellten den größten Anteil der Produkte dar, 7 % der Produkte waren Biozidprodukte.

Biozidprodukte wurden in 75 % der Haushalte inventarisiert, im Durchschnitt wurden 1,7 dieser Produkte pro Haushalt gefunden. Am weitesten verbreitet waren Desinfektionsmittel (PA 1-4), gefolgt von Insektiziden (PA 18) und Repellentien (PA 19). Haushalte aus dem städtischen Wohngebiet C besaßen signifikant mehr Oberflächendesinfektionsmittel (PA 2) als die beiden anderen Wohngebiete. Auch der Bildungsabschluss des Haushaltsmitgliedes mit dem höchsten Einkommen korreliert signifikant ($p<0{,}05$) mit der Anzahl der gescannten Desinfektionsmittel. Je höher der Bildungsabschluss war, desto mehr Desinfektionsmittel waren im jeweiligen Haushalt zu finden. Für Insektizide galt das Gegenteil, je höher die Ausbildung, desto weniger Insektizide wurden genutzt. Insektizide wurden signifikant häufiger in Einfamilienhäusern als in Wohnungen inventarisiert. Dies ist vermutlich auf die dörfliche Lage der Häuser mit angrenzenden Gärten zurückzuführen, da in solchen Lagen leichter Insekten eingeschleppt werden können. Repellentien wurden insbesondere in Haushalten gefunden, deren Mitglieder Tiere mit Fell, Kinder zwischen 3 und 6 Jahren oder ein höheres Haushaltsnettoeinkommen hatten.

Insgesamt wurden 79 verschiedene biozide Wirkstoffe 4 106-mal auf den Produkten gelistet (European Chemicals Agency 2015). Biozide Wirkstoffe wurden in allen Haushalten gefunden, am häufigsten wurden die Wirkstoffe auf Wasch- und Reinigungsmitteln (41 % der Wirkstofflistungen) und Körperpflegeprodukten (49 %) gelistet (Abbildung 3). Auf diesen Produkten waren insgesamt 42 verschiedene biozide Wirkstoffe zu finden. Der Einsatz von bioziden Wirkstoffen in Körperpflegeprodukten wird grundsätzlich nicht im Rahmen der Umweltrisikobewertung der Biozid-Verordnung bewertet, da diese Produkte durch Artikel 2(2j) der Biozid-Verordnung von dieser ausgenommen sind. Körperpflegeprodukte fallen unter die *Verordnung (EG) Nr. 1223/2009 über kosmetische Mittel*, die die Umweltrisikobewertung an die REACH-Verordnung delegiert (European Union 2009). Der Einsatz der bioziden Wirkstoffe in Wasch- und Reinigungsmitteln wird nur unter der Risikobewertung der Biozid-Verordnung betrachtet, wenn es sich um Konservierungsmittel handelt, die als Schutzmittel für Produkte während der Lagerung (PA 6) gelistet sind.

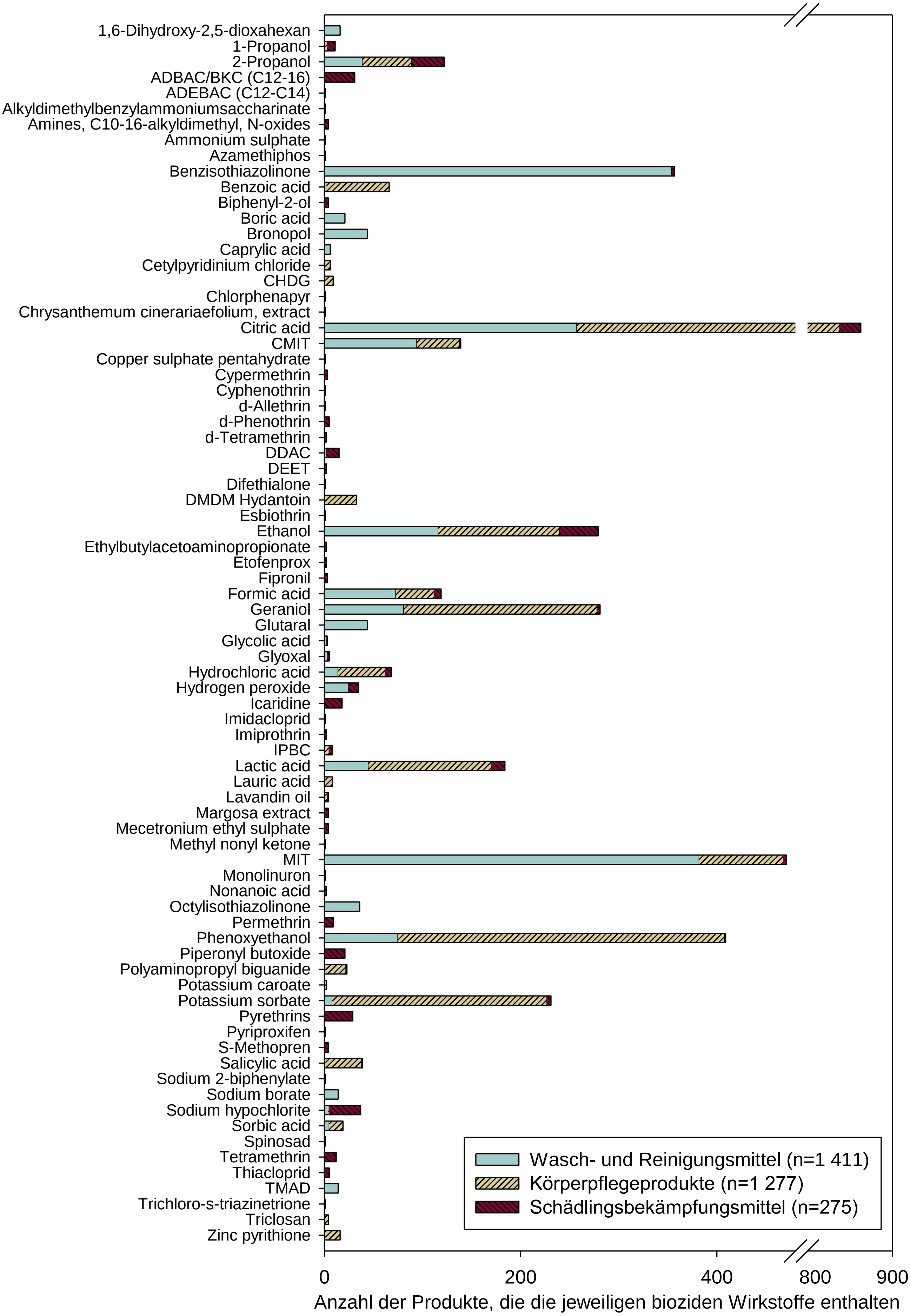

Abbildung 3: Inventarisierte biozide Wirkstoffe nach Produktkategorien

Für jeden der 79 bioziden Wirkstoffe wurde geprüft, ob dessen Verwendung in Wasch- und Reinigungsmitteln, Körperpflegeprodukten oder anderen Mitteln zur Bekämpfung von Schädlingen jeweils unter die Umweltrisikobewertung der Biozid-Verordnung fällt. Insgesamt fallen nur 36 % der inventarisierten Einsätze unter diese Risikobewertung.

1. Gemäß den Inhaltsstofflisten der **Wasch- und Reinigungsmittel** wurden dort 562-mal biozide Wirkstoffe verwendet, die derzeit nicht als Schutzmittel für Produkte während der Lagerung (PA 6) bewertet werden oder bereits bewertet worden sind. Dies stellt 14 % der inventarisierten Anwendungen biozider Wirkstoffe dar.
2. Auf den **Körperpflegeprodukten** wurden 2 023-mal biozide Wirkstoffe aufgelistet (49 %). Diese Anwendungen fallen generell nicht unter die Biozid-Verordnung.
3. Des Weiteren wurden 33-mal biozide Wirkstoffe in anderen **Schädlingsbekämpfungsmitteln** gefunden, die nicht unter die Biozid-Verordnung fallen (1 %).

Durch die Verwendung von bioziden Wirkstoffen in Anwendungen, die nicht unter die Biozid-Verordnung fallen, werden die Einträge von bioziden Wirkstoffen ins Abwasser während der Umweltrisikobewertung unterschätzt. Dies ist für 64 % der Anwendungen der Fall. Einige dieser Anwendungen werden unter anderen gesetzlichen Regelungen hinsichtlich ihrer Umweltauswirkungen bewertet. Dies gilt zum Beispiel für den Einsatz der Wirkstoffe in Pflanzenschutzmitteln oder Körperpflegeprodukten. Während es sich jedoch bei der Pflanzenschutzmittel-Verordnung ebenfalls um ein Gesetzeswerk handelt, welches sich mit Produkten mit intendierter Wirkung auf Organismen befasst, ist dies bei Körperpflegeprodukten nicht der Fall. Hier wird die Umweltrisikobewertung unter REACH durchgeführt, einer Gesetzgebung für Stoffe ohne beabsichtigte Wirkung. Dies wurde bereits von Tarazona (2014) kritisiert.

Doch selbst wenn alle Anwendungen der bioziden Wirkstoffe unter den unterschiedlichen Gesetzgebungen ausführlich bewertet werden würden, so würden die Umweltrisiken immer noch unterschätzt werden. Diese Unterschätzung resultiert daraus, dass den Wirkwerten innerhalb der einzelnen Risikobewertungen zu geringe berechnete Expositionsdaten gegenübergestellt werden. Für eine realistischere Umweltrisikobewertung müssten die Emissionen aus allen Produktkategorien addiert werden. Eine derartige aggregierte Expositionsberechnung wird derzeit jedoch nicht praktiziert (Dudzina et al. 2015). Dieses Beispiel zeigt die Grenzen der regulatorischen Risikobewertung: Obwohl die Komplexität der Bewertung bereits sehr hoch ist, gibt es immer noch blinde Flecken, die mit den bestehenden Methoden der Umweltrisikobewertung nicht erfasst werden (Backhaus et al. 2010).

4.2 Wahrnehmung von Biozidprodukten durch die Haushaltsmitglieder

Mittels eines Fragebogens wurden Mitglieder der besuchten Haushalte zu ihrer Wahrnehmung von Biozidprodukten und ihren Informationsquellen zu Schädlingen befragt. Die Ergebnisse werden im Detail in Artikel 2 diskutiert.

Zunächst wurden die Befragten nach ihrem Verständnis des Begriffes „Biozid" gefragt, anschließend wurde der Begriff ihnen für die weitere Beantwortung des Fragebogens erklärt. 39 % der Befragten hatten den Begriff noch nie zuvor gehört. Die Ergebnisse unterscheiden sich sehr zwischen den unterschiedlichen Wohngebieten, im Wohngebiet A gab die Mehrheit der Befragten an, den Begriff bereits gehört zu haben, in den Wohngebieten B und C nur eine Minderheit. Auch die Schulbildung hat einen Einfluss darauf, ob der Begriff bekannt ist. Je höher der Schulabschluss, desto eher wurde angegeben, dass der Begriff schon einmal gehört wurde. In den Wohngebieten A und B wurden die Befragten anschließend mittels einer offenen Frage gefragt, was sie unter dem Begriff „Biozid" verstehen würden (Tabelle 2). Im Wohngebiet C wurde diese Frage von der interviewenden Person nicht gestellt. 29 % verstehen unter dem Begriff „etwas Biologisches/ökologische Schädlingsbekämpfung", während nur 21 % bei dem Begriff an „Gift/Schädlingsbekämpfung" dachten. Dieses Missverständnis liegt vermutlich an dem deutschen Präfix „bio", der im Allgemeinen für ökologisch angebaute Produkte steht. Während die Befragten den Begriff als positive Metapher interpretierten, dachte die Legislative an die wörtliche Bedeutung des Begriffes: „tötet Leben". Dieses, von der Gesetzgebung unbeabsichtigte, metaphorische Missverständnis hat vermutlich direkten Einfluss auf die Nutzung von Biozidprodukten, da Metaphern starken Einfluss auf das Handeln haben (Lakoff und Johnson 2014). Die missverständliche Wortwahl erschwert deshalb vermutlich die Risikokommunikation in Deutschland und anderen Ländern, in denen das Präfix „bio" ähnlich positiv belegt ist. Weiterhin wird die Risikokommunikation mittels des Begriffes „Biozid" dadurch erschwert, dass 28 % der Befragten gar keine Idee äußern konnten, was der Begriff bedeuten könnte.

Tabelle 2: Antworten auf die Frage, was der Begriff „Biozid" bedeuten könnte

Kategorisierte Antworten	n	%
„Etwas Biologisches/ ökologische Schädlingsbekämpfung"	33	29
„Keine Idee"	32	28
„Gift/Schädlingsbekämpfung"	24	21
„Etwas Negatives"	12	11
Zuordnung zu anderen Produktkategorien, wie z.B. Wasch- und Reinigungsmittel	7	6
Andere Antworten	5	4

Nach diesen einleitenden Fragen wurde den Befragten der Begriff „Biozid" erläutert. Sie wurden gebeten, die Produktkategorien Biozidprodukte, Pflanzenschutzmittel, Wasch- und Reinigungsmittel und Körperpflegeprodukte hinsichtlich der empfundenen Gefahr zu ordnen. Die als am gefährlichsten eingeschätzte Kategorie sollte auf Platz 1 eingeordnet werden und die am wenigsten gefährlichste auf Platz 4 (Abbildung 4). Grundsätzlich wurden Wasch- und Reinigungsmittel und Körperpflegeprodukte als am wenigsten gefährlich angesehen. Die Reihenfolge dieser beiden Kategorien blieb in allen Wohngebieten gleich, während die Reihenfolge von Biozidprodukten und Pflanzenschutzmitteln schwankte. Im ländlichen Wohngebiet A wurden Pflanzenschutzmittel als am gefährlichsten wahrgenommen und im städtischen Wohngebiet C Biozidprodukte. Dies könnte daran liegen, dass im Wohngebiet A ein höherer Anteil den Begriff „Biozid“ schon einmal gehört hatte. Grundsätzlich werden Produkte, mit denen man vertrauter ist, als weniger gefährlich wahrgenommen (European Chemicals Agency 2012). Andererseits sind die Befragten im Wohngebiet A ebenfalls stärker mit Pflanzenschutzmitteln vertraut, da nur in diesem Wohngebiet Pflanzenschutzmittel inventarisiert wurden.

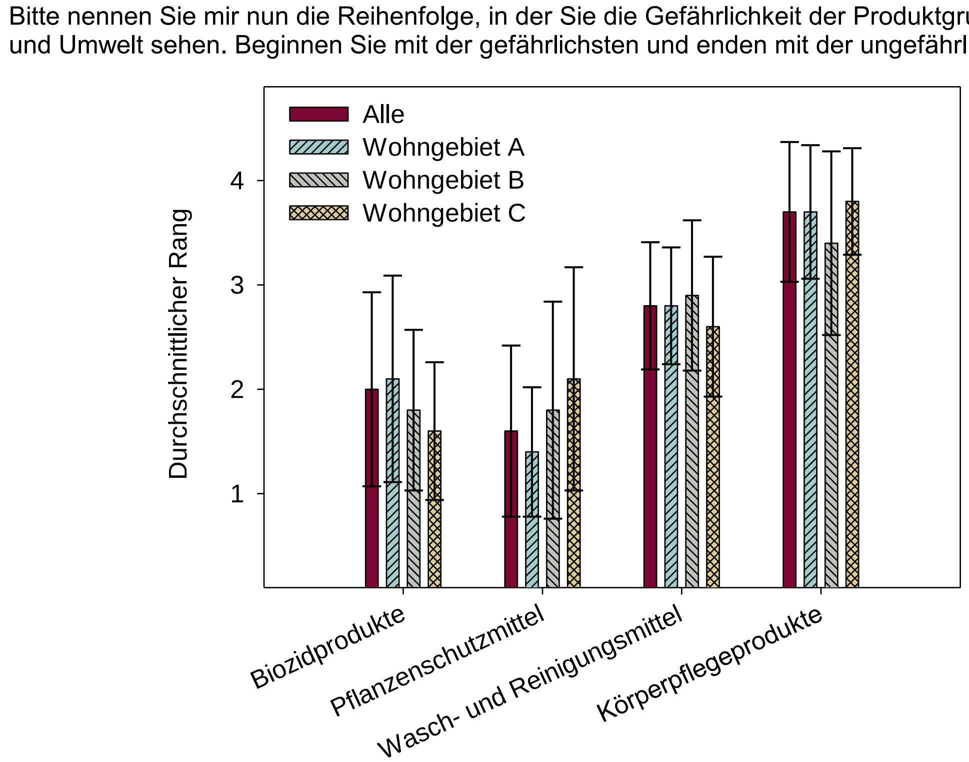

Abbildung 4: Ranking der Produktkategorien hinsichtlich der empfundenen Gefahr (mit Standardfehler, n=133)

Alle Befragten wurden gebeten anzugeben, welche Biozidprodukte sie besaßen. Basierend auf den Angaben der Befragten waren Produkte der folgenden bioziden Produktarten in den Haushalten vorhanden: Desinfektionsmittel (PA 1, 2, 3, 4, 5), Schutzmittel für Fassaden (PA 7, 10), Holzschutzmittel (PA 8), Rodentizide (PA 14), Insektizide (PA 18), Repellentien (PA 19) und Einbalsamierungsmittel (PA 22). Diese Ergebnisse wurden den Inventaren (siehe Artikel 1) gegenübergestellt, die ebenfalls für die Haushalte erstellt wurden. In 80 % der Haushalte stimmten die Produktangaben und -inventare nicht vollständig überein. Insbesondere Oberflächendesinfektionsmittel (PA 2) wurden von den Haushaltsmitgliedern oft nicht angegeben, obwohl sie im Haushalt vorhanden waren. Dies kann als Hinweis darauf verstanden werden, dass sich die Befragten der Nutzung von Reinigungsmitteln mit desinfizierender Wirkung nicht immer bewusst sind. Saisonal genutzte Biozidprodukte wie Insektizide oder Repellentien wurden von den Befragten oft genannt, aber nicht inventarisiert. Dies zeigt die begrenzte

Nutzbarkeit der zwei Methoden zur Charakterisierung von Haushalten, einerseits von Produktinventaren und andererseits der Befragungen. Beide Methoden können einzeln keine vollständige Übersicht der vorhandenen Produkte geben. Die Notwendigkeit der Kombination von verschiedenen Erhebungsinstrumenten wurde bereits von Eriksson et al. (2003) diskutiert.

Die Ergebnisse des Fragebogens zeigen auch, dass insbesondere Informationen zur Kontrolle von Insekten, Schimmel und Bakterien für die Befragten relevant wären, weil diese Schäd- und Lästlinge am häufigsten auftreten. Informationsmaterialen im Internet zu biozidfreien bzw. zu präventiven Maßnahmen gegen diese Organismen haben vermutlich die größte Reichweite. Das Internet wurde im Rahmen der Befragung von 69 % als die Quelle angegeben, in der die Befragten nach Informationen zur Bekämpfung von Schädlingen suchen würden. Dabei werden vor allem Suchmaschinen genutzt, was deutlich macht, dass die Verwendung von bekannten Begriffen auf Webseiten wichtig ist. Während in Deutschland die Bevölkerung von behördlicher Seite auf dem Biozid-Portal www.biozid.info über präventive und alternative Maßnahmen aufgeklärt wird, wird die dänische Bevölkerung über eine Kampagne namens „Biocider er hverdagsgifter“ (eigene Übersetzung: „Biozide sind Alltagsgifte“) informiert. Hier wird der künstliche Begriff „Biozid“ in Alltagssprache übersetzt. Dies erscheint in Anbetracht der oben beschriebenen Missdeutung des Biozid-Begriffs sinnvoll. Zur Information über bestimmte Produkte sind Etiketten die wichtigste Informationsquelle (Epp et al. 2010; European Commission 2011). Diese eignen sich jedoch nicht zur Information über präventive Maßnahmen. In den Antworten der Befragten zeichnete sich ab, dass die Etiketten jedoch zur Kommunikation von Risikominderungsmaßnahmen sehr wichtig sind. Ein Großteil der Befragten gab an, die Gebrauchsanweisung auf den Etiketten immer oder meistens zu lesen. Sie nannten eine zu kleine Schriftgröße oder unverständliche Angaben als Hindernisse zur Befolgung der Anweisungen.

Grundsätzlich sahen die Befragten es als wichtig an, Maßnahmen zu ergreifen, die die Chemikalienkonzentrationen in Oberflächengewässern senken können. Besonders Verhaltensänderungen der Bevölkerung und gesetzliche Auflagen für die Hersteller wurden als wichtige Maßnahmen bewertet. Eine bessere technische Ausrüstung von Kläranlagen wurden dagegen für weniger sinnvoll gehalten. Dies zeigt ein grundsätzliches Verständnis der Befragten für eine Reduktion von Emissionen an der Quelle anstatt eines ausschließlichen Einsatzes von „end-of-pipe“ Technologien. Ein ähnlicher Trend wurde bereits von Stemplewski et al. (2014) beobachtet. Es ist jedoch fraglich, ob die Bevölkerung derzeit über Kommunikationsmaßnahmen zu den Risiken durch biozide Wirkstoffe erreicht werden kann, um Verhaltensänderungen zu erreichen. Die Ergebnisse zeigen, dass es häufig schon am Verständnis des Begriffes „Biozid“ mangelt und die Befragten sich des Einsatzes von Biozidprodukten unter Umständen nicht bewusst sind. Es fehlen deshalb Ansatzpunkte, an die bei Informationskampagnen angeknüpft werden könnte. Man sollte überlegen, ob zum Schutz der exponierten Personen Maßnahmen ergriffen werden müssen, die die Exposition gegenüber bioziden Wirkstoffen auf anderen Wegen reduzieren können. Derartige Maßnahmen können beispielsweise Verkaufsbeschränkungen oder die Substitution bestimmter Wirkstoffe sein.

4.3 Eintrag biozider Wirkstoffe aus Haushaltsprodukten in das Abwasser

Die Abwasserproben des Wohngebiets A wurden auf 14 verschiedene biozide Wirkstoffe untersucht. Die Ergebnisse werden detailliert im Artikel 3 dargestellt und diskutiert. In den 14h-Mischproben wurden 10 Substanzen in mindestens 10 % der Proben gefunden (Tabelle 3). Lediglich CMIT, DCOIT, PBO und TET wurden nicht oberhalb der Bestimmungsgrenze (LOQ) gemessen.

Tabelle 3: Gesamtkonzentrationen und Häufigkeiten der Nachweise der Wirkstoffe

	BIT	BKC	CAR	CMIT	DCOIT	DEET	DIU	ICA	OIT	PBO	TCS	TEB	TER	TET
							Straße 1							
Nachweis in Proben [n=19; %]	100	100	15	0	0	100	0	100	5	0	95	0	11	0
Maximum C_{total} [ng/L]	6 261	15 340	47	0	0	12 808	0	436	16	0	319	0	2	0
Durchschnitt C_{total} [ng/L]	1 750	4 740	4	0	0	2 121	0	180	1	0	139	0	0.17	0
Standardabweichung C_{total} [ng/L]	1 624	3 985	13	0	0	3 649	0	141	4	0	118	0	0.6	0
							Straße 2							
Nachweis in Proben [n=25; %]	100	100	56	0	0	100	60	100	20	0	100	6	100	0
Maximum C_{total} [ng/L]	2 885	19 090	268	0	0	4 401	11	6 452	13	0	928	2	465	0
Durchschnitt C_{total} [ng/L]	980	7 756	38	0	0	718	30	1 517	7	0	386	7	85	0
Standardabweichung C_{total} [ng/L]	623	4 909	71	0	0	1 218	37	2 068	28	0	207	6	123	0

Die 1h-Proben zeigen unterschiedliche Emissionsmuster der verschiedenen Substanzen, diese sind aber nur für DEET und BKC signifikant unterschiedlich. Beide zeigen mittags deutlich höhere Abwasserkonzentrationen als morgens. Ein ähnliches Muster ist bei den gemessenen BIT-Konzentrationen zu sehen. Die Produktinventare zeigen, dass BKC und BIT häufig in Oberflächendesinfektionsmitteln bzw. Wasch- und Reinigungsmitteln eingesetzt werden. Diese werden im Wohngebiet A vermutlich eher tagsüber als in den Morgen- oder Abendstunden verwendet, da in diesem Wohngebiet viele Bewohner nicht mehr berufstätig sind. Emissionsmuster und die Produktinventare deuten hier also beide daraufhin, dass diese Wirkstoffe vor allem durch Putzen und Waschen eingetragen werden. Dies wurde für BKC bereits vermutet (Butkovskyi et al. 2016). Nimmt man an, dass ähnliche Emissionsmuster darauf hindeuten, dass die Wirkstoffe durch die gleichen Produkte oder Aktivitäten eingetragen werden, so ist zu vermuten, dass auch DEET, welches seine Konzentrationsmaxima auch mittags hat, vor allem durch Waschen eingetragen wird.

Der maßgebliche Einsatz von Repellentien gegen Mücken und Zecken im Sommer spiegelt sich in den deutlich höheren Konzentrationen von DEET und ICA im Sommer wieder, die auch schon vorher beobachtet wurden (Engelmann 2016; Merel et al. 2015). Beide Wirkstoffe werden jedoch das ganze Jahr über in allen Proben gemessen, obwohl der Einsatz der Produkte in Deutschland eher saisonal ist (Abbildung 5). Um mögliche Gründe für das durchgehende Auftreten der beiden Wirkstoffe zu finden, wurde das Waschwasser von Wäsche untersucht, die während der Applikation ICA- und DEET-haltiger Produkte getragen wurde. Die Ergebnisse zeigen, dass die Wirkstoffe auch nach drei Waschgängen noch aus der Wäsche ausgetragen werden. Dies kann eine mögliche Erklärung dafür sein, dass die Wirkstoffe auch im Winter, in allerdings deutlich geringeren Konzentrationen, die zudem über den Herbst abnehmen, im Abwasser gemessen werden konnten.

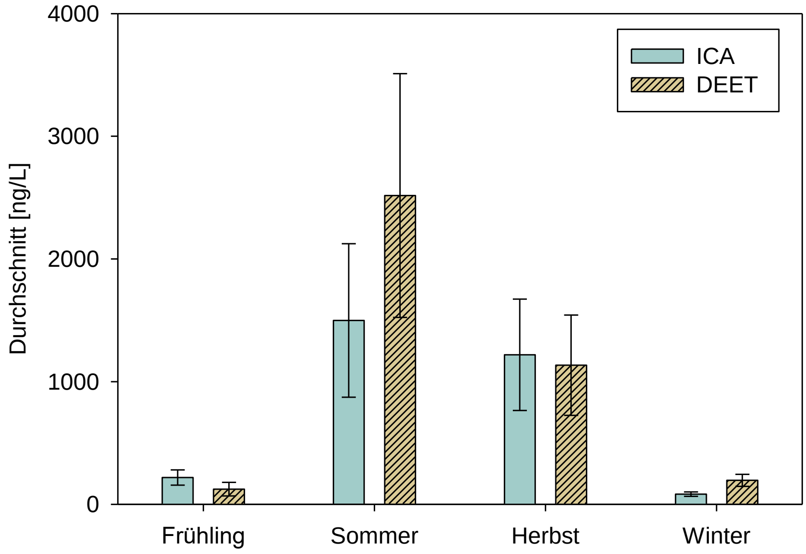

Abbildung 5: Saisonale Unterschiede der Konzentrationen von ICA und DEET in den 14h-Proben (mit Standardfehler, Frühling: n=7; Sommer: n=13; Herbst: n=13; Winter: n=11)

Anders als ICA und DEET, die nur über Biozidprodukte eingetragen werden, scheinen die wichtigsten Emissionsquellen von TCS Körperpflegeprodukte zu sein. Bei der Inventarisierung wurde der Wirkstoff ausschließlich in Zahnpasta gefunden. Die gemessenen TCS-Konzentrationen von im Durchschnitt 303 ± 212 ng/L können laut Expositionsberechnungen aus den inventarisierten Zahnpastatuben resultieren. Diese Hypothese wird dadurch unterstützt, dass die TCS-Konzentrationen in der Straße 2 deutlich höher waren als in Straße 1 und die TCS-haltigen Zahnpastatuben ausschließlich in Straße 2 inventarisiert wurden. Dass dennoch TCS auch im Abwasser von Straße 1 oberhalb der Nachweisgrenze gemessen werden konnte, kann daran liegen, dass in beiden Straßen nicht alle Haushalte an der Befragung teilgenommen haben. Deshalb kann auch in Straße 1 TCS-haltige Zahnpasta vorhanden gewesen sein. Auch Deodorants und medizinische Cremes könnten zusätzliche Quellen sein, diese wurden jedoch nicht inventarisiert. Zudem ist zu beachten, dass die Inventarisierung zu Beginn der Probenahme bereits ein Jahr zurücklag und sich die Produktzusammensetzung der Haushalte in der Zwischenzeit geändert haben kann. Während der Inventarisierung war die Verwendung von TCS in Desinfektionsmitteln für die persönliche Hygiene (PA 1), wie zum Beispiel Handdesinfektionsmittel, noch erlaubt, mittlerweile ist der Einsatz in Biozidprodukten jedoch vollständig verboten.

Neben den in den inventarisierten Produkten enthaltenen bioziden Wirkstoffen wurden auch die Wirkstoffe CAR, DIU, TEB und TER im Abwasser gemessen, die nicht in den Produkten gefunden wurden. Dabei handelt es sich um Materialschutzmittel, die zum Beispiel aus Farben, Putzen oder auch Silikondichtungen ausgewaschen, und so ins Abwasser eingetragen werden können (Burkhardt et al. 2007). Häufig werden sie als Materialschutzmittel im Außenbereich eingesetzt, zum Beispiel in Fassadenfarben. Grundsätzlich dürften aus dem Außenbereich durch Regen ausgewaschene Stoffe nicht im untersuchten Abwasser zu finden sein, da es sich um eine Trennkanalisation handelt, in der das Regenwasser getrennt vom häuslichen Abwasser geführt wird. Untersuchungen des örtlichen Wegezweckverbandes nach Abschluss der Messungen zeigten jedoch, dass ein Fehlanschluss in Straße 2 vorlag, durch welchen Regenwasser in das häusliche Abwasser eingeleitet wurde. Dieser Fehlanschluss kann die Funde der Materialschutzmittel in den Proben erklären.

Die Ergebnisse der Messungen und Produktinventare zeigen, dass der Einsatz der gemessenen Wirkstoffe unter unterschiedliche Regelungsbereiche fällt und für die Bevölkerung nicht immer ersichtlich ist:

- **Einsatz in Biozidprodukten**: Einige Wirkstoffe wie ICA, DEET oder BKC werden hauptsächlich über die Verwendung von Biozidprodukten eingetragen. Diese Produkte fallen unter die Biozid-Verordnung.
- **Einsatz in Wasch- und Reinigungsmitteln**: Der Einsatz von BIT und OIT als Konservierungsmittel in Wasch- und Reinigungsmitteln fällt zwar unter die Umweltrisikobewertung der Biozid-Verordnung, für die Bevölkerung ist aber nicht offensichtlich, dass es sich dabei um ein Produkt handelt, das auch biozide Wirkstoffe enthält und entsprechend verantwortungsvoll zu nutzen ist.
- **Einsatz in Körperpflegeprodukten**: TCS wird vor allem über den Einsatz von Körperpflegeprodukten eingetragen, der nicht unter die Biozid-Verordnung fällt.
- **Einsatz in Baumaterialien**: Substanzen, die zum Schutz von Materialien eingesetzt werden (CAR, DIU, TEB und TER), fallen unter die Biozid-Verordnung. Ihr Einsatz ist den Haushaltsmitgliedern jedoch in der Regel nicht bekannt.

Abhängig von der Substanz müssen also unterschiedliche Maßnahmen ergriffen werden, um Emissionen biozider Wirkstoffe aus Haushalten wirksam minimieren zu können.

4.4 Verwendung der Produktinventare für andere Stoffgruppen - Duftstoffe

Um die Übertragbarkeit der Methode auf andere Stoffgruppen zu überprüfen, wurde in den erhobenen Produktinventaren zusätzlich geprüft, welche allergenen Duftstoffe auf Wasch- und Reinigungsmitteln deklariert wurden. Die Auswertung wird ausführlich in Artikel 4 diskutiert. Die 26 Duftstoffe, die laut der Detergenzien-Verordnung auf den Verpackungen angegeben werden müssen, wurden fast 2 000-mal gelistet, im Durchschnitt enthielt jedes Wasch- und Reinigungsmittel 1,4 allergene Duftstoffe. 46 % der inventarisierten Wasch- und Reinigungsmittel enthielten mindestens einen der allergenen Duftstoffe. Limonene, Hexylcinnamal und Butylphenyl methylpropional wurden am häufigsten genannt. Die maximale Anzahl allergener Duftstoffe in einem Wasch- und Reinigungsmittel war acht.

Mittels hierarchischer Clusteranalyse wurde untersucht, welche allergenen Duftstoffe häufig gemeinsam verwendet werden. Innerhalb eines Produktes wurden Hexyl cinnamal und Butylphenyl methylpropional am häufigsten zusammen in Inhaltsstofflisten genannt. Betrachtet man alle in einem Haushalt vorhandenen allergenen Duftstoffe in Wasch- und Reinigungsmitteln, traten Eugenol, Coumarin und Cinnamyl alcohol am häufigsten gemeinsam auf. Die Wirkung dieser gemeinsam auftretenden Duftstoff-Mischungen sollte aus diesem Grund genauer untersucht werden.

Die Ergebnisse zeigen, dass Wasch- und Reinigungsmittel bei der Einschätzung der Exposition der Bevölkerung gegenüber allergenen Duftstoffen berücksichtigt werden müssen. Dies wird in aktuellen Risikobetrachtungen oft vernachlässigt. Um die Exposition realitätsnah abschätzen zu können, müssten Wasch- und Reinigungsmittel in bestehende Expositionsmodelle integriert werden (Comiskey et al. 2017; Safford et al. 2017).

5 Schlussfolgerungen und Empfehlungen

Ziel dieser Arbeit war es, Emissionsquellen biozider Wirkstoffe in Haushalten zu identifizieren. Zu diesem Zwecke wurden Haushaltsmitglieder innerhalb eines Wohngebiets im Norden Deutschlands dazu befragt, was sie mit Bioziden verbinden, wie sie deren Risiken einschätzen und was für Biozidprodukte sie nutzen. Zudem wurden für die Haushalte Produktinventare erstellt, um herauszufinden, in welchen Produktkategorien welche Wirkstoffe tatsächlich verwendet werden. Zur Überprüfung der Inventare wurde das Abwasser des Wohngebietes nach der Inventarisierung untersucht und die Ergebnisse dieser Analysen mit den Produktinventaren verglichen.

Diese Methode der Inventarisierung ist auch für andere Stoffgruppen nutzbar, so lange Angaben zu den Stoffen auf Etiketten Pflicht sind. Dieses konnte am Beispiel der Duftstoffe gezeigt und bestätigt werden. Produktinventare sollten jedoch nicht ausschließlich zur Charakterisierung von Abwasser herangezogen werden. Dieses könnte dazu führen, dass bestimmte Emissionen vernachlässigt werden.

Die Ergebnisse zeigen, dass Haushalte eine wichtige Emissionsquelle für biozide Wirkstoffe in das Abwasser darstellen – neben bekannten Emissionsquellen aus Außenanwendungen, wie zum Beispiel Fassaden. Dies bestätigt Vermutungen vorheriger Studien (Bollmann et al. 2014a; Launay et al. 2016; Wittmer et al. 2010). Durch die besonderen Gegebenheiten des Studiengebiets konnten auch Erkenntnisse darüber gewonnen werden, welche Konzentrationen durch die Innenraumanwendung der Wirkstoffe erwartet werden können und welche saisonalen Variationen durch die Anwendung in Haushalten erklärt werden können. Dies kann Betreibern von Kläranlagen helfen, den Beitrag von spezifischen Emissionsquellen im Einzugsgebiet der Kläranlage besser einordnen zu können. So könnten mögliche Schwankungen und Anstiege in den Abwasserkonzentrationen, die von den beobachteten Emissionsmustern aus Innenraumanwendungen abweichen, einen Hinweis über andere Emissionsquellen in den Einzugsgebieten liefern. Die Produktinventare der Haushalte zeigen jedoch auch, dass die emittierten Substanzen je nach Wohngebiet sehr unterschiedlich sein können. So wurden in den städtischen Wohngebieten deutlich mehr Desinfektionsmittel inventarisiert, der Eintrag von BKC in urbanes Abwasser könnte zum Beispiel dementsprechend höher sein.

Zielgerichtete Maßnahmen zur Minderung von bioziden Wirkstoffen im Abwasser sind notwendig, da beispielsweise die in dieser Arbeit untersuchten Stoffe CAR, DEET, DIU, TEB, TER und TCS bereits im Ablauf deutscher Kläranlagen in Konzentrationen oberhalb der jeweiligen Qualitätsnorm gemessen wurden (Engelmann 2016). Es existieren zwei Konzepte, die an unterschiedlichen Stellen ansetzten, um den Eintrag dieser Stoffe in die Umwelt zu minimieren: zum einen die Reduktion von Schadstoffen an der Quelle, zum anderen eine verbesserte Elimination in der Kläranlage durch nachgeschaltete Maßnahmen. Zum Beispiel kann die Reinigungsleistung von Kläranlagen durch zusätzliche Reinigungsstufen, wie zum Beispiel Aktivkohlefilter oder die erweiterte Oxidation verbessert werden (Ribeiro et al. 2015). Dieser Weg wird derzeit von der Schweiz beschritten. In Deutschland könnten derartige Aufrüstungen über eine Erhöhung der Abwasserabgabe finanziert werden (Gawel et al. 2015). Behandlungen wie Ozonierung oder UV-Bestrahlung bauen die Schadstoffe jedoch oft nicht vollständig ab, sondern tragen zur Bildung von Transformationsprodukten bei (Alfiya et al. 2017; Herrmann et al. 2016; Herrmann et al. 2015a; Lutterbeck et al. 2015). Die Eigenschaften dieser Transformationsprodukte sind oft nicht bekannt, *in-silico*-Ergebnisse deuten bei einigen Produkten jedoch darauf hin, dass die Toxizität im Vergleich zur Ausgangssubstanz erhöht sein kann.

Aus diesen Gründen sollten derartige nachgeschaltete Maßnahmen nur dann eingesetzt werden, wenn Maßnahmen an der Quelle nicht ausreichen oder gar nicht möglich sind (Hillenbrand und Tettenborn 2017). Maßnahmen zur Reduzierung von Emissionen aus Haushalten können bei den Herstellern von Produkten oder Chemikalien oder den anwendenden Personen ansetzen. Die in dieser Arbeit dokumentierten komplexen Anwendungsmuster biozider Wirkstoffe in Haushalten machen es den Haushaltsmitgliedern schwer, zu verstehen, wann sie biozide Wirkstoffe anwenden und bei der Handhabung entsprechende Vorsicht walten lassen sollten. Die Ergebnisse der Befragung zeigen, dass vielen Befragten selbst grundlegendes Wissen über Biozidprodukte fehlt, der Begriff „Biozid" ist weitestgehend unbekannt bzw. missverstanden. Ob Emissionsminderungsmaßnahmen, die bei Verhaltensänderungen der Bevölkerung durch Information oder Sensibilisierung ansetzen, erfolgsversprechend sind, ist deshalb fraglich. Kampagnen müssten hier zunächst einmal ein entsprechendes Bewusstsein schaffen. Dass Kampagnen einen positiven Einfluss auf die Angaben von Befragten haben können, wurde bereits gezeigt (Lippeverband 2016). Allerdings steht der Nachweis, dass aus dem Wissen auch veränderte Handlungen resultieren, noch aus. Untersuchungen, die Produktinventare oder Abwasserkonzentrationen vor und nach Aufklärungskampagnen untersuchen, könnten hier weitere Informationen liefern.

Gemeinsam mit Informationskampagnen könnten zusätzliche Maßnahmen einen größeren Effekt auf die Anwendung biozider Wirkstoffe in Haushalten haben. Der Preis eines Produktes ist ein erheblicher Faktor bei der Auswahl von Haushaltsprodukten (Glegg und Richards 2007; Howells 2005; Kollmuss und Agyeman 2002). Aus diesem Grund könnte eine Abgabe auf Produkte, die biozide Wirkstoffe enthalten, ein wirksames Instrument sein. In Dänemark gibt es bereits eine Abgabe für Biozidprodukte (Skatteministeriet 2015) und eine risikobasierte Abgabe für Pflanzenschutzmittel ist in Deutschland in der Diskussion (Möckel et al. 2015). Derartige Abgaben könnten für Hersteller beispielsweise ein Anreiz sein, Packungsgrößen so anzupassen, dass der Zusatz von Konservierungsmitteln nicht mehr nötig ist, weil die Produkte schneller verbraucht werden. Im Rahmen von Life-Cycle-Assessments ist jedoch abzuwägen, ob der damit verbundene erhöhte Ressourcenaufwand für Verpackungen derartige Maßnahmen sinnvoll erscheinen lässt. Weitere Instrumente, um die Anwendung von Biozidprodukten auf das notwendige Mindestmaß zu beschränken, könnten ein Selbstbedienungsverbot für bestimmte Biozidprodukte oder Verkaufsverbote im Internet sein. Auch Ökolabel für alternative oder präventive Maßnahmen könnten weiter gefördert werden. In Deutschland existiert ein „Blauer Engel"-Ökolabel für Schädlingsbekämpfung im Innenraum, das den Gebrauch biozider Wirkstoffe ausdrücklich ausschließt (RAL gGmbH

2011). Dieses Label beinhaltet präventive Maßnahmen, wie Fliegengitter, oder alternative Maßnahmen, wie biozidfreie Fruchtfliegenfallen. Der Einsatz des Blauen Engels könnte für die Kaufenden ein wichtiges Kaufkriterium sein, da dieses Label eine hohe Glaubwürdigkeit besitzt (Glegg und Richards 2007; Stieß und Birzle-Harder 2013). Ökolabel eignen sich jedoch nicht zur Bewerbung genereller präventiver Maßnahmen gegen Schädlinge, wie zum Beispiel das Lagern von Essen in geschlossenen Behältnissen oder gute Hygienestandards. Aus diesem Grund dürfen derartige Labels nicht das einzige Kommunikationsinstrument sein.

Weitere Maßnahmen sollten früher in der Wertschöpfungskette ansetzen, dies könnte zum Beispiel die Substitution bestimmter Wirkstoffe im Rahmen der Formulierung von Produkten sein. Wirkstoffe, die hinsichtlich ihrer Abbaubarkeit strukturell optimiert wurden, könnten bevorzugt eingesetzt werden. Als letztes Instrument zur Reduktion des Einsatzes von bioziden Wirkstoffen könnten auch generelle Verbote bestimmter Anwendungen erlassen werden. Dies wurde in den Vereinigten Staaten von Amerika für Handdesinfektionsmittel im nicht-professionellen Bereich praktiziert. Der Einsatz von 19 desinfizierenden Wirkstoffen wurde verboten, da die vermarktenden Firmen keine Daten einreichen konnten, um zu zeigen, dass es einen zusätzlichen Nutzen durch den Einsatz der Produkte im Vergleich zum Händewaschen mit normaler Seife gibt (Food and Drug Administration 2016). Diese Regulierung geht deutlich weiter als die bestehende EU-Gesetzgebung, wo ein fehlender Nutzen des eingesetzten bioziden Wirkstoffes noch kein Grund ist, eine Produktzulassung zu versagen. Da in Artikel 17(5) der Biozid-Verordnung bereits gefordert wird, dass „[…] der Einsatz von Biozidprodukten auf das notwendige Mindestmaß begrenzt wird […]“, könnte eine breitere Interpretation dieses Artikels als Ausgangspunkt derartiger Regulierungen dienen.

Grundsätzlich werden bereits heute die Umweltrisiken der bioziden Wirkstoffe durch die Umweltrisikobewertung der Biozid-Verordnung im Rahmen der Produktzulassung reguliert. Die Ergebnisse der erstellten Produktinventare zeigen jedoch, dass als Quelle für biozide Wirkstoffe eine Vielzahl unterschiedlicher Produkte verantwortlich sein kann und dass diese Produkte nicht alle unter die Risikobewertung fallen. Die Untersuchung der Produktkategorien, die in den Haushalten biozide Wirkstoffe enthalten, deutet darauf hin, dass die Umweltrisikobewertung aktuell die Risiken unterschätzt. Grundsätzlich würde es die Umweltrisikobewertung erheblich realistischer machen, wenn alle Anwendungen eines Wirkstoffes gemeinsam betrachtet und bewertet werden würden (Evans et al. 2016). Dies würde allerdings einen Komplexitätsanstieg der Umweltrisikobewertung bedeuten, die im regulatorischen Alltag vermutlich nicht zu handhaben ist (Backhaus et al. 2010). Aus diesem Grund ist ein regulatorischer Maßnahmen-Baukasten wünschenswert, mit dem der Einsatz biozider Wirkstoffe in den unterschiedlichen Einsatzbereichen zielgerichtet auf die notwendigen Anwendungen reduziert werden kann. Dies wäre eine sinnvolle Umsetzung des Artikels 17(5). Für Pflanzenschutzmittel gibt es so einen Baukasten bereits mit der *Richtlinie 2009/128/EG über einen Aktionsrahmen der Gemeinschaft für die nachhaltige Verwendung von Pestiziden*. Dieser Maßnahmenkatalog könnte für die Anwendung biozider Wirkstoffe adaptiert werden (UBA 2014).

6 Fazit

Diese Arbeit liefert wichtige Erkenntnisse zur genaueren Beurteilung der Quellen biozider Wirkstoffe im häuslichen Abwasser. Ein Vergleich mit den Zielen, die in Kapitel 2 dargestellt wurden, liefert folgende Ergebnisse:

1. In jedem Haushalt war mindestens ein Produkt vorhanden, welches biozide Wirkstoffe enthielt. Dieses waren häufig Schutzmittel für Produkte während der Lagerung (PA 6).
2. In einem Großteil der Haushalte (75 %) waren Biozidprodukte vorhanden. Dabei stellten Desinfektionsmittel (PA 1-4), Insektizide (PA 18) und Repellentien (PA 19) den größten Anteil dar.
3. Nur 36% der beobachteten Anwendungen biozider Wirkstoffe fiel unter die Umweltrisikobewertung der Biozid-Verordnung. Der überwiegende Anteil der Anwendungen war dementsprechend nicht durch die Risikobewertung abgedeckt.
4. Insbesondere bei Desinfektionsmitteln und Insektiziden waren sich die Befragten der Nutzung von Biozidprodukten häufig nicht bewusst, der Begriff „Biozid" wurde oft missverstanden.
5. Die in den Haushalten häufig vorhandenen Schutzmittel für Produkte während der Lagerung konnten in bis zu 100 % der Abwasserproben nachgewiesen werden.
6. Biozide Wirkstoffe, die eher saisonal eingesetzt werden, wie beispielsweise Repellentien gegen Mücken (PA 19), wurden dennoch über das ganze Jahr hinweg in den Abwasserproben gemessen.

Die Ergebnisse belegen erstmals die Vermutung, dass in Haushalten wichtige Quellen für biozide Wirkstoffe im Abwasser vorhanden sind, die nicht vernachlässigt werden dürfen. Die innovative Kombination interdisziplinärer Methoden konnte zeigen, dass es in Haushalten zahlreiche Produkte gibt, aus denen biozide Wirkstoffe ins Abwasser eingetragen werden können und dass die Umweltrisikobewertung diese Emissionen derzeit unterschätzt. Diese Methoden sind auch für andere Stoffgruppen anwendbar, wie am Beispiel der Duftstoffe gezeigt werden konnte. Dank der umfangreichen und an die Emissionsmuster von Haushalten angepassten Probenahmestrategie und Substanzauswahl wurde das häusliche Abwasser erstmals umfangreich hinsichtlich biozider Wirkstoffe charakterisiert. Die dargestellten komplexen Eintragspfade und -quellen sind für die Befragten schwer zu durchschauen. Reduktionsmaßnahmen sollten sich deshalb nicht darauf beschränken, die Bevölkerung über Biozidprodukte aufzuklären und zu sensibilisieren. Um die Verschmutzung des Abwassers durch biozide Wirkstoffe wirksam zu reduzieren und damit einen kleinen Beitrag zur Einhaltung der Grenzen der planetaren Tragfähigkeit für chemische Verschmutzungen zu leisten, sollten geeignete Maßnahmenkonzepte vielmehr früher in der Wertschöpfungskette ansetzen.

7 Literatur

Alfiya, Y., Dubowski, Y., Friedler, E., Olsson, O., Westphal, J. (2017): Photodegradation of micropollutants using V-UV/UV-C processes; Triclosan as a model compound. Science of the Total Environment 601-602, 397–404

ANSES (2010): Exposition de la population generale aux residus de pesticides en France. In: https://www.anses.fr/fr/content/exposition-de-la-population-générale-aux-pesticides, 02.10.2017

Backhaus, T., Brooks, B. W., Kapustka, L. (2010): Chemical risk assessment: pressures, perceptions and expectations. Integrated Environmental Assessment and Management 6 (3), 323–324

Barco-Bonilla, N., Romero-González, R., Plaza-Bolaños, P., Garrido Frenich, A., Martínez Vidal, José Luis (2010): Analysis and study of the distribution of polar and non-polar pesticides in wastewater effluents from modern and conventional treatments. Journal of Chromatography A 1217 (50), 7817–7825

BBSR (2015): Raumbeobachtung. In: http://78.47.125.117/raumbeobachtung/#, 09.10.2015

BBSR (31.12.2009): Raumtypen 2010. In: http://www.bbsr.bund.de/BBSR/DE/Raumbeobachtung/Raumabgrenzungen/Raumtypen2010_vbg/Download_RefTypenLageSied.xls?__blob=publicationFile&v=2, 28.02.2017

Beck, U. (2017): Die Metamorphose der Welt. Suhrkamp, Berlin

Bennett, D. H., Wu, X. M., Teague, C. H., Lee, K., Cassady, D. L., Ritz, B., Hertz-Picciotto, I. (2012): Passive sampling methods to determine household and personal care product use. Journal of Exposure Science and Environmental Epidemiology 22 (2), 148–160

Bollmann, U. E., Tang, C., Eriksson, E., Jönsson, K., Vollertsen, J., Bester, K. (2014a): Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources. Water Research 60, 64–74

Bollmann, U. E., Vollertsen, J., Carmeliet, J., Bester, K. (2014b): Dynamics of biocide emissions from buildings in a suburban stormwater catchment - concentrations, mass loads and emission processes. Water Research 56, 66–76

Bruinen de Bruin, Y., Hakkinen, P. B., Lahaniatis, M., Papameletiou, D., del Pozo, C., Reina, V., van Engelen, J., Heinemeyer, G., Viso, A. C., Rodriguez, C., Jantunen, M. (2007): Risk management measures for chemicals in consumer products: documentation, assessment, and communication across the supply chain. Journal of Exposure Science and Environmental Epidemiology 17 Suppl 1, 55–66

Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (2017): Register of approved plant protection products (Verzeichnis zugelassener Pflanzenschutzmittel). In: https://apps2.bvl.bund.de/psm/jsp/index.jsp, 26.10.2017

Burkhardt, M., Kupper, T., Hean, S., Haag, R., Schmid, P., Kohler, M., Boller, M. (2007): Biocides used in building materials and their leaching behavior to sewer systems. Water Science and Technology 56 (12), 63–67

Butkovskyi, A., Rijnaarts, H. H. M., Zeeman, G., Hernandez Leal, L. (2016): Fate of personal care and household products in source separated sanitation. Journal of Hazardous Materials 320, 427–434

Chen, Z.-F., Ying, G.-G., Lai, H.-J., Chen, F., Su, H.-C., Liu, Y.-S., Peng, F.-Q., Zhao, J.-L. (2012): Determination of biocides in different environmental matrices by use of ultra-high-performance liquid chromatography-tandem mass spectrometry. Analytical and Bioanalytical Chemistry 404 (10), 3175–3188

Comiskey, D., Api, A. M., Barrett, C., Ellis, G., McNamara, C., O'Mahony, C., Robison, S. H., Rose, J., Safford, B., Smith, B., Tozer, S. (2017): Integrating habits and practices data for soaps, cosmetics and air care products into an existing aggregate exposure model. Regulatory Toxicology and Pharmacology 88, 144–156

Corcellas, C., Eljarrat, E., Barceló, D. (2015): First report of pyrethroid bioaccumulation in wild river fish: a case study in Iberian river basins (Spain). Environment International 75, 110–116

COWI (2009): Assessment of different options to adress risks from the use phase of biocides. In: ec.europa.eu/environment/archives/ppps/pdf/final_report0309.pdf, 03.08.2018

Daughton, C. G. (2014): The Matthew Effect and widely prescribed pharmaceuticals lacking environmental monitoring: case study of an exposure-assessment vulnerability. Science of the Total Environment 466-467, 315–325

Diamond, M. L., de Wit, Cynthia A, Molander, S., Scheringer, M., Backhaus, T., Lohmann, R., Arvidsson, R., Bergman, Å., Hauschild, M., Holoubek, I., Persson, L., Suzuki, N., Vighi, M., Zetzsch, C. (2015): Exploring the planetary boundary for chemical pollution. Environment International 78, 8–15

Dudzina, T., Delmaar, C. J. E., Biesterbos, J. W. H., Bakker, M. I., Bokkers, Bas G H, Scheepers, P. T. J., van Engelen, Jacqueline G M, Hungerbuehler, K., Goetz, N. von (2015): The probabilistic aggregate consumer exposure model (PACEM): validation and comparison to a lower-tier assessment for the cyclic siloxane D5. Environment International 79, 8–16

Engelmann, U. (2016): Biocidal active substances in municipal wastewater in Saxony (Biozid-Wirkstoffe in kommunalen Abwassereinleitungen in Sachsen). KA - Korrespondenz Abwasser, Abfall 5, 388-402

Epp, A., Hertel, R. F., Böl, G.-F. (03/2010): Chemie im Alltag. BfR-Wissenschaft 03/2010, Berlin

Eriksson, E., Auffahrt, K., Eilersen, A.-M., Henze, M., Ledin, A. (2003): Household chemicals and personal care products as sources for xenobiotic organic compounds in grey wastewater. Water SA 29 (2), 135–146

European Chemicals Agency (24.07.2017a): Biocidal active substances. In: https://echa.europa.eu/information-on-chemicals/biocidal-active-substances, 24.07.2017

European Chemicals Agency (2017b): Registered substances. In: https://echa.europa.eu/web/guest/information-on-chemicals/registered-substances, 24.07.2017

European Chemicals Agency (14.06.2015): Biocidal active substances. In: http://echa.europa.eu/information-on-chemicals/biocidal-active-substances;jsessionid=3A5ED4D17DE2F7E107A219F152954286.live2?p_auth=5gyycIgb&p_p_id=echarevbiocides_WAR_echarevbiocidesportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&_echarevbiocides_WAR_echarevbiocidesportlet_viewTab=Search&_echarevbiocides_WAR_echarevbiocidesportlet_javax.portlet.action=tabsAction&tabs1=Summary, 14.06.2015

European Chemicals Agency (2012): Communication on the safe use of chemicals. In: https://echa.europa.eu/documents/10162/13559/clp_study_en.pdf/33dd7bf1-93bc-4d30-8e8d-6f51d838851b, 03.08.2018

European Commission (2017): EU pesticides database. In: http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN, 11.08.2017

European Commission (2016): Special Eurobarometer 456 Chemical safety. In: http://ec.europa.eu/commfrontoffice/publicopinion/index.cfm/ResultDoc/download/DocumentKy/78785, 03.08.2018

European Commission (2011): Special Eurobarometer 360 Consumer understanding of labels and the safe use of chemicals. In: http://ec.europa.eu/commfrontoffice/publicopinion/index.cfm/ResultDoc/download/DocumentKy/56099, 03.08.2018

European Court of Justice (16.07.1998): Gut Springenheide and Tusky v Oberkreisdirektor des Kreises Steinfurt

European Union (2013a): Decision No 1386/2013/EU of the European parliament and of the council of 20 November 2013 on a General Union Environment Action Programme to 2020 ‘Living well, within the limits of our planet’

European Union (2013b): Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products. BPR

European Union (2009): Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products

European Union (2004): Regulation (EC) No 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents

Evans, R. M., Martin, O. V., Faust, M., Kortenkamp, A. (2016): Should the scope of human mixture risk assessment span legislative/regulatory silos for chemicals? Science of the Total Environment 543 (Pt A), 757–764

Food and Drug Administration (06.09.2016): Safety and Effectiveness of Consumer Antiseptics; Topical Antimicrobial Drug Products for Over-the-Counter Human Use Docket No. FDA-1975-N-0012. Bd. 81

Gawel, E., Köck, W., Schindler, H., Holländer, R., Lautenschläger, S. (2015): Mikroverunreinigungen und Abwasserabgabe. UBA-Texte 26/2015, Dessau-Roßlau

Glegg, G. A., Richards, J. P. (2007): Chemicals in household products: problems with solutions. Environmental Management 40 (6), 889–901

Herrmann, M., Menz, J., Gassmann, M., Olsson, O., Kümmerer, K. (2016): Experimental and in silico assessment of fate and effects of the antipsychotic drug quetiapine and its bio- and phototransformation products in aquatic environments. Environmental Pollution 218, 66–76

Herrmann, M., Menz, J., Olsson, O., Kümmerer, K. (2015a): Identification of phototransformation products of the antiepileptic drug gabapentin. Biodegradability and initial assessment of toxicity. Water Research 85, 11–21

Herrmann, M., Olsson, O., Fiehn, R., Herrel, M., Kümmerer, K. (2015b): The significance of different health institutions and their respective contributions of active pharmaceutical ingredients to wastewater. Environment International 85, 61–76

Hertz-Picciotto, I., Cassady, D., Lee, K., Bennett, D. H., Ritz, B., Vogt, R. (2010): Study of Use of Products and Exposure-Related Behaviors (SUPERB): study design, methods, and demographic characteristics of cohorts. Environmental Health 9, 54

Hillenbrand, T., Tettenborn, F. (2017): Empfehlungen des Stakeholder-Dialogs "Spurenschadstoffstragie des Bundes" an die Politik zur Reduktion von Spurenstoffeinträgen in die Gewässer. In: https://www.dialog-spurenstoffstrategie.de/spurenstoffe-wAssets/docs/PolicyPapier_FINAL.pdf, 03.08.2018

Howells, G. (2005): The Potential and Limits of Consumer Empowerment by Information. Journal of Law and Society 32 (3), 349–370

Kollmuss, A., Agyeman, J. (2002): Mind the Gap. Why do people act environmentally and what are the barriers to pro-environmental behavior? Environmental Education Research 8 (3), 239–260

Kümmerer, K., Dionysiou, D. D., Fatta-Kassinos, D. (2015): Long-Term Strategies for Tackling Micropollutants. In: The Handbook of Environmental Chemistry. Springer, Berlin, Heidelberg

Kümmerer, K., Henninger, A. (2003): Promoting resistance by the emission of antibiotics from hospitals and households into effluent. Clinical Microbiology and Infection 9 (12), 1203–1214

Lakoff, G., Johnson, M. (2014): Leben in Metaphern. Konstruktion und Gebrauch von Sprachbildern. Carl-Auer-Verlag, Heidelberg

Lao, W., Tsukada, D., Greenstein, D. J., Bay, S. M., Maruya, K. A. (2010): Analysis, occurrence, and toxic potential of pyrethroids, and fipronil in sediments from an urban estuary. Environmental Toxicology and Chemistry 29 (4), 843–851

Launay, M. A., Dittmer, U., Steinmetz, H. (2016): Organic micropollutants discharged by combined sewer overflows - Characterisation of pollutant sources and stormwater-related processes. Water Research 104, 82–92

Lippeverband (2016): Den Spurenstoffen auf der Spur in Dülmen - Herkunftsanalyse und Sensibilisierung zur Vermeidung des Eintrages von Spurenstoffen in Dülmen; Abschlussbericht, gerichtet an das Ministerium für Klimaschutz, Umwelt, Landwirtschaft, Natur- und Verbraucherschutz des Landes Nordrhein-Westfalen. AZ 500-8657198/0001.F

Loos, R., Carvalho, R., António, D. C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R. H., Schwesig, D., Gawlik, B. M. (2013): EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Research 47 (17), 6475–6487

Lutterbeck, C. A., Wilde, M. L., Baginska, E., Leder, C., Machado, Ê. L., Kümmerer, K. (2015): Degradation of 5-FU by means of advanced (photo)oxidation processes: UV/H2O2, UV/Fe2+/H2O2 and UV/TiO2--Comparison of transformation products, ready biodegradability and toxicity. Science of the Total Environment 527-528, 232–245

Medizinische Medien Informations GmbH (2017): 'Gelbe Liste Online'. In: https://www.gelbe-liste.de/, 24.07.2017

Merel, S., Nikiforov, A. I., Snyder, S. A. (2015): Potential analytical interferences and seasonal variability in diethyltoluamide environmental monitoring programs. Chemosphere 127, 238–245

Midden, C., del Pozo, C., Poumadère, M., Wiedemann, P. (2011): In-depth Study of Hazard Perception of Household Chemical Products: Consequences for the Communication of Information on Safe Use to the General Public. In: https://echa.europa.eu/documents/10162/13559/clp_study_en.pdf/33dd7bf1-93bc-4d30-8e8d-6f51d838851b, 03.08.2018

Möckel, S., Gawel, E., Bretschneider, W., Kästner, M., Liess, M., Knillmann, S. (2015): Eine Abgabe auf Pflanzenschutzmittel für Deutschland. Natur und Recht 37 (10), 669–677

Ort, C., Lawrence, M. G., Rieckermann, J., Joss, A. (2010a): Sampling for pharmaceuticals and personal care products (PPCPs) and illicit drugs in wastewater systems: are your conclusions valid? A critical review. Environmental Science & Technology 44 (16), 6024–6035

Ort, C., Lawrence, M. G., Reungoat, J., Mueller, J. F. (2010b): Sampling for PPCPs in wastewater systems: comparison of different sampling modes and optimization strategies. Environmental Science & Technology 44 (16), 6289–6296

Rahlenbeck, S., Müller-Stöver, I., Doggett, S. (2013): Insect protection: How to lower the risk of bites (Insektenschutz: Wie man das Stichrisiko senkt). Deutsches Ärzteblatt 110 (29-30), A1432-A1434

RAL gGmbH (2011): Basic Criteria for Award of the Environmental Label Non-Tocic Indoor Pest Control and Prevention RAL-UZ 34. In: https://www.blauer-engel.de/en/products/home-living/indoor-pest-control/indoor-pest-control-and-prevention, 15.11.2017

Ribeiro, A. R., Nunes, O. C., Pereira, M. F. R., Silva, A. M. T. (2015): An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environment International 75, 33–51

Rockström, J., Steffen, W., Noone, K., Persson, A., Chapin, F. S., Lambin, E. F., Lenton, T. M., Scheffer, M., Folke, C., Schellnhuber, H. J., Nykvist, B., de Wit, Cynthia A, Hughes, T., van der Leeuw, Sander, Rodhe, H., Sörlin, S., Snyder, P. K., Costanza, R., Svedin, U., Falkenmark, M., Karlberg, L., Corell, R. W., Fabry, V. J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P., Foley, J. A. (2009): A safe operating space for humanity. Nature 461 (7263), 472–475

Safford, B., Api, A. M., Barratt, C., Comiskey, D., Ellis, G., McNamara, C., O'Mahony, C., Robison, S., Rose, J., Smith, B., Tozer, S. (2017): Application of the expanded Creme RIFM consumer exposure model to fragrance ingredients in cosmetic, personal care and air care products. Regulatory Toxicology and Pharmacology 86, 148–156

Singer, H., Jaus, S., Hanke, I., Lück, A., Hollender, J., Alder, A. C. (2010): Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water. Environmental Pollution 158 (10), 3054–3064

Skatteministeriet (26.02.2015): LBK nr 232 af 26/02/2015 Bekendtgørelse af lov om afgift af bekæmpelsesmidler

Statistisches Bundesamt (2010): Demographische Standards. Ausgabe 2010. Statistik und Wissenschaft, Wiesbaden

Stemplewski, J., Pfeiffer, E., Nafo, I., Liesenfeld, J., Müller, R., Stachowiak, J. (2014): Herausforderung Spurenstoffe im Wasser. Empirische Befunde zum Umgang mit Medikamenten. KA - Korrespondenz Abwasser, Abfall 10, 886–893

Stieß, I., Birzle-Harder, B. (2013): Der Blaue Engel – ein Klassiker mit Potenzial. Eine empirische Studie zu Verbraucherakzeptanz und Marktdurchdringung des Umweltzeichens. ISOE-Studientexte, Frankfurt am Main

Stiftung Warentest (2017): Insect protection (Insektenabwehrmittel). In: https://www.test.de/medikamente/selbstmedikation/haut/insektenstiche/insektenstiche/insektenabwehrmittel/, 28.08.2017

Tarazona, J. V. (2014): Environmental Risk Assessment, Cosmetic and Consumer Products. In: Encyclopedia of Toxicology. Elsevier, 394–397

Ternes, T. A., Joss, A., Siegrist, H. (2004): Scrutinizing Pharmaceuticals and Personal Care Products in Wastewater Treatment. Environmental Science & Technology 38 (20), 392A–399A

Terzopoulou, E., Voutsa, D., Kaklamanos, G. (2015): A multi-residue method for determination of 70 organic micropollutants in surface waters by solid-phase extraction followed by gas chromatography coupled to tandem mass spectrometry. Environmental Science and Pollution Research International 22 (2), 1095–1112

Tran, N. H., Hu, J., Ong, S. L. (2013): Simultaneous determination of PPCPs, EDCs, and artificial sweeteners in environmental water samples using a single-step SPE coupled with HPLC-MS/MS and isotope dilution. Talanta 113, 82–92

UBA (2014): Biocides - Proposal for a concerted European approach towards a sustainable use. In: https://www.umweltbundesamt.de/publikationen/biocides-approach-towards-a-sustainable-use, 03.08.2018

United Nations (2017): Sustainable Development Goals. In: https://sustainabledevelopment.un.org/sdgs, 24.08.2017

Verlicchi, P., Al Aukidy, M., Jelic, A., Petrović, M., Barceló, D. (2014): Comparison of measured and predicted concentrations of selected pharmaceuticals in wastewater and surface water: a case study of a catchment area in the Po Valley (Italy). Science of the Total Environment 470-471, 844–854

Weigel, S., Kuhlmann, J., Hühnerfuss, H. (2002): Drugs and personal care products as ubiquitous pollutants: occurrence and distribution of clofibric acid, caffeine and DEET in the North Sea. Science of the Total Environment 295 (1-3), 131–141

Wick, A., Fink, G., Ternes, T. A. (2010): Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectrometry. Journal of Chromatography A 1217 (14), 2088–2103

Wittmer, I. K., Scheidegger, R., Bader, H.-P., Singer, H., Stamm, C. (2011): Loss rates of urban biocides can exceed those of agricultural pesticides. Science of the Total Environment 409 (5), 920–932

Wittmer, I. K., Bader, H.-P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., Carlsson, C., Stamm, C. (2010): Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. Water Research 44 (9), 2850–2862

Woutersen, M., Tiesjema, B., Jeurissen, S. M. F., de Bruijn, A. C. P., Herremans, J. M. M., Hegger, I. (2015): Producten op de grensvlakken Warenwet - Wet op de medische hulpmiddelen - Biocidenverordening. RIVM Rapport 2015-0184, Bilthoven

Wu, X. M., Bennett, D. H., Ritz, B., Cassady, D. L., Lee, K., Hertz-Picciotto, I. (2010): Usage pattern of personal care products in California households. Food and Chemical Toxicology 48 (11), 3109–3119

Zhang, C., Cui, F., Zeng, G.-M., Jiang, M., Yang, Z.-Z., Yu, Z.-G., Zhu, M.-Y., Shen, L.-Q. (2015): Quaternary ammonium compounds (QACs): A review on occurrence, fate and toxicity in the environment. Science of the Total Environment 518-519, 352–362

8 Artikel zur kumulativen Dissertation

Artikel 1

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Artikel 2

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Artikel 3

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Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater

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ABSTRACT

The aim of this study was to investigate the role of household products as possible sources of biocidal active substances in municipal wastewater and their regulation under the Biocidal Products Regulation (EU) 528/2012. In 131 households, we investigated the prevalence of products used to control pests, washing and cleaning agents and select personal care products with high release to wastewater. Inventories of these products were established with the help of barcode scanning. All uses of biocidal active substances were evaluated regarding their assessment under the Biocidal Products Regulation.

2963 products were scanned in total, with 48% being washing and cleaning agents, 43% personal care products and 9% products used to control pests. Biocidal active substances were found in each household. These were observed primarily in washing and cleaning agents and personal care products (90%), while only a small percentage of the observations of biocidal active substances was in biocidal products. 64% of the observations of biocidal active substances were in applications that do not fall under the Biocidal Products Regulation and are thus not subject to its environmental risk assessment.

This study shows clearly that risks for the environment are underestimated because unregulated emissions to wastewater occur. It demonstrates that there are gaps in the current chemical legislation that lead to a release of substances into wastewater that were not subject to environmental risk assessment under the Biocidal Products Regulation. This is one example of the limitations of scientific risk assessment of chemicals – its complexity is immense. From our point of view, the results underline the importance of a sustainable use of the substances as this is the only way to decrease yet unidentified risks.

1. Introduction

Contamination of the environment with chemicals is still a challenge, and preventive approaches are needed to mitigate global chemical pollution (Diamond et al., 2015). Emissions of micropollutants from households are one of the threats to the water quality of aquatic systems. Recently, biocidal active substances (BAS), defined as "substance[s] or […] micro-organism[s] that [have] an action on or against harmful organisms" (European Union, 2013), have come into focus since they were first observed in the aquatic environment. Recent studies have shown that BAS can be found in different water bodies (Brausch and Rand, 2011; Buergi et al., 2007; Reemtsma et al., 2006; Weigel et al., 2002), biota (Corcellas et al., 2015; Rüdel et al., 2013) and also in human urine (Frederiksen et al., 2014; Heffernan et al., 2015; Larsson et al., 2014). They can pose a risk for organisms due to their, by definition, intended effects on organisms. These effects are not limited to the environment, but can also be relevant for human health. Potential risks have been identified e.g. for pest control using sprays, spraying of disinfectants or cleaning of surfaces with concentrates (Hahn et al., 2010). BAS can be sensitizing (e.g. methylchloroisothiazolinone/methylisothiazolinone (Geier et al., 2012)) and their contribution to evolving resistances against antibiotics due to cross-resistance is still under discussion (SCENIHR, 2009). The use of the disinfectant benzalkonium chloride for example could trigger antibiotic resistance against fluoroquinolones (Buffet-Bataillon et al., 2016). Especially the use of disinfectants in households has been discussed because the inappropriate use of non-approved disinfectants can lead to risks (Pieper et al., 2014) and the benefit of disinfecting soaps containing triclosan is questioned (Kim et al., 2015).

Approaches to reduce environmental contamination at the source are needed for these kinds of micropollutants instead of end-of-pipe technologies (Kümmerer et al., 2015). The manifold emission routes of biocides due to their diverse applications make, however, this approach

Abbreviations: BAS, biocidal active substance; BP, biocidal products; ERA, environmental risk assessment; BPR, EU Biocidal Products Regulation 528/2012; PCP, personal care products; PPP, plant protection products; PT, product type; STP, sewage treatment plants; WCA, washing and cleaning agents.

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exceedingly difficult. BAS can be released into the environment via direct and indirect emissions. Direct emissions can occur e.g. through run-off from building materials such as roofs or outdoor paints on facades (Bollmann et al., 2014b; Burkhardt et al., 2011; Gromaire et al., 2015). Indirect emissions to the environment can occur through sewage treatment plants (STP), where not all substances are completely removed (Chen et al., 2012; Gasperi et al., 2014; Kupper et al., 2006; Morasch et al., 2010; Singer et al., 2010; Weston et al., 2013; Wick et al., 2010). Households are likely to be major contributors to the total amount of BAS in STP. However, the specific sources within households are not yet fully understood (Bollmann et al., 2014a; Wittmer et al., 2011).

1.1. Regulation

In the EU, biocidal products (BP) are regulated under the *Regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products* (BPR). Applications for approval of BAS falling under BPR have to be submitted for each of the 22 different product types (PT), as described in Annex V of the BPR, in which the substance is intended to be used for a biocidal purpose. The European Chemicals Agency lists 262 BAS whose risks are currently assessed by the Member States ("under review") or are already approved in the EU. Approval has been sought for 685 active substance-PT combinations (European Chemicals Agency, 2015b). But BAS can simultaneously be used in other product groups, which do not fall under the BPR, e.g. plant protection products (PPP), personal care products (PCP) or washing and cleaning agents (WCA). Article 2 of the BPR defines exemptions for these products falling under the scope of other regulatory instruments. The regulatory differentiation between BP and product groups falling under other regulations is complex (Woutersen et al., 2015). This can lead to borderline cases, for which it has to be decided on a case-to-case basis under which provision a product is regulated (European Commission, 2015). This decision is based on the intended field of application of a product.

The consequence is that emissions of identical substances from applications, which are subject to different regulations, are not aggregated during the separate risk assessments. Thus, possible wastewater emissions of BAS are not completely evaluated and environmental risks are underestimated. Information and data are, therefore, needed to close this knowledge gap regarding these possible emissions of BAS from households into wastewater and to what extent they are regulated under BPR. Only with this knowledge, it is possible to fully understand the environmental risks posed by BAS.

1.2. Information on ingredients

Information on the ingredients of products in Europe is regulated under the respective legislation for product categories. As BAS can be found as ingredients in WCA, PCP and BP, the regulatory background for the labelling of these products is important. This background allows for a qualitative assessment of all BAS used in these categories, but not for quantitative questions:

- In accordance with Annex VII of *Regulation (EC) 648/2004 on Detergents*, manufacturers of detergents have to make available a list of names of ingredients on a website (European Union, 2005). However, no information is given on the amounts of the respective substances in the products.
- For PCP, Article 19(1) of the *Regulation on Cosmetic Products* requires a list of ingredients on the packaging. As in the case of WCA, no information on amounts is required. To gain information regarding the exact amounts of the substances, product testing would be necessary, which is not possible in light of the huge number of products (Dudzina et al., 2014).
- For BP, the authorisation holders are, as stipulated by Article 69(2) of the BPR, required to state the identity of every active substance and its concentration on the label of the products.

1.3. Data collection

Consumption data from households would be the most convenient way to collect information on emissions of BAS from households, as it has been done for pharmaceuticals in the past (Herrmann et al., 2015; Le Corre et al., 2012). However, unlike for pharmaceuticals, consumption data for BAS is currently not available. Besides a chemical characterisation of wastewater from households, the enquiry of consumption data by product inventories is a promising approach to examine emissions from households into wastewater. For a collection of data on the prevalence of BAS, different approaches can be used, e.g. telephone interviews, self-administered (e.g. Internet) surveys or on-site visits (Hertz-Picciotto et al., 2010). Each of these methods has disadvantages. Accurate reporting of used products cannot be expected during telephone interviews (Wu et al., 2010), internet surveys have low response rates and on-site visits such as household visits are intrusive (Hertz-Picciotto et al., 2010) and time-consuming for researchers (Weegels and van Veen, 2001). However, on-site visits are the most promising approach to collect detailed information. During the visits, it is especially important for the acceptance of households, to establish trust between researchers and interviewees and to minimise the time needed (Hertz-Picciotto et al., 2010). A highly sufficient approach to reduce the time required is the use of barcode scanners to inventory present products either by the researcher (Bennett et al., 2012) or by the consumer (Hall et al., 2007). Household investigations that included BAS, but were not focused on them, were conducted in Europe, e.g. in 30 households in one building in Copenhagen by on-site visits (Eriksson et al., 2003), in 2281 households in France by telephone interviews and 23 households close to Angers and Nantes in France by on-site visits (ANSES, 2010). Among other factors, such as age, gender or education, the living conditions are considered to be an important factor for the use of biocidal products (ANSES, 2010). However, until now no studies exist examining the correlation of the use of biocidal products and demographic factors in detail.

1.4. Objectives

Because the studies mentioned above have focused on certain product groups, either on PPP and BP or on PCP and WCA, their results give no overall picture of the sources of BAS in households. In addition, the use of the BAS in households has never been evaluated regarding its coverage by environmental risk assessments. For this reason, the objective of our study was to generate new and urgently needed data on the overall prevalence of BAS in household products in different categories: We aim to identify possible emission sources of BAS from households into wastewater and to examine whether the respective products are subject to environmental risk assessment (ERA) under the BPR. In the following, we present (1) which BAS are used in the studied households and (2) the products they are found in. The uses of BAS in different product categories are then (3) evaluated regarding their regulation under BPR or other legislation.

For this study, we chose on-site visits as a method to collect data and tested the applicability of product inventories using barcode scanners in households of three neighbourhoods in northern Germany. The product inventories were limited to products with a relevant release to wastewater because we considered this to be the most important exposure pathway of BAS from household products into the environment.

2. Material and methods

2.1. Study sites

In total, product inventories in 131 households were recorded. To account for different living conditions, that have been deemed to be an important factor for the use of biocidal products by ANSES (2010), three neighbourhoods were included in this study. These are representative of the three different urban–rural typologies in Europe: predominantly urban, intermediate and predominantly rural regions (BBSR, 2009). All study sites are located in the northern part of Germany. Households were contacted, and in each household, one individual was asked whether he or she would be willing to participate in the study. Following the recommendations by the German Federal Statistical Office, a household in this study was defined as an economic community and not simply as group of people living together to account for shared flats (Statistisches Bundesamt, 2010).

Neighbourhood A represents a predominantly rural region. It is part of a series of municipalities with a population density of 172 inhabitants/km^2 (BBSR, 2015). While the entire series of municipalities is categorized as intermediate (BBSR, 2009), the neighbourhood studied here can be defined as predominantly rural due to the low proportion of urban areas (only 3.3%, personal communication with BBSR, 12 October 2015). The neighbourhood is a housing estate dominated by single-family homes and is located in a village of approx. 3000 inhabitants. The initial goal was to conduct a complete survey in a neighbourhood of 145 households. 92 households of this neighbourhood participated by inventorying their household products.

Neighbourhood B represents intermediate regions. It is located in a town of 33,000 inhabitants with a population density of 245 inhabitants/km^2 (BBSR, 2015); the proportion of urban areas in this region is 36.6% (personal communication with BBSR, 12 October 2015). The neighbourhood is dominated by multi-family homes. 19 households in this neighbourhood participated in the study. The choice of households was convenience sampling based on their willingness to participate in the study.

Neighbourhood C represents predominantly urban regions. It is located in Hamburg with a total of 1.7 mio. inhabitants and a population density of 2296 inhabitants/km^2 (BBSR, 2015). This neighbourhood consists of multi-family homes with a high proportion of shared flats. 20 households in this neighbourhood participated in the study. The choice of households was convenience sampling based on their willingness to participate in the study.

As expected, the three neighbourhoods represent very different living conditions (Table 1). While the inhabitants of Neighbourhood A (rural) by the majority live in single-family homes ($n = 84$; 89.4%), in the intermediate and predominantly urban regions 100% live in flats in multi-family homes. The average size of the living area is, accordingly, different (136 m^2 in Neighbourhood A versus 65 and 67 m^2 in Neighbourhoods B and C). Neighbourhood A has a high average number of household members above 65 and higher total net household incomes.

Table 1
Demographic characteristics of the neighbourhoods.

	Neighbourhood A		Neighbourhood B		Neighbourhood C	
Characteristics	*n*	%/an[a]	*n*	%/an[a]	*n*	%/an[a]
Gender						
Female	64	68.1	12	63.2	16	80.0
Male	30	31.9	7	36.8	4	20.0
Age interviewee						
17–30	1	1.1	7	36.8	10	50.0
31–40	17	18.1	2	10.5	5	25.0
41–50	8	8.5	1	5.3	3	15.0
51–60	16	17.0	4	21.1	2	10.0
61–70	24	25.5	1	5.3	0	0.0
71–80	21	22.3	3	15.8	0	0.0
81–92	5	5.3	1	5.3	0	0.0
Not specified	2	2.1	0	0.0	0	0.0
Number and average number household members (an)						
Children under 3	9	0.1	4	0.2	5	0.3
Children under 6	7	0.2	1	0.3	0	0.3
Children under 18	25	0.5	5	0.6	0	0.3
Members between 18 and 65	113	1.2	20	1.1	39	2.0
Members above 65	73	0.8	6	0.3	0	0.0
Highest education level[b]						
Without graduation	1	1.1	2	10.5	0	0.0
Graduation after 9 years	30	31.9	5	26.3	0	0.0
Graduation after 10 years	25	26.6	7	36.8	4	20.0
Graduation after ≥12 years	34	36.2	2	10.5	16	80.0
Other	2	2.1	3	15.8	0	0.0
Not specified	2	2.1	0	0.0	0	0.0
Job training[b,c]						
No job training (yet)	4	4.3	3	15.8	4	20.0
Apprenticeship	71	75.5	12	63.2	10	50.0
Forman or similar	11	11.7	0	0.0	1	5.0
University degree	32	34.0	2	10.5	9	45.0
Other	0	0.0	1	5.3	0	0.0
Not specified	2	2.1	1	5.3	0	0.0
Total net household income						
<850 €	1	1.1	3	15.8	5	25.0
851–1500 €	7	7.4	6	31.6	4	20.0
1501–2000 €	6	6.4	7	36.8	2	10.0
2001–3000 €	25	26.6	1	5.3	2	10.0
3001–4000 €	26	27.7	0	0.0	4	20.0
4001–5000 €	10	10.6	0	0.0	0	0.0
5001–6000 €	5	5.3	0	0.0	2	10.0
>6000 €	7	7.4	0	0.0	0	0.0
Not specified	7	7.4	2	10.5	1	5.0
Living conditions						
Single-family homes	84	89.4	0	0	0	0.0
Flat (with partner/family)	10	10.6	19	100.0	13	65.0
Shared flat	-[d]	-[d]	0	0	7	35.0
Ø m^2	136		65		67	

[a] an: Average number of household members.
[b] Of the household member with the highest income.
[c] Multiple selections possible.
[d] Not a possible choice in the questionnaires for Neighbourhood A.

2.2. Product categories

BAS can occur in various product groups in households. Besides other products for the control of pests (e.g. PPP) that may use the same active substances, BAS can also be found in PCP or WCA. In these products, they can be used as preservatives for the control of microorganisms or for other purposes. For this reason, to identify all possible sources of BAS in households, it is not enough to inventory only BP. In this study, the following product groups were inventoried:

- all products for the control of pests (incl. BP, PPP, products against fleas and lice on humans and pets) with a relevant release to wastewater;
- all WCA;
- certain PCP types with high release to wastewater: shampoo, body wash, bath additives, conditioner, soap, toothpaste, mouth wash, body lotion, hand cream, hair styling products, hair dye and make-up remover.

The inventory of BP was limited to PT with a release to wastewater as outlined in the Emission Scenario Documents used for the ERA under BPR (European Chemicals Agency, n.d.). PPP were included because an emission to wastewater could occur when application equipment is cleaned indoors. The inventory of PCP was limited to the selection of products listed above to reduce the amount of time needed per household. Because preservatives were considered to be the most prevalent type of BAS in PCP, the selection was based on the theoretically possible emission (E_{theo} [g/day]) of preservatives to wastewater, which is described by Eq. (1):

$$E_{theo} = c_{max} \times A_{daily} \quad (1)$$

Annex V of *Regulation (EC) 1223/2009 on Cosmetic Products* (European Union, 2009b) defines maximum concentrations in ready for use preparations (c_{max} [%]) of preservatives in PCP for different application types (rinse-off, oral, leave-on, hair, eye, other products and deodorants). These were multiplied by the estimated daily amount applied (A_{daily} [g/day]) for several important PCP types (Scientific Committee on Consumer Safety, 2012). Based on these results, PCP types with a theoretically possible emission of BAS preservatives to wastewater above 0.01 g/day were selected for inventorying. A comparable set of products was given in Ledin et al. (2003).

2.3. Approach used for data collection and evaluation

Households received information on the study prior to data collection. During the study, all households were approached in person by an interviewer during different times of the day if no one was at home during the first visit. If a possible participant was at home, the person was asked if he or she would be willing to participate and whether he or she had time. If the latter was not the case, an appointment was made for another time.

Interviewees were allowed to choose whether they would rather walk around in the household together with the interviewer for scanning or whether they preferred to gather the products themselves and present them for scanning. Barcodes of all products in the households belonging to the product categories described above were scanned with an Inateck BCST-10 barcode scanner. After each product, a barcode representing the respective product category (pest control products, WCA, PCP) was scanned to simplify subsequent data analysis. If products did not have a barcode or the barcode was unreadable, we followed the approach by Bennett et al. (2012) and scanned an internal barcode for the respective product and recorded the name.

Statistical questions that were included in a questionnaire were based on the recommendations of the German Federal Statistical Office (Statistisches Bundesamt, 2010). Therefore, demographic results can be compared to German census data.

The approach was tested in classic pre-tests ($n = 20$) in randomly chosen households that were not situated in the neighbourhoods studied here. A public database was used to match the scanned barcodes with information regarding names of the products and ingredients (Bennett et al., 2012). If a product was not found in this database, an online search was conducted. If a barcode was linked to a product name, but no information regarding ingredients was available in the database, ingredients were checked on the websites of the manufacturers. BAS in the products were identified by comparing their CAS- and EC-numbers with the European Chemicals Agency-list of BAS as of 14 June 2015 (European Chemicals Agency, 2015a). The results were tested for normal distribution with the Shapiro-Wilk test. Possible correlations between household parameters and BP on stock were analysed with Spearman's rank correlation coefficient if at least one variable was not on a ratio scale, but ordinally coded or not normally distributed. A Chi-squared test was used if nominally scaled variables were part of the tested data. Significances in differences were determined with *t*-test or Mann–Whitney Rank Sum Test for not normally distributed variables, and pairwise comparison was done with Dunn's Method. All statistical calculations were done with SigmaPlot for Windows 12.5 (Systat Software, Inc.).

3. Results and discussion

3.1. Scanned products

In total, 2963 products with BAS were scanned in 131 households (Fig. 1). For 96.3% of the barcodes ($n = 2853$), the names of the products could be retrieved, and for 93.4%, the ingredients were available ($n = 2767$). These numbers are higher than those found in a study conducted in California, where readability of barcodes of household and personal care products ranged from 86 to 3% for different product groups (Bennett et al., 2012). As the product groups of this Californian study were not categorized according to European law, like in our study, the retrieval rates of the different product groups were not directly comparable.

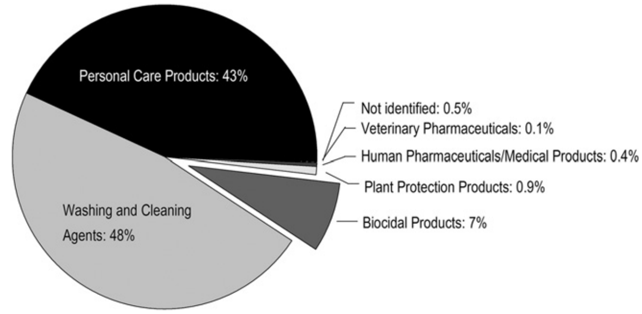

Fig. 1. Distribution of the scanned products by product category.

The majority of the scanned products were WCA (48%, $n = 1411$) and PCP (43%, $n = 1277$), and products for the control of pests constituted 9% of the scanned products ($n = 275$). In this product category, the products were further separated during the evaluation based on their intended use: BP, PPP, human pharmaceuticals/medical products and veterinary pharmaceuticals. BP represented the highest proportion (7%, $n = 220$), followed by PPP (0.9%, $n = 26$), human pharmaceuticals/ medical products (0.4%, $n = 12$) and veterinary pharmaceuticals (0.1%, $n = 3$). It has to be noted that not all human and veterinary pharmaceuticals or medical products in stock were scanned, but only products against fleas and lice on humans and pets. In addition, not all PPP present in the households were scanned, because the interviewees may have related the study only to indoor (="household") uses, even though emission to wastewater from products used outdoors would also be possible when they are, for example, used to clean equipment inside. The results of this study should thus not be used to evaluate the overall use of PPP in households.

3.2. Biocidal active substances present in households

BAS that are currently under review or already authorised (European Chemicals Agency, 2015a) were present in 100% of the households. Fig. 2 displays the 79 BAS that were listed as ingredients across all scanned products and the number of times each was observed. In total, BAS were found 4106 times in the lists of ingredients of the scanned products, independent of the purpose of the substance in the products. The products which accounted for the majority of BAS observations were PCP (49.3%) and WCA (41.1%). The five most abundant active substances were citric acid ($n = 859$), methylisothiazolinone ($n = 471$), phenoxyethanol ($n = 409$), benzisothiazolinone ($n = 357$) and geraniol ($n = 281$). This finding is in line with Ledin et al. (2003), who also found citric acid and phenoxyethanol to be among the most abundant BAS in household products. Rotsidou and Scrimshaw (2015) identified methylisothiazolinone and phenoxyethanol as the most used preservatives in the dishwashing liquids they inventoried in UK households ($n = 52$), and citric acid as the BAS most used as a preservative in body washes. In the products they inventoried, geraniol was found as well, but not in such a high frequency as in our study.

The diversity of substances in the three product categories in our study is very variable. While 1411 WCA were scanned and contained in total 32 different BAS, and 1277 PCP contained in total 27 different BAS, the 275 pest control products scanned contained 59 different BAS. Studies evaluating the prevalence of pest control products in households are rare in the literature, but a study in France also revealed a large variety of active substances for the control of pests in households (ANSES, 2010). This study lists 106 active substances that were found in households ($n = 1585$), However, not all of them are BAS because the French study also included PPP active substances. Disinfectants and preservatives were also not part of the study, so its findings regarding active substances are not directly comparable with our evaluation.

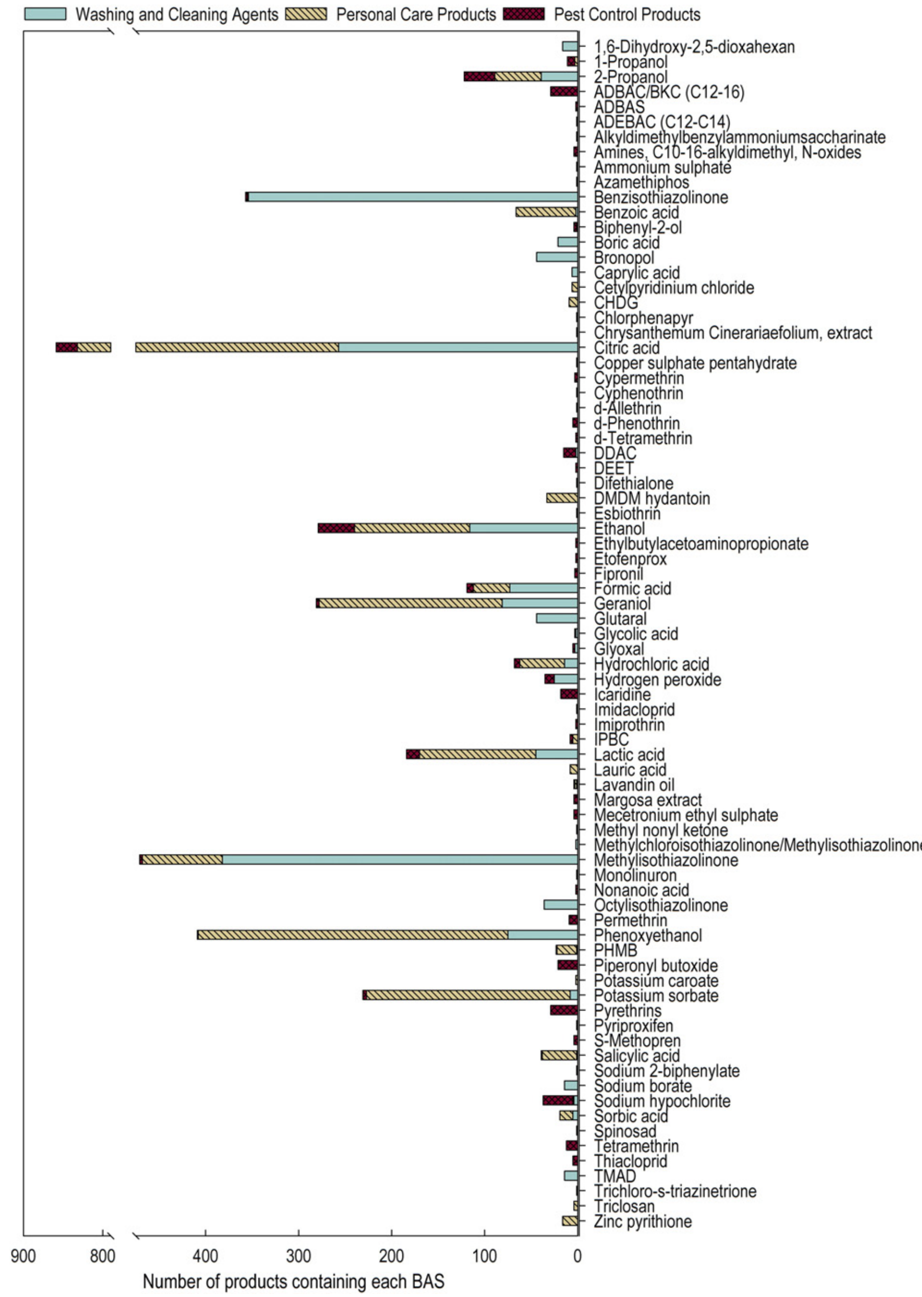

Fig. 2. Absolute numbers of observations for the 79 different BAS across all scanned products.

Among the PT that were part of both studies, a similar range of substances can be seen. Pyrethroids were present in households in both France and Germany, as well as piperonyl butoxide, S-methoprene, pyriproxyfen or fipronil.

3.3. Products containing biocidal active substances

3.3.1. Biocidal products

The results show that BP were found in 75% of the households. On average, each household possessed 1.7 BP, with a range of 0 to 10 products. Disinfectants represented the largest group among the product types detected, with 69% of the products belonging to PT 1–4 (Fig. 3). Insecticides (PT 18, 24%) and repellents (PT 19, 9%) were also found relatively often. In the study in France mentioned above, households ($n = 23$) possessed on average 19 pesticides (ANSES, 2010). However, the number of products also included PPP, which were not completely inventoried in our study, so the results are not directly comparable. In the French households, insecticides constituted 36% of the total number of inventoried products, disinfectants being the second largest group (28%). This difference to our results can be explained by the inclusion in the French study of PPP, which are often applied against insects.

The observed BP were further evaluated regarding their use conditions and the significant correlations of household variables and the amount of products of the different PTs are presented here. Shapirow-Wilk tests of normal distribution showed that the data is not normally distributed. To evaluate the parameters that might significantly determine the use of BP, we calculated Spearman correlation coefficients (r_S) if data with ratio or ordinal scales was involved or used the Chi-squared test if nominally scaled data was analysed. However, for the Chi-squared tests minimum size of expected frequencies was not reached for some categories, so the results should be evaluated critically.

A weak correlation between living conditions and the use of insecticides (PT 18) can be seen. Households with large living areas ($r_s =$

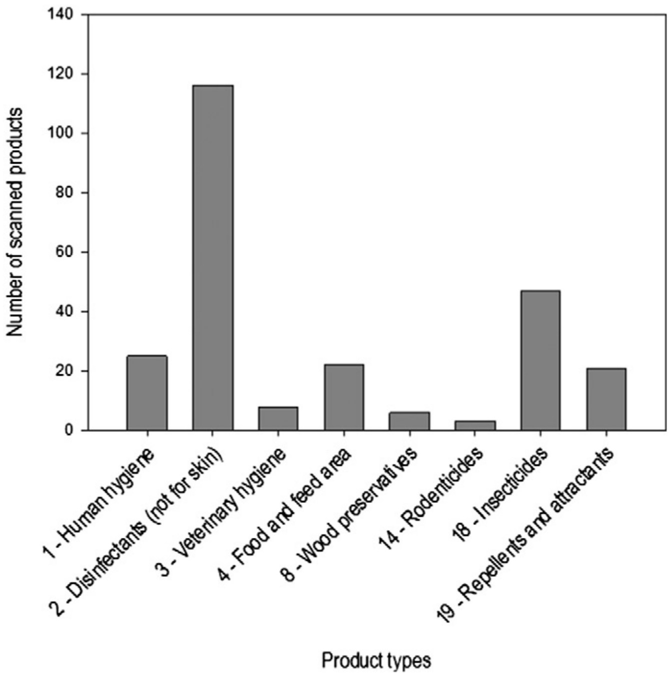

Fig. 3. Distribution pattern of scanned BP in households for different PT.

0.251, $p = 0.004$) and, accordingly, households situated in single-family homes ($p = 0.02$, $\alpha = 0.050{:}0.891$, degree of freedom (df) = 8) tend to have more insecticides in stock. This is in line with the study in 23 households in France (ANSES, 2010). Households in which the main income earners have higher educational levels, tend to have fewer insecticides ($r_s = -0.203$, $p = 0.02$). This can be explained by the fact that, among the households studied, people with higher educational levels tended to live in flats rather than in single-family homes ($p = 0.02$, $\alpha = 0.050{:}0.929$, df = 12). The results also showed that significantly more insecticides are used in the rural Neighbourhood A than in the two other neighbourhoods (significant differences between Neighbourhood A and C: $p = 0.003$ and Neighbourhood A and B: $p = 0.013$). This may be related to the distribution between flats and single-family homes, as Neighbourhood A comprise significantly more single-family homes.

The number of furry pets ($r_s = 0.263$, $p = 0.002$) and the number of children aged between 3 and 6 years ($r_s = 0.185$, $p = 0.03$) correlated positively with the presence of repellents (PT 19), as did a higher net income ($r_s = 0.25$, $p = 0.004$) and a larger living area ($r_s = 0.172$, $p = 0.05$). A reason for this may be that, within the neighbourhoods studied, the proportion of households with a higher net income and larger living areas is higher in the rural area, where repellents might be more used, than in the cities. Relations between education and repellent use have been observed in other studies: In California, it has been shown that people with a college degree use more repellents than people without a degree (Wu et al., 2010), while variability of the number of BP has also been related to profession for French households (ANSES, 2010). We were not able to verify this correlation of education and the use of repellents directly. However, our data shows a correlation between education and total net income ($r_s = 0.178$, $p = 0.04$) and, thus, supports the results of the aforementioned studies.

Even though the sample sizes for the different neighbourhoods are different, tendencies regarding the use of disinfectants can still be detected when comparing the different groups. The households in the urban environment use significantly more disinfectants and algaecides not intended for direct application to humans or animals (PT 2) than those in the intermediate or predominantly rural regions. Significant differences both between the Neighbourhoods A and C ($p = 0.049$) and between B and C ($p = 0.018$) can be seen. Households with a higher educational level of the main income earners used significantly more disinfectants ($p = 0.05$, $\alpha = 0.050{:}0.762$, df = 6). A relationship between the number of furry pets and the use of disinfectants (PT 2) is plausibly apparent, but not significant in the data ($r_s = 0.166$, $p = 0.06$). The number of children would conceivably be a relevant factor for the use of disinfectants but, as households with children were underrepresented in the data, this hypothesis could not be verified. The aforementioned study in California found no significant correlation between households with young children and the prevalence of antibacterial soap, hand sanitizers or disinfectant sprays. However, there was a marginal significant difference of the weekly used amount of disinfectant sprays, which was higher in households with young children (Bennett et al., 2012).

3.3.2. Other products

BP were not the only products that contained BAS (Fig. 2). Overall, WCA and PCP contained 42 different BAS (Table 2). 50% of these ($n = 21$) are currently under review or already approved for use as in-can preservatives (PT 6) under BPR. This means that an ERA is done for the respective substances as preservatives. However, this ERA under BPR only covers their use as preservatives in WCA. This is not a problem in itself, but a gap arises because the use of the same BAS as a preservative in PCP is not covered by the BPR but instead falls under the *Regulation on Cosmetic Products*, which delegates the ERA to *Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)* (European Union, 2007). Thus, the evaluation of whether the use of a BAS is covered by ERA under BPR depends on the specific product category under which that BAS is used.

The other 21 substances are not currently under review or approved for use in PT 6 under the BPR. For these 21 substances, no specific ERA is conducted under BPR, either for use in PCP or WCA. To our knowledge, the present study is the first to make this differentiation.

3.4. Evaluation of regulation under BPR

For all the BAS mentioned in the lists of ingredients of the scanned products, it was evaluated whether the use of the substance in the respective product is covered by the ERA of BPR. The following uses that are not covered were identified:

1. In WCA, BAS which are not currently evaluated or approved for a use as a preservative (PT 6) were used 562 times. This represents 13.7% of the observations of BAS in all products.
2. In PCP, BAS were used 2023 times (49.3%). In general, the use of BAS in PCP is not evaluated under the BPR, whether used as a preservative or not.
3. Additionally, BAS were found 33 times in pest control products other than BP (0.8%).

Thus, it is an important contribution of this study to clearly highlight an important reason why risks for the environment are underestimated: because unregulated household emissions to municipal wastewater may occur. In total, 63.8% of the BAS uses observed here were not covered by the ERA under the BPR ($n = 2618$).

Some uses are in fact subject to ERA under other legislation, such as substances in PPP under *Regulation (EC) No 1107/2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC* (European Union, 2009a), or substances in PCP, whose ERA is delegated to REACH. However, REACH is not designed for ERA of substances with intended effects on target organisms; this is why, in principle, all active substances are subject to risk assessments under their own regulations (like the BPR). But this is not true for biologically active preservatives in PCP, an omission which has already been criticised by Tarazona (2014). Example risk assessments for preservatives in PCP show possible risks for STP (Carbajo et al., 2015) and preservatives have been identified as classes of "down-the-drain" chemicals used in households, which may be of concern (Rotsidou and Scrimshaw, 2015).

Table 2
Regulatory status of BAS contained in scanned WCA and PCP under the BPR.

	Under review/Approved for product type (PT)[a] (European Chemicals Agency, 2015b)																
Biocidal active substances	1	2	3	4	5	6	7	8	9	10	11	12	13	18	19	21	22
Under review/approved for PT 6																	
1,6-Dihydroxy-2,5-dioxahexan		×				×					×	×	×				
Benzisothiazolinone		×				×			×	×	×	×	×				
Biphenyl-2-ol	×	×	×	×		×	×		×	×			×				
Bronopol		×				×			×		×	×					×
CMIT/MIT		×		×		×					×	×	×				
DDAC	×	×	×	×		×		×		×	×	×					
DMDM hydantoin						×							×				
Formic acid		×	×	×	×	×					×	×					
Glutaral		×	×	×		×					×	×					
Hydrogen peroxide	×	×	×	×	×	×					×	×					
IPBC						×	×	×	×	×			×				
Lactic acid	×	×	×	×		×											
Methylisothiazolinone						×					×	×	×				
Octylisothiazolinone						×	×	×	×	×	×		×				
Pheno×yethanol	×	×		×		×							×				
PHMB[b]	×[b]	×	×	×	×	×[b]			×[b]		×						
Potassium sorbate						×		×									
Sodium 2-biphenylate	×	×	×	×		×	×		×	×			×				
Sorbic acid						×											
TMAD		×				×					×	×	×				
Zinc pyrithione		×				×	×		×	×						×	
Not under review/not approved for PT 6																	
1-Propanol	×	×		×													
2-Propanol	×	×		×													
Ammonium sulfate											×	×					
Benzoic acid			×	×													
Boric acid								×									
Caprylic acid				×										×			
Cetylpyridinium chloride		×															
CHDG	×	×	×														
Citric acid	×																
Ethanol	×	×		×													
Geraniol														×	×		
Glycolic acid		×	×	×													
Glyoxal		×	×	×													
Hydrochloric acid		×															
Lauric Acid															×		
Lavandin oil															×		
Potassium caroate		×	×	×	×												
Salicylic acid		×	×	×													
Sodium borate								×									
Sodium hypochlorite	×	×	×	×	×						×	×					
Triclosan[c]	×[c]																

[a] According to Annex V of BPR: 1: Human hygiene; 2: Disinfectants and algaecides not intended for direct application to humans or animals; 3: Veterinary hygiene; 4: Food and feed area; 5: Drinking water; 6: Preservatives for products during storage; 7: Film preservatives; 8: Wood preservatives; 9: Fibre, leather, rubber and polymerised materials preservatives; 10: Construction material preservatives; 11: Preservatives for liquid-cooling and processing systems; 12: Slimicides; 13: Working or cutting fluid preservatives; 18: Insecticides, acaricides and products to control other arthropods; 19: Repellents and attractants; 21: Antifouling products; 22: Embalming and taxidermist fluids.

[b] As of 27 January 2016 the European Commission decided not to approve PHMB for the use in PT 1, 6 and 9 (European Commission, 2016a). As the use was still permitted during the inventorying period, the regulatory status of the substances at that time was used for the evaluation.

[c] As of 27 January 2016 the European Commission decided not to approve Triclosan for the use in PT 1 (European Commission, 2016b). As the use was still permitted during the inventorying period, the regulatory status of the substances at that time was used for the evaluation.

But even if the regulations for each substance were to include detailed ERA regarding all its respective uses, the aggregate environmental exposure due to its different uses falling under different regulatory areas would still be neglected. An aggregated exposure assessment would be necessary to conduct realistic chemical risk assessments, but this is not current practice (Dudzina et al., 2015). This is one example of the limitations of the risk assessment of chemicals: Although the complexity of these assessments is already high, there are still black spots that are missed by existing methods (Backhaus et al., 2010).

3.5. Limitations of the study

3.5.1. Method

The response rate for Neighbourhood A was 65%. This is much higher than in the abovementioned study in California, which had a response rate of 39% (Bennett et al., 2012), but slightly lower than in a comparable, but smaller, study in Denmark, which had a response rate of 79% (Eriksson et al., 2003). Response rates for Neighbourhoods B and C cannot be calculated because these neighbourhoods were each only visited for two weeks, due to limited time. It was not possible to contact all households in these neighbourhoods in this time window.

Interviewees were allowed to choose whether they would rather walk around in the household together with the interviewer as the scanning was performed, or whether they preferred to gather the products from around the household themselves and present them for scanning. The second option has the drawback that interviewees might miss products whose relevance they were not aware of. The same problem was reported by Bennett et al. (2012). To reduce possible mistakes, a list of all relevant product categories was given to the participants. At the end of the scanning process, the attention of participants was again drawn to this list to remind them of potential omissions they had made. The evaluation of a sub-set of households ($n = 83$) showed significant differences in the number of products that were scanned, depending on whether the interviewer walked around in the household ($n = 56$) or whether the products were gathered and presented by the interviewees ($n = 27$). Differences were significant for the number of scanned WCA (*t*-test, $p \leq 0.001$, $\alpha = 0.050{:}0.979$, two-tailed, df = 81), for the number of scanned PCP (Mann–Whitney Rank Sum Test, $p \leq 0.001$) and number of scanned BP (Mann–Whitney Rank Sum Test, $p = 0.002$). Despite the possibility of such mistakes, the benefit of this option is that it is less intrusive than the interviewer walking around in the house and therefore also increases acceptance. Thus, the risk of products being missed was deemed acceptable. Nonetheless, it must be kept in mind that the number of products in households is as a consequence somewhat underestimated.

Overall, the participants were predominantly female (69%). However, as the products of all household members were scanned, this bias should not have a large effect on the product inventory. A previous study did report male interviewees mentioning a significantly higher number of products (ANSES, 2010). However, this effect was limited to products used in the garden, so again a large effect on the present results is not expected for this study, which focuses on household products.

Furthermore, the survey method is only applicable to regularly used products. Products that are used once every few years are usually not in stock in households and were thus not representatively inventoried. Again, this leads to a possible underestimation of BAS emissions because long-term emissions from these infrequently used products might still occur. An example is outdoor paint, from which BAS can be released continuously even long after initial application. This is especially relevant for wastewater in neighbourhoods with combined sewer systems, where the run-off from façades also flows into the wastewater.

During pre-tests, we tried to gain information regarding the frequency of use of each product. However, providing this information turned out to be very difficult for participants so this approach was not pursued during the household visits. This difficulty in recalling past behaviour has been observed in other studies as well (Moran et al., 2012). Another potential problem is participants not reporting "embarrassing" products. Thus, we also offered interviewees in Neighbourhood A the possibility to anonymously report products that might be embarrassing, with the goal of minimizing the number of products not reported by interviewees. Post-paid envelopes with a short information leaflet were handed out after each household visit. Despite this opportunity of reporting products later, only two households did so. The reported products were not particularly embarrassing products, but simply products they had forgotten (e.g. hair dye, body milk, window cleaner), and the data was not detailed enough to be used.

Generally, the method of barcode scanning can be used everywhere as long as information regarding ingredients of products is available and barcodes are used on the products. However, products sold over non-standard distribution channels may require more complicated treatment. In particular, products without their own barcode were assigned internal barcodes in this study, as described above. In general, if it is necessary to do this during household visits, it will increase the time needed per household and might correspondingly decrease response rates.

Another important detail concerning the type of results obtained in this study is that they will only be comparable within one regulatory region (e.g. EU), because product categories might be assigned differently in different regions. For example, disinfectant soaps or repellents, which are BP in the EU, are sometimes considered as PCP (Brausch and Rand, 2011; Peck, 2006; Wu et al., 2010).

3.5.2. Representativeness

Even though sample size was limited, a comparison of the demographic characteristics of the study sites with average characteristics of the respective regions generally agreed well (see Supplementary information S1, Statistisches Bundesamt, 2013). However, it is noticeable that the study sites generally had much fewer children than the average German region of the site's respective type. This might influence the results, which were therefore not evaluated for correlations concerning children, even though households with children are present in the sample.

The rural Neighbourhood A had slightly more inhabitants with higher total net household income, and categorized as having higher (primary or secondary) educational levels or university degrees, than rural regions in general. As a consequence, the merged results of all neighbourhoods also show higher educational levels, university degrees and higher total net household incomes than Germany on average. Intermediate Neighbourhood B had lower total net household incomes than average intermediate regions in Germany. Inhabitants of urban Neighbourhood C more frequently had a higher education level (graduation after 12 years or more) and a university degree than average predominantly urban regions in Germany.

Notwithstanding these slight differences, the good agreement of the sample characteristics with average data for corresponding regions and Germany in general promises that the results should be transferable for Germany and thence to other industrialised countries. However, there might be other parameters that influence the presence of BP in households that are currently unknown and were thus not included in the study. For example, an important factor might be which supermarkets are nearby as these are presumably the first choice for shopping and thus their product range may influence the products present in households.

3.5.3. Plausibility

In order to assess whether the method of product scanning was successful to inventory all products containing BAS in households with emission to wastewater, the results are compared with recent monitoring results of BAS in municipal wastewater and STP effluent throughout Europe (Table 3).

This comparison with the data from the literature shows that, while some BAS that are found in wastewater were also detected in the scanned products, other BAS found in wastewater were not scanned in the households. These substances, like diuron, isoproturon or carbendazim, are often components of outdoor paints and might enter combined sewer systems via stormwater. As outdoor paints are not usually stocked in households, products containing these substances may not have been comprehensively inventoried in our survey. This confirms the conclusion of Eriksson et al. (2003) that a product inventory is insufficient for a full characterisation of wastewater. Product inventory can be an important tool to identify specific sources, but it should be complemented by chemical analyses.

For other substances, the monitoring results support the scanning results and indicate a measureable contribution from the household products to wastewater. However, some of the substances were detected only in a few products, which alone are not enough to explain positive monitoring results. For example, in the case of triclosan, the results show that this BAS was only found four times, as an ingredient in toothpaste ($n = 131$). Considering the findings of several studies which have detected triclosan in wastewater, the data obtained here cannot account for the concentrations measured in these studies. Possible explanations are that not all products containing triclosan were inventoried (e.g. deodorant or treated articles like kitchenware or functional clothing) or that the monitoring results from earlier studies no longer reflect current use. Chemical analyses of the wastewater of Neighbourhood A are therefore scheduled in the near future to allow for direct comparison to the survey results there. The interpretation of the concentrations of salicylic acid is difficult. Salicylic acid can be emitted both from its use in PCP products that were scanned and from human pharmaceuticals that were not scanned. Its concentrations in wastewater as listed in the table above thus result not only from its use in PCP, but also from pharmaceuticals. In the other direction, for some BAS that were frequently detected in the scanned products, such

Table 3
Measured concentrations of BAS in wastewater and STP influent and effluent.

Substance	Matrix	Measured maximum concentration	Reference	Found in products?
Bayrepel-acid (metabolite of icaridin)	STP effluent	0.1–1 μg L^{-1}	Reemtsma et al. (2006)	Yes (Icaridin)
Benzalkonium chloride (C12–18)	STP influent	170,000 ng L^{-1}	Clara et al. (2007)	Yes
Carbendazim	STP effluent	70 ng L^{-1}	Singer et al. (2010)	No
	STP influent	143 ng L^{-1}	Wick et al. (2010)	
	STP influent	78 ng L^{-1}	Bollmann et al. (2014a)	
	STP influent	<670 ng L^{-1}	Kupper et al. (2006)	
Cybutryne	STP effluent	5 ng L^{-1}	Singer et al. (2010)	No
	STP influent	21 ng L^{-1}	Wick et al. (2010)	
	STP influent	8 ng L^{-1}	Bollmann et al. (2014a)	
DCOIT	STP influent	Detected, but not quantified	Bollmann et al. (2014a)	No
DDAC (C10–18)	STP influent	200,000 ng L^{-1}	Clara et al. (2007)	Yes
DEET	STP effluent	0.1–1 μg L^{-1}	Reemtsma et al. (2006)	Yes
Diuron	STP effluent	40 ng L^{-1}	Singer et al. (2010)	No
	STP influent	39 ng L^{-1}	Bollmann et al. (2014a)	
	STP influent	68 ng L^{-1}	Wick et al. (2010)	
Isoproturon	STP effluent	30 ng L^{-1}	Singer et al. (2010)	No
	STP influent	39 ng L^{-1}	Wick et al. (2010)	
	STP influent	43 ng L^{-1}	Bollmann et al. (2014a)	
Methylisothiazolinone	STP influent	Detected, but not quantified	Bollmann et al. (2014a)	Yes
Octylisothiazolinone	STP influent	11 ng L^{-1}	Wick et al. (2010)	Yes
	STP influent	Detected, but not quantified	Bollmann et al. (2014a)	
Permethrin	STP influent	<670 ng L^{-1}	Kupper et al. (2006)	Yes
Piperonyl butoxide	Wastewater	172 ng L^{-1}	Rodil et al. (2009)	Yes
Propiconazole	STP influent	16 ng L^{-1}	Wick et al. (2010)	No
	STP influent	4540 ng L^{-1}	Bollmann et al. (2014a)	
Salicylic acid	STP effluent	0.36 ng L^{-1}	Su et al. (2014)	Yes
	STP influent	89,133 ng L^{-1}	Kosma et al. (2014)	
	STP effluent	682.5 ng L^{-1}	Kosma et al. (2014)	
	Wastewater	6067 ng L^{-1}	Rodil et al. (2009)	
Tebuconazole	STP influent	78 ng L^{-1}	Bollmann et al. (2014a)	No
	STP influent	8.9 ng L^{-1}	Wick et al. (2010)	
Terbutryn	STP effluent	20 ng L^{-1}	Singer et al. (2010)	No
	STP influent	116 ng L^{-1}	Wick et al. (2010)	
	STP influent	62 ng L^{-1}	Bollmann et al. (2014a)	
Triclosan	STP influent	1742 ng L^{-1}	Kosma et al. (2014)	Yes
	STP influent	841 ng L^{-1}	Wick et al. (2010)	
	Wastewater	<5260 ng L^{-1}	Gasperi et al. (2014)	

citric acid or ethanol, positive monitoring results in the wastewater studies are not available and unlikely due to their rapid biodegradation.

For a high number of substances, no monitoring results for their presence in wastewater are available. This does not necessarily mean that they are not present, but could simply imply that not all relevant substances in wastewater have been monitored yet. This could be the result of a process that Daughton (2014) calls the “Matthew Effect”. Chemicals that have already been frequently detected in the environment tend to become the focus for scientists more than the so-called “Matthew Effect Orphaned Chemicals,” which have been less often observed. As the regulation of BAS is relatively new – the *Directive 98/8/EC concerning the placing of biocidal products on the market* only entered into force in 1998 (European Union, 1998) – there is still much ignorance concerning their occurrence in the environment. Thus, our results contribute urgently needed information regarding their potential occurrence in wastewater. Accordingly, these new findings can be used to adjust corresponding BAS monitoring programs to allow for target-oriented and thus cost-efficient monitoring programs.

4. Conclusions

The analysis of the regulatory background in our study shows that the environmental risks of BAS are underestimated: Considering the number of observations of BAS in the scanned products, PCP and WCA clearly outnumber BP as emission sources of active substances in wastewater. Consequently, risks are underestimated because not all of these emission sources are considered during ERA under BPR. If risks are identified under this ERA, risk mitigation measures only tackling the use of BP will not be sufficient for all BAS, because emissions to wastewater might still occur from other product categories.

It is questionable whether complex cases, in which the use of BAS is subject to different legislations, could, in practice, be covered by existing risk assessment concepts. To solve this problem, it would be necessary to increase the complexity of these assessments and to aggregate ERA throughout all legislation. From our point of view, a precautionary approach to reduce possible, maybe yet unidentified, risks by these substances in general, while keeping effort for industry and regulators to a manageable level, would be to limit their use to in fact essential uses. This would be in line with the principles of sustainable chemistry to avoid or reduce emissions of hazardous substances and their emissions to the environment and a small step towards staying within the planetary boundaries for chemical pollution. A sustainable use of BAS should thus be further promoted to complement the important prospective risk assessments of BAS and closing existing gaps.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2016.07.007.

Conflict of interest

Stefanie Wieck is also working at the German Federal Environment Agency. This paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

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References

ANSES, 2010. Exposition de la population generale aux residus de pesticides en France. https://www.anses.fr/fr/content/exposition-de-la-population-g%C3%A9n%C3%A9rale-aux-pesticides (accessed October 09, 2015).

Backhaus, T., Brooks, B.W., Kapustka, L., 2010. Chemical risk assessment: pressures, perceptions and expectations. Integr. Environ. Assess. Manag. 6 (3), 323–324.

BBSR, 2009. Raumtypen 2010. http://www.bbsr.bund.de/BBSR/DE/Raumbeobachtung/Raumabgrenzungen/Raumtypen2010_vbg/Download_RefTypenLageSied.xls?__blob=publicationFile&v=2 (accessed October 06, 2015).

BBSR, 2015. Raumbeobachtung. http://78.47.125.117/raumbeobachtung/# (accessed October 09, 2015).

Bennett, D.H., Wu, X.M., Teague, C.H., Lee, K., Cassady, D.L., Ritz, B., et al., 2012. Passive sampling methods to determine household and personal care product use. J. Expo. Sci. Environ. Epidemiol. 22 (2), 148–160.

Bollmann, U.E., Tang, C., Eriksson, E., Jönsson, K., Vollertsen, J., Bester, K., 2014a. Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources. Water Res. 60, 64–74.

Bollmann, U.E., Vollertsen, J., Carmeliet, J., Bester, K., 2014b. Dynamics of biocide emissions from buildings in a suburban stormwater catchment - concentrations, mass loads and emission processes. Water Res. 56, 66–76.

Brausch, J.M., Rand, G.M., 2011. A review of personal care products in the aquatic environment: environmental concentrations and toxicity. Chemosphere 82 (11), 1518–1532.

Buergi, D., Knechtenhofer, L., Meier, I., Giger, W., 2007. Projekt BIOMIK: Biozide als Mikroverunreinigungen in Abwasser und Gewässern. Teilprojekt 1: Priorisierung von bioziden Wirkstoffen. Zürich.

Buffet-Bataillon, S., Tattevin, P., Maillard, J., Bonnaure-Mallet, M., Jolivet-Gougeon, A., 2016. Efflux pump induction by quaternary ammonium compounds and fluoroquinolone resistance in bacteria. Future Microbiol 11 (1), 81–92.

Burkhardt, M., Zuleeg, S., Vonbank, R., Schmid, P., Hean, S., Lamani, X., et al., 2011. Leaching of additives from construction materials to urban storm water runoff. Water Sci. Technol. 63 (9), 1974.

Carbajo, J.B., Perdigón-Melón, J.A., Petre, A.L., Rosal, R., Letón, P., García-Calvo, E., 2015. Personal care product preservatives: risk assessment and mixture toxicities with an industrial wastewater. Water Res. 72, 174–185.

Chen, Z., Ying, G., Lai, H., Chen, F., Su, H., Liu, Y., et al., 2012. Determination of biocides in different environmental matrices by use of ultra-high-performance liquid chromatography-tandem mass spectrometry. Anal. Bioanal. Chem. 404 (10), 3175–3188.

Clara, M., Scharf, S., Scheffknecht, C., Gans, O., 2007. Occurrence of selected surfactants in untreated and treated sewage. Water Res. 41 (19), 4339–4348.

Corcellas, C., Eljarrat, E., Barceló, D., 2015. First report of pyrethroid bioaccumulation in wild river fish: a case study in Iberian river basins (Spain). Environ. Int. 75, 110–116.

Daughton, C.G., 2014. The Matthew effect and widely prescribed pharmaceuticals lacking environmental monitoring: case study of an exposure-assessment vulnerability. Sci. Total Environ. 466–467, 315–325.

Diamond, M.L., de Wit, C.A., Molander, S., Scheringer, M., Backhaus, T., Lohmann, R., et al., 2015. Exploring the planetary boundary for chemical pollution. Environ. Int. 78, 8–15.

Dudzina, T., von Goetz, N., Bogdal, C., Biesterbos, W H]–>J.W.H., Hungerbühler, K., 2014. Concentrations of cyclic volatile methylsiloxanes in European cosmetics and personal care products: prerequisite for human and environmental exposure assessment. Environ. Int. 62, 86–94.

Dudzina, T., Delmaar, J E]–>C.J.E., Biesterbos, W H]–>J.W.H., Bakker, M.I., Bokkers, G H]–>B.G.H., Scheepers, T J]–>P.T.J., et al., 2015. The probabilistic aggregate consumer exposure model (PACEM): validation and comparison to a lower-tier assessment for the cyclic siloxane D5. Environ. Int. 79, 8–16.

Eriksson, E., Auffahrt, K., Eilersen, A., Henze, M., Ledin, A., 2003. Household chemicals and personal care products as sources for xenobiotic organic compounds in grey wastewater. Water SA 29 (2), 135–146.

European Chemicals Agency, 2015a. Biocidal active substances. http://echa.europa.eu/information-on-chemicals/biocidal-active-substances;jsessionid=3A5ED4D17DE2F7E107A219F152954286.live2?p_auth=5gyycIgb&p_p_id=echarevbiocides_WAR_echarevbiocidesportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&_echarevbiocides_WAR_echarevbiocidesportlet_viewTab=Search&_echarevbiocides_WAR_echarevbiocidesportlet_javax.portlet.action=tabsAction&tabs1=Summary (accessed June 14, 2015).

European Chemicals Agency, 2015b. Biocidal active substances. http://echa.europa.eu/information-on-chemicals/biocidal-active-substances;jsessionid=3A5ED4D17DE2F7E107A219F152954286.live2?p_auth=5gyycIgb&p_p_id=echarevbiocides_WAR_echarevbiocidesportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&_echarevbiocides_WAR_echarevbiocidesportlet_viewTab=Search&_echarevbiocides_WAR_echarevbiocidesportlet_javax.portlet.action=tabsAction&tabs1=Summary (accessed October 02, 2015).

European Chemicals Agency, d. Emission scenario documentshttp://echa.europa.eu/en/guidance-documents/guidance-on-biocides-legislation/emission-scenario-documents (accessed January 27, 2016, n.d.).

European Commission, 2015. Manual of decisions for implementation of directive 98/8/EC concerning the placing on the market of biocidal products. https://circabc.europa.eu/d/a/workspace/SpacesStore/d0155521-069e-4e8c-91cc-126006d32a83/Manual%20of%20decisions%20(obsolete%20as%20of%2001.10.2015 (accessed March 03, 2016).

European Commission, 2016a. Commission implementing decision (EU) 2016/109 of 27 January 2016 not to approve PHMB (1600; 1.8) as an existing active substance for use in biocidal products for product-types 1, 6 and 9. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=OJ:JOL_2016_021_R_0013 (accessed February 04, 2016).

European Commission, 2016b. Commission implementing decision (EU) 2016/110 of 27 January 2016 not approving triclosan as an existing active substance for use in biocidal products for product-type 1. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=OJ:JOL_2016_021_R_0014 (accessed February 04, 2016).

European Union, 1998. Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 Concerning the Placing of Biocidal Products on the Market: BPD.

European Union, 2005. Regulation (EC) no 648/2004 of the European Parliament and of the Council of 31 March 2004 on Detergents.

European Union, 2007. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Establishing a European Chemicals Agency, Amending Directive 1999/45/EC and Repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

European Union, 2009a. Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 Concerning the Placing of Plant Protection Products on the Market and Repealing Council Directives 79/117/EEC and 91/414/EEC.

European Union, 2009b. Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on Cosmetic Products.

European Union, 2013. Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 Concerning the Making Available on the Market and Use of Biocidal Products: BPR.

Frederiksen, H., Jensen, T.K., Jørgensen, N., Kyhl, H.B., Husby, S., Skakkebæk, N.E., et al., 2014. Human urinary excretion of non-persistent environmental chemicals: an overview of Danish data collected between 2006 and 2012. Reproduction 147 (4), 555–565.

Gasperi, J., Geara, D., Lorgeoux, C., Bressy, A., Zedek, S., Rocher, V., et al., 2014. First assessment of triclosan, triclocarban and paraben mass loads at a very large regional scale: case of Paris conurbation (France). Sci. Total Environ. 493, 854–861.

Geier, J., Lessmann, H., Schnuch, A., Uter, W., 2012. Recent increase in allergic reactions to methylchloroisothiazolinone/methylisothiazolinone: is methylisothiazolinone the culprit? Contact Dermatitis 67 (6), 334–341.

Gromaire, M.C., Van de Voorde, A., Lorgeoux, C., Chebbo, G., 2015. Benzalkonium runoff from roofs treated with biocide products - in situ pilot-scale study. Water Res. 81, 279–287.

Hahn, S., Schneider, K., Gartiser, S., Heger, W., Mangelsdorf, I., 2010. Consumer exposure to biocides—identification of relevant sources and evaluation of possible health effects. Environ. Health Glob. Access Sci. Source 9, 7.

Hall, B., Tozer, S., Safford, B., Coroama, M., Steiling, W., Leneveu-Duchemin, M.C., et al., 2007. European consumer exposure to cosmetic products, a framework for conducting population exposure assessments. Food Chem. Toxicol. 45 (11), 2097–2108.

Heffernan, A.L., Baduel, C., Toms, M L]–>L.M.L., Calafat, A.M., Ye, X., Hobson, P., et al., 2015. Use of pooled samples to assess human exposure to parabens, benzophenone-3 and triclosan in Queensland, Australia. Environ. Int. 85, 77–83.

Herrmann, M., Olsson, O., Fiehn, R., Herrel, M., Kümmerer, K., 2015. The significance of different health institutions and their respective contributions of active pharmaceutical ingredients to wastewater. Environ. Int. 85, 61–76.

Hertz-Picciotto, I., Cassady, D., Lee, K., Bennett, D.H., Ritz, B., Vogt, R., 2010. Study of Use of Products and Exposure-Related Behaviors (SUPERB): study design, methods, and demographic characteristics of cohorts. Environ. Health Glob. Access Sci. Source 9, 54.

Kim, S.A., Moon, H., Lee, K., Rhee, M.S., 2015. Bactericidal effects of triclosan in soap both in vitro and in vivo. J. Antimicrob. Chemother.

Kosma, C.I., Lambropoulou, D.A., Albanis, T.A., 2014. Investigation of PPCPs in wastewater treatment plants in Greece: occurrence, removal and environmental risk assessment. Sci. Total Environ. 466–467, 421–438.

Kümmerer, K., Dionysiou, D.D., Fatta-Kassinos, D., 2015. Long-Term Strategies for Tackling Micropollutants. Springer Berlin Heidelberg, Berlin, Heidelberg.

Kupper, T., Plagellat, C., Brändli, R.C., de Alencastro, L.F., Grandjean, D., Tarradellas, J., 2006. Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment. Water Res. 40 (14), 2603–2612.

Larsson, K., Ljung Björklund, K., Palm, B., Wennberg, M., Kaj, L., Lindh, C.H., et al., 2014. Exposure determinants of phthalates, parabens, bisphenol A and triclosan in Swedish mothers and their children. Environ. Int. 73, 323–333.

Le Corre, K.S., Ort, C., Kateley, D., Allen, B., Escher, B.I., Keller, J., 2012. Consumption-based approach for assessing the contribution of hospitals towards the load of pharmaceutical residues in municipal wastewater. Environ. Int. 45, 99–111.

Ledin, A., Auffahrt, K., Eriksson, E., Smith, M., Eilersen, A.M., Mikkelsen, P.S., et al., 2003. Udvikling af metode til karakterisering af gråt spildevand: Miljøstyrelsen.

Moran, R.E., Bennett, D.H., Tancredi, D.J., Wu, X., Ritz, B., Hertz-Picciotto, I., 2012. Frequency and longitudinal trends of household care product use. Atmos. Environ. 55, 417–424.

Morasch, B., Bonvin, F., Reiser, H., Grandjean, D., de Alencastro, L.F., Perazzolo, C., et al., 2010. Occurrence and fate of micropollutants in the Vidy Bay of Lake Geneva, Switzerland. Part II: micropollutant removal between wastewater and raw drinking water. Environ. Toxicol. Chem. 29 (8), 1658–1668.

Peck, A.M., 2006. Analytical methods for the determination of persistent ingredients of personal care products in environmental matrices. Anal. Bioanal. Chem. 386 (4), 907–939.

Pieper, C., Schwebke, I., Noeh, I., Uhlenbrock, K., Hübner, N., Solecki, R., 2014. Antimicrobial products in the domestic area - a consideration of the effects on human health and the environment as well as on the benefit for consumers. Hyg. Med. 39 (3), 68–76.

Reemtsma, T., Weiss, S., Mueller, J., Petrovic, M., González, S., Barcelo, D., et al., 2006. Polar pollutants entry into the water cycle by municipal wastewater: a European perspective. Environ. Sci. Technol. 40 (17), 5451–5458.

Rodil, R., Quintana, J.B., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2009. Multi-residue analytical method for the determination of emerging pollutants in water by solid-phase extraction and liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1216 (14), 2958–2969.

Rotsidou, M., Scrimshaw, M.D., 2015. An approach for prioritizing "down-the-drain" chemicals used in the household. Int. J. Environ. Res. Public Health 12 (2), 1351–1367.

Rüdel, H., Böhmer, W., Müller, M., Fliedner, A., Ricking, M., Teubner, D., et al., 2013. Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: results from the German Environmental Specimen Bank. Chemosphere 91 (11), 1517–1524.

SCENIHR, 2009. Assessment of the Antibiotic Resistance Effects of Biocides (Brussels).

Scientific Committee on Consumer Safety, 2012. The SCCS'S Notes of Guidance for the Testing of Cosmetic Substances and their Safety Evaluation. European Commission, Brüssel.

Singer, H., Jaus, S., Hanke, I., Lück, A., Hollender, J., Alder, A.C., 2010. Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water. Environ. Pollut. 158 (10), 3054–3064.

Statistisches Bundesamt, 2010. Demographische Standards: Ausgabe 2010. Statistik und Wissenschaft Vol. 17 (Wiesbaden).

Statistisches Bundesamt, 2013. Ergebnisse für den/die Haupteinkommensbezieher/-in am Ort der Hauptwohnung als Repräsentant/-in für den jeweiligen Privathaushalt für das Jahr 2011. https://www.destatis.de/DE/Methoden/DemografischeRegionaleStandards/MZ2011_heb.xls?__blob=publicationFile (accessed October 06, 2015).

Su, L., Khunjar, W.O., Aga, D.S., 2014. Analysis of trace organic pollutants in wastewater to assess biodegradation using wrong-way-round ionization in liquid chromatography/tandem mass spectrometry. Rapid Commun. Mass Spectrom. 28 (11), 1265–1272.

Tarazona, J.V., 2014. Environmental Risk Assessment, Cosmetic and Consumer Products. Encyclopedia of Toxicology. Elsevier, pp. 394–397.

Weegels, M.E., van Veen, M.P., 2001. Variation of consumer contact with household products: a preliminary investigation. Risk Anal. 21 (3), 499–511.

Weigel, S., Kuhlmann, J., Hühnerfuss, H., 2002. Drugs and personal care products as ubiquitous pollutants: occurrence and distribution of clofibric acid, caffeine and DEET in the North Sea. Sci. Total Environ. 295 (1–3), 131–141.

Weston, D.P., Ramil, H.L., Lydy, M.J., 2013. Pyrethroid insecticides in municipal wastewater. Environ. Toxicol. Chem. 32 (11), 2460–2468.

Wick, A., Fink, G., Ternes, T.A., 2010. Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1217 (14), 2088–2103.

Wittmer, I.K., Scheidegger, R., Bader, H., Singer, H., Stamm, C., 2011. Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409 (5), 920–932.

Woutersen, M., Tiesjema, B., Jeurissen, S.M.F., de Bruijn, A.C.P., Herremans, J.M.M., Hegger, I., 2015. Producten op de grensvlakken Warenwet - Wet op de medische hulpmiddelen - Biocidenverordening. Bilthoven. RIVM Rapport 2015–0184.

Wu, X.M., Bennett, D.H., Ritz, B., Cassady, D.L., Lee, K., Hertz-Picciotto, I., 2010. Usage pattern of personal care products in California households. Food Chem. Toxicol. 48 (11), 3109–3119.

Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater

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Supplementary information

S1. Comparison of demographic characteristics

Table 1: The demographic data of the different neighbourhoods is compared with average data for these regions in Germany based on the "Mikrozensus 2011" (available online at https://www.destatis.de/DE/Methoden/DemografischeRegionaleStandards/MZ2011_heb.xls?__blob=publicationFile, updated on 2013, checked on 10/6/2015).

Demographic characteristics	Neighbourhood A		Rural Regions		Neighbourhood B		Intermediate Regions		Neighbourhood C		Predominantly Urban		Total Study Sites		Total Germany	
	n	%/an [a]	n (1000)	%/an [a]	n	%/an [a]	n (1000)	%/an [a]	n	%/an [a]	n (1000)	%/an [a]	n	%/an [a]	n (1000)	%/an [a]
Gender																
Female	64	68.1	-	-	12	63.2	-	-	16	80.0	-	-	92	69.2	-	-
Male	30	31.9	-	-	7	36.8	-	-	4	20.0	-	-	41	30.8	-	-
Age interviewee																
17-30	1	1.1	-	-	7	36.8	-	-	10	50.0	-	-	18	13.5	-	-
31-40	17	18.1	-	-	2	10.5	-	-	5	25.0	-	-	24	18.0	-	-
41-50	8	8.5	-	-	1	5.3	-	-	3	15.0	-	-	12	9.0	-	-
51-60	16	17.0	-	-	4	21.1	-	-	2	10.0	-	-	22	16.5	-	-
61-70	24	25.5	-	-	1	5.3	-	-	0	0.0	-	-	25	18.8	-	-
71-80	21	22.3	-	-	3	15.8	-	-	0	0.0	-	-	24	18.0	-	-
81-92	5	5.3	-	-	1	5.3	-	-	0	0.0	-	-	6	4.5	-	-
Not specified	2	2.1	-	-	0	0.0	-	-	0	0.0	-	-	2	1.5	-	-
Number and average number of household members																
Children under 3	9	0.1	261	1.0	4	0.2	655	1.0	5	0.3	1031	1.0	18	0.2	1947	1.0
Children under 6	16	0.2	542	1.2	5	0.3	1347	1.2	5	0.3	2069	1.2	26	0.3	3958	1.2
Children under 18	41	0.5	1900	1.6	10	0.6	4742	1.6	5	0.3	6312	1.6	56	0.5	12955	1.6
Members 18-65	113	1.2	-	-	20	1.1	-	-	39	2.0	-	-	172	1.4	-	-
Members > 65	73	0.8	-	-	6	0.3	-	-	0	0.0	-	-	79	0.4	-	-
Highest education level [b]																
Without graduation	1	1.1	112	2.1	2	10.5	334	2.5	0	0.0	904	4.3	3	2.3	1357	3.4
Graduation after 9 years	30	31.9	2359	43.2	5	26.3	5930	45.0	0	0.0	7129	33.6	35	26.3	15417	38.7
Graduation after 10 years	25	26.6	1034	18.9	7	36.8	2818	21.4	4	20.0	4281	20.2	36	27.1	8133	20.4
Graduation after ≥12 years	34	36.2	984	18.0	2	10.5	3089	23.4	16	80.0	7808	36.8	52	39.1	11881	29.8
Other	2	2.1	950	17.4	3	15.8	975	7.4	0	0.0	1018	4.8	5	3.8	2943	7.4
Not specified	2	2.1	21	0.4	0	0.0	36	0.3	0	0.0	62	0.3	2	1.5	119	0.3

Demographic characteristics	Neighbourhood A		Rural Regions		Neighbourhood B		Intermediate Regions		Neighbourhood C		Predominantly Urban		Total Study Sites		Total Germany	
	n	%/an [a]	n (1000)	%/an [a]	n	%/an [a]	n (1000)	%/an [a]	n	%/an [a]	n (1000)	%/an [a]	n	%/an [a]	n (1000)	%/an [a]
Job training [b,c]																
No job training (yet)	4	4.3	876	16.0	3	15.8	2309	17.5	4	20.0	5037	23.8	11	6.7	8226	20.6
Apprenticeship	71	75.5	3260	59.7	12	63.2	7478	56.7	10	50.0	10063	47.5	93	57.1	20801	52.2
Forman or similar	11	11.7	560	10.3	0	0.0	1399	10.6	1	5.0	1695	8.0	12	7.4	3654	9.2
University degree	32	34.0	572	10.5	2	10.5	1783	13.5	9	45.0	4096	19.3	43	26.4	6449	16.2
Other	0	0.0	164	3.0	1	5.3	168	1.3	0	0.0	224	1.1	1	0.6	556	1.4
Not specified	2	2.1	29	0.5	1	5.3	48	0.4	0	0.0	86	0.4	3	1.8	163	0.4
Total net household income																
< 850 € [d]	1	1.1	625	11.5	3	15.8	1241	9.4	5	25.0	2966	14.1	9	6.8	4830	12.1
851 - 1500 €	7	7.4	1236	22.7	6	31.6	2703	20.6	4	20.0	4560	21.5	17	12.8	8499	21.3
1501 - 2000 €	6	6.4	861	15.8	7	36.8	2056	15.6	2	10.0	3297	15.5	15	11.3	6215	15.6
2001 - 3000 € [e]	25	26.6	1145	21	1	5.3	2742	20.8	2	10.0	4064	19.2	28	21.1	7951	19.9
3001 - 4000 € [f]	26	27.7	756	13.9	0	0.0	1977	14.9	4	20.0	2614	12.3	30	22.6	5347	13.4
4001 - 5000 €	10	10.6	297	5.5	0	0.0	870	6.6	0	0.0	1174	5.5	10	7.5	2341	5.9
5001 - 6000 €	5	5.3	128	2.4	0	0.0	380	2.9	2	10.0	562	2.7	7	5.3	1070	2.7
> 6000 €	7	7.4	106	2	0	0.0	413	3.2	0	0.0	666	3.2	7	5.3	1188	3
Not specified	7	7.4	219	4	2	10.5	715	5.4	1	5.0	1285	6.1	10	7.5	2218	5.6
Living conditions																
Single-family homes	84	89.4	-	-	6	31.6	-	-	5	25.0	-	-	95	71.4	-	-
Flat (with partner/family)	10	10.6	-	-	13	68.4	-	-	8	40.0	-	-	31	23.3	-	-
Shared flat	- [g]	- [g]	-	-	0	0	-	-	7	35.0	-	-	7	5.3	-	-
Ø m²	136	-	-	-	65	-	-	-	67	-	-	-	-	-	-	-

[a] an: Average number of household members
[b] Of the household member with the highest income
[c] Multiple selections possible
[d] For Mikrozensus-data: <900€
[e] For Mikrozensus-data: 2000 – 2900 €
[f] For Mikrozensus-data: 2900 – 4000 €
[g] Not a possible choice in the questionnaires for neighbourhood A

Artikel 2

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Consumers' perceptions of biocidal products in households

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ABSTRACT

Biocidal products are commonly used in households and can pose a risk to human health and the environment. The aim of this study was to evaluate consumers' use and understanding of biocidal products in order to identify starting points for minimising their exposure to these products and reducing possible emissions to the environment. In a case study, standardised questionnaires were used to interview consumers in 133 households in three neighbourhoods in Northern Germany, representing the urban–rural typologies in Europe: predominantly urban, intermediate and predominantly rural regions. The questions focussed on the comprehension of the term 'biocide', pest control habits, sources of information, risk perception of different product groups and possible emission reduction measures.

Only 21% of the respondents understood the term 'biocide' correctly, whereas 29% thought of 'something that had to do with organic pest control', and 28% were not able to think of a possible meaning. The risk perception of biocidal products compared to plant protection products varied depending on the living conditions. In the urban neighbourhood, biocidal products were perceived as more dangerous than in the rural area. The main pests to be fought were ants, mould and fruit fly. The results of the study indicate that there is a considerable difference between the types of biocidal products that interviewees claimed to own and those that they actually did have in their households. Most notably, respondents did not realise that they owned surface disinfectants. This result indicates that consumers often seem not to be aware of using specific biocidal products. Also, this shows the limitations of collecting data on products owned with only one method, as the results from products inventories of the households deviate from the data collected in interviews.

Our results show that the term 'biocide' is not fully understood by many people. To communicate possible risks of biocidal products, other terms would have to be used. Online information regarding general facts on necessary general hygiene measures and biocidal products against bacteria and insects are likely to be of highest relevance for consumers. However, risk communication for biocidal products in general is difficult because consumers are often not aware of using biocidal products. For this reason, information and awareness raising campaigns should be accompanied by further measures such as sales restrictions for specific user-groups or prohibitions of certain uses for a sustainable use of biocidal products.

1. Introduction

1.1. Information of consumers regarding household chemicals

Chemical products are often used in households and can pose risks towards the health of consumers (Buffet-Bataillon et al., 2016; Geier et al., 2012; Hahn et al., 2010; Horton et al., 2011; Llop et al., 2013; Presgrave et al., 2008; Ruckart et al., 2004; Webber et al., 2017) and the environment (Brausch and Rand, 2011; Buergi et al., 2007; Corcellas et al., 2015; Kosma et al., 2014; Rüdel et al., 2013; Ternes et al., 2004; Weigel et al., 2002). Biocidal products constitute a specific group within household chemicals, next to, for example, washing and cleaning agents and personal care products. Biocidal products are regulated in *Regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products* (BPR). They are defined as products 'with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on any harmful organism by any means other than mere physical or mechanical action' (European Union, 2013b). Biocidal active substances can also be incorporated in personal care products and washing and cleaning agents as in-can preservatives. The benefits of the use of biocidal products in households have been questioned, especially for disinfectants (Food and Drug Administration, 2016; Kim et al., 2015; Larson et al., 2004; Pieper et al., 2014). It is therefore very important

Abbreviations: BPR, Biocidal Products Regulation (EU) 528/2012; df, degrees of freedom; PT, product type

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that consumers use these products only if necessary and, if needed, in an appropriate and a safe manner. For this reason, consumers need to be informed about risk mitigation measures for biocidal products and understand why they should comply (Bruinen de Bruin et al., 2007; Ternes et al., 2004).

In today's world, politics and economy often expect consumers to be 'reasonably well informed and reasonably observant and circumspect' (European Court of Justice, 1998). They are expected to make informed choices, e.g. buying and applying household chemicals, based on what is known about risks for humans or the environment (European Union, 2013a). However, this paradigm has been questioned regularly, as studies have shown that consumers often know very little about the different types of chemical products they use in their households (Epp et al., 2010; European Commission, 2016b, 2011; Glegg and Richards, 2007). Until now, the attitudes towards biocidal products in particular have never been studied, other than for human pharmaceuticals or washing and cleaning agents (Adomßent, 2015; Bearth et al., 2017; Bound and Voulvoulis, 2005; Götz and Keil, 2007; Stemplewski et al., 2014). Only some biocidal product types were studied together with other product groups (Armes et al., 2011; Bennett et al., 2012; Moran et al., 2012; Wu et al., 2011). The hitherto available results indicate that biocidal products are perceived as less dangerous than plant protection products (ANSES, 2010).

The perceived risks by consumers usually differ from the risks detected during regulatory risk assessments (Kraus et al., 1992). The severity of ecotoxicological risk is calculated using hazard and the probability of exposure. However, Kraus et al. (1992) show that consumers have difficulties understanding that the exposure is influencing the risk. This makes the communication of risks by chemicals difficult (OECD, 2002; Scheer et al., 2010). At the same time, consumers are confronted with professional marketing experts (Howells, 2005) and advertising campaigns that do not necessarily allow them to base their purchase decisions on an informed risk assessment, as it has previously been shown for household disinfectants (Wieck, 2015). This is particularly problematic because risks and benefits of household chemicals often cannot be perceived directly (Beck, 2017). The OECD guidance document on risk communication for chemical risk management offers suggestions on how to draft communication strategies on chemical topics. Two-way communication would be ideal (OECD, 2002). However, it is difficult to reach a broad audience with it, so one-way communication is often used. Especially for those information offers, for example print and online, it is crucial to know the needs of the recipients and starting points, depending on the topic (OECD, 2002). It is therefore of great importance to close the knowledge gaps on the perception of biocidal products by consumers for a targeted information campaign. At the same time, it has to be kept in mind that even if information is available, it only has a limited effect on consumer behaviour (Howells, 2005). For this reason, this study will discuss possibilities for consumer protection that go beyond information and awareness raising campaigns.

1.2. Data collection on perception of biocidal products by consumers

Methods to evaluate the knowledge of consumers regarding products are usually based on questionnaires. These can be done by online, self-administered questionnaires, via telephone or face-to-face. While response rates and engagement of the interviewees is higher in face-to-face settings than online, these are also more time-consuming and costly (Hertz-Picciotto et al., 2010). Some large studies have evaluated the knowledge and assessment of household chemicals in general by consumers. Studies on chemicals in general by the German Federal Institute for Risk Assessment and the European Chemicals Agency were conducted with more than 1000 participants by telephone (Epp et al., 2010) and up to more than 27000 participants face-to-face, respectively (European Commission, 2016b, 2011; Midden et al., 2011). Other studies focussed on specific biocidal product types amongst other product groups (ANSES, 2010; Bennett et al., 2012; Moran et al., 2012). While most of the studies used quantitative approaches with structured questionnaires, others used qualitative interviews (Midden et al., 2011) or both (Glegg and Richards, 2007). However, up to now no one has explored the perception of biocidal products in general by consumers, focussing on their particularities such as terms and the diversity of uses. In addition, most studies investigating product inventories use answers of consumers on products owned and used without validating the responses. This makes an assessment of the validity of these studies difficult. Inventories could be verified by comparing data on products obtained by questionnaires to product inventories established by third parties of the same households. For the households examined in this study, we already had product inventories available (Wieck et al., 2016) making a comparison of the two survey methods possible.

1.3. Objectives

As the above-mentioned studies did not evaluate consumers' perception of biocidal products in particular, the objective of this study is to analyse consumers' use and understanding of this product group and to evaluate how they could be further encouraged to use them in a sustainable way. Additionally, this study compares data collected using questionnaires about products owned to data from product inventories based on barcode scans in the same households, which validates the data collected by both methods. In the following, we present the results of a standardised quantitative questionnaire in three neighbourhoods. Based on these results, we identify consumers' status quo perception of biocidal products and derive possible starting points to adjust consumer protection strategies supporting a more sustainable use.

2. Material and methods

2.1. Study design

Interviews were conducted in person with one willing household member of 133 households in three neighbourhoods in Northern Germany (BBSR, 2009), representing the three different urban–rural typologies in Europe (Eurostat, 2017). Neighbourhood A represents predominantly rural regions. It is dominated by single-family homes within a small town of approximately 3000 inhabitants. Neighbourhood B represents the intermediate regions and is dominated by multi-family homes within a town of 33000 inhabitants. Neighbourhood C is characteristic of the predominantly urban regions and lies within Hamburg (1.8 Mio. inhabitants). This neighbourhood consists of multi-family homes with a high proportion of shared flats. Table 1 (Wieck et al., 2016, modified) depicts the demographic characteristics of all interviewees and households.

After agreeing to participate in the study, a trained interviewer asked questions from a standardised questionnaire and noted responses on the questionnaire form. These sessions were structured and the trained interviewer only asked questions from the questionnaire, using it similar to a script. After the questionnaire was completed, the trained interviewer took barcode scans of all biocidal products, washing and cleaning agents and wastewater-relevant personal care products in the households. The results of the barcode scans are published in Wieck et al. (2016), the results of the questionnaires are presented in this publication.

To recruit participants in Neighbourhood A, all households were sent a letter from the cooperating local disposal company in agreement with the town mayor. This letter contained information regarding the project and the planned study. The interviews were conducted between March and May 2015. In this neighbourhood, the goal was to obtain a complete survey of the neighbourhood's entire 145 households. Therefore, all households in the neighbourhood were contacted several times to achieve this goal and no sampling strategy was necessary. In the end, 94 households within this neighbourhood participated in the

Table 1
Demographic characteristics of the interviewed neighbourhoods (Wieck et al., 2016, modified).

Characteristics	Neighbourhood A		Neighbourhood B		Neighbourhood C	
	n	%	n	%	n	%
Gender						
Female	64	68.1	12	63.2	16	80.0
Male	30	31.9	7	36.8	4	20.0
Interviewee age						
17–30	1	1.1	7	36.8	10	50.0
31–40	17	18.1	2	10.5	5	25.0
41–50	8	8.5	1	5.3	3	15.0
51–60	16	17.0	4	21.1	2	10.0
61–70	24	25.5	1	5.3	0	0.0
71–80	21	22.3	3	15.8	0	0.0
81–92	5	5.3	1	5.3	0	0.0
Not specified	2	2.1	0	0.0	0	0.0
Household members						
Single household	17	18.1	6	31.6	5	25.0
Household with 2 adults	40	42.6	5	26.3	7	35.0
Household with 1 child	16	17.0	6	31.6	5	25.0
Household with 2 children	5	5.3	2	10.5	0	0.0
Household with 3 children	3	3.2	0	0.0	0	0.0
Other	13	13.8	0	0.0	3	15.0
Highest school leaving certificate [a]						
Without graduation	1	1.1	2	10.5	0	0.0
Graduation after 9 years	30	31.9	5	26.3	0	0.0
Graduation after 10 years	25	26.6	7	36.8	4	20.0
Graduation after ≥12 years	34	36.2	2	10.5	16	80.0
Other	2	2.1	3	15.8	0	0.0
Not specified	2	2.1	0	0.0	0	0.0
Job training [a,b]						
No job training (yet)	4	4.3	3	15.8	4	20.0
Apprenticeship	71	75.5	12	63.2	10	50.0
Master craftsman diploma (‘Meister’) or similar	11	11.7	0	0.0	1	5.0
University degree	32	34.0	2	10.5	9	45.0
Other	0	0.0	1	5.3	0	0.0
Not specified	2	2.1	1	5.3	0	0.0
Total net household income						
< 850 €	1	1.1	3	15.8	5	25.0
851–1500 €	7	7.4	6	31.6	4	20.0
1501–2000 €	6	6.4	7	36.8	2	10.0
2001–3000 €	25	26.6	1	5.3	2	10.0
3001–4000 €	26	27.7	0	0.0	4	20.0
4001–5000 €	10	10.6	0	0.0	0	0.0
5001–6000 €	5	5.3	0	0.0	2	10.0
> 6000 €	7	7.4	0	0.0	0	0.0
Not specified	7	7.4	2	10.5	1	5.0

[a] Of the household member with the highest income.
[b] Multiple selections possible.

interviews leading to a response rate of 65%.

In Neighbourhoods B and C, a convenience sampling strategy was used based on the willingness of a household member to participate in the study. In Neighbourhood B, 80 households were mailed a letter from Leuphana University of Lüneburg, containing information regarding the project and the planned study. The questionnaire and barcode scanning were conducted between July and August 2015. 19 households completed the survey, leading to a response rate of 24%. In Neighbourhood C, a notice from Leuphana University of Lüneburg containing information regarding the project and the planned study was posted in multi-family homes. The questionnaire and barcode scanning were conducted between June and July 2015. 20 households participated in the study. To account for the shared flats in Neighbourhood C, we defined, in line with the definition used by the German Federal Statistical Office (Statistisches Bundesamt, 2010), a household as an economic community and not simply as group of people living together. As it remained unknown how many households according to this definition were situated in the multi-family homes, the response rate for this neighbourhood cannot be calculated.

2.2. Questionnaire

The questionnaire was designed to evaluate consumers' perception and biocidal products use and to compare this to other household products such as plant protection products, washing and cleaning agents and personal care products. Biocidal product types (PT) are defined in Annex V of the BPR. Those that are relevant for consumers and are further considered in our questionnaire include: disinfectants for various purposes (PT 1-3, 5), products to protect materials such as film preservatives (PT 7), wood preservatives (PT 8), construction material preservatives (PT 10), products to control specific pests such as rodenticides (PT 14), insecticides (PT 18), repellents and attractants (PT 19) and embalming and taxidermist fluids (PT 22) (COWI, 2009). The questionnaire was designed with the questionnaire tool EvaSys (Electric Paper Evaluationssysteme GmbH, Lüneburg, Germany), which also was used to scan the completed questionnaires. The standardised questionnaire consisted of a mixture of open and closed questions. The survey items covered the topics, understanding of the term ‘biocide’, sources of information, pest control habits, risk perception in comparison to other household chemicals and views towards possible risk reduction measures. A translation of the questions can be found in the supplementary material. Following the questions regarding the understanding of the term 'biocides', the meaning of the term was explained to the interviewees to avoid misunderstandings during the rest of the interview. To characterise the households and interviewees, household parameters and demographic details were gathered. Demographic questions were based on the recommendations of the German Federal Statistical Office (Statistisches Bundesamt, 2010), which enables the comparison of the demographic results to German census data. For this reason, education and professional training of the main income earners of the households were requested, not those of the interviewees. The questionnaire was tested in classic pre-tests in randomly chosen households (n = 20) not belonging to the neighbourhoods.

All statistical calculations were completed with IBM SPSS Statistics 24.0.0.0 (IBM, Armonk, USA). Variables on a ratio scale were centred if they had no meaningful zero and nominally scaled variables were recoded using effect coding. Pearson's chi-squared test was used to detect correlations for data sets containing nominally scaled variables. For sets with the expected values in any of the cells of the contingency table below 5, Fisher's exact test was used. To model the relationship between variables, linear regression was used with data-based, stepwise choice of predictors. P-values below 0.05 were considered significant.

3. Results and discussion

3.1. The term 'biocide'

Before the term 'biocide' was mentioned and explained in the questionnaire, interviewees were asked whether they had heard the term before. 39% had never heard the term before. Rural Neighbourhood A differs from the intermediate Neighbourhood B and urban Neighbourhood C. In the first, the majority of all interviewees had heard the term 'biocide' before (61%), whereas in the other neighbourhoods, the majority had not (Chi-square (degrees of freedom (df): 2) = 9.782; p = 0.008). Also, the education background of household members had an influence on whether the interviewees said that they had already heard the term. Whereas only 43% of the interviewees in households in which the main income earner had completed 9 years in school stated that they had heard the term, 67% had done so in households in which the main income earners had completed 10 years of school, and 71% if the main income earner had completed 12 or more years in school. These differences were significant between main income earners finishing 9 and 10 years of school (Chi-square (df: 2) = 6.507; p = 0.039); and between main income earners finishing 9 and 12 or more years of school (Chi-square (df: 2) = 7.170; p = 0.028).

In the Neighbourhoods A and B, interviewees were additionally asked what they tend to associate with the term 'biocide' (Table 2). 29% thought of '*something that has to do with* "*organic*"/*organic pest control*', while only 21% thought of '*poison or pest control*'. 28% were not able to name any possible meaning. There were no significant correlations between the correct understanding of the term and other variables besides having completed a master craftsman diploma or a similar degree (Fishers Exact (p = 0.049)). As these results indicate, many interviewees were familiar with the term but only some of them actually knew what it meant. There was also no correlation between the correct understanding of the term and education variables, even though members of households characterised by higher educational levels stated more often to have heard the term before. Thus, it might be possible that these interviewees were less willing to admit that they had not heard the term.

Table 2
Categorised answers to the open question 'If you would hear the term "biocides", what would you think that it means?'.

Categorised answers	n	%
'Something that has to do with "organic"/organic pest control'	33	29
No idea	32	28
'Poison or pest control'	24	21
'Something negative'	12	11
'Assignment to other product groups such as WCA'	7	6
Other	5	4

We assume that the misunderstanding of the term 'biocides' is probably due to the German prefix for organic products. Organically produced consumer products often are marketed with the name prefix 'bio', for this reason consumers may have positive associations when they hear the term 'biocides'. While consumers, then, might interpret the prefix as metaphoric for something good, legislators in particular intended it to be understood literally in its direct translation from Greek, 'life', with the full meaning of 'biocide' being 'killing life'. Lakoff and Johnson (2014) assume that metaphors influence human actions, so this metaphoric understanding might have a direct influence on consumers' behaviour regarding biocidal products. Moreover, consumers who do not understand the meaning at all might not be aware of the fact that they handle products with an intended effect on organisms and might use those products with less care (see Section 3.3 for further discussion). There are, however, no studies that have examined these assumptions or the use of biocidal products in daily life. Given this misunderstanding of the term, one needs to consider how it could and should be used for risk communication purposes in Germany. The situation may be different in other countries, where, for example, English is spoken, and the prefix 'bio' is not used for marketing organically produced products.

We are not aware on other studies that have examined the understanding of the term 'biocides'. For this reason, our study is the first to draw attention to this important obstacle for risk communication. The importance of national linguistic differences has already been raised in the context of risk communication by the European Commission (2011). They asked people in European member states in the respective national language which product might be more hazardous, one with the word 'danger' on it or with the word 'warning'. In Germany, 67% of the respondents thought that 'danger' was the stronger word, whereas in Estonia, 53% chose the product with the word 'warning'. This illustrates the importance of national risk communication strategies. In countries such as Germany, it would be important to focus awareness raising campaigns on other terms than 'biocide' and to invest in additional efforts to disseminate the term. In Denmark, for example, the information campaign on biocidal products is called 'Biocider er hverdagsgifter' ('Biocides are everyday-poisons', our translation) and found at www.hverdagsgifte.dk. With this expression, the abstract word 'biocide' is translated into more common language.

3.2. Risk perception

The interviewees were asked to rank the product groups washing and cleaning agents, personal care products, plant protection products and biocidal products based on their perception of their risks regarding human health and the environment (Fig. 1). The most dangerous product group was to be ranked on a scale as 1 and the least dangerous one as 4. Washing and cleaning agents and personal care products were perceived as less risky than plant protection products and biocidal products. This finding is in line with previous research (Epp et al., 2010; Glegg and Richards, 2007). This indicates that if interviewees correctly identify the purpose of a given product they are able to correctly assess their risks (see Section 3.3 for further discussion). While the ranking order of personal care products and washing and cleaning agents remained the same in all neighbourhoods (average of 2.8 for washing and cleaning agents and 3.7 for personal care products), the ranking of biocidal products and plant protection products differed from neighbourhood to neighbourhood. Plant protection products were perceived

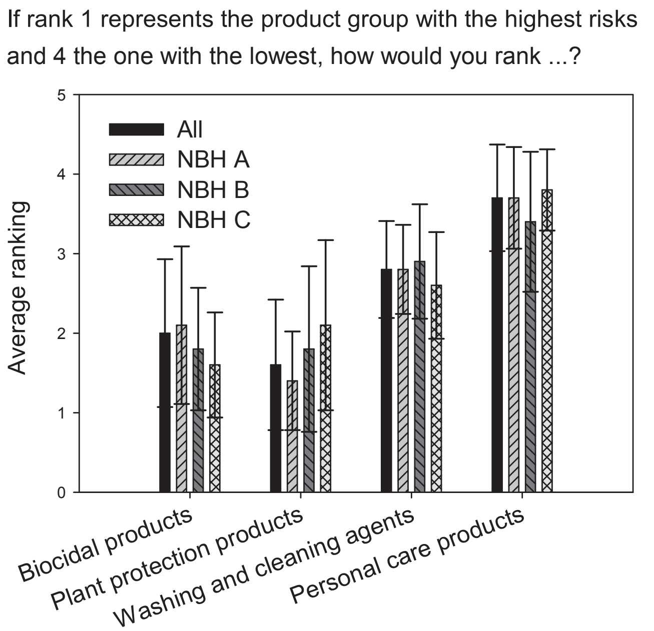

Fig. 1. Ranking of product groups in terms of perceived risk by interviewees. Rank 1 represents the highest perceived risk, whereas 4 represents the lowest. Error bars are included. NBH: neighbourhood.

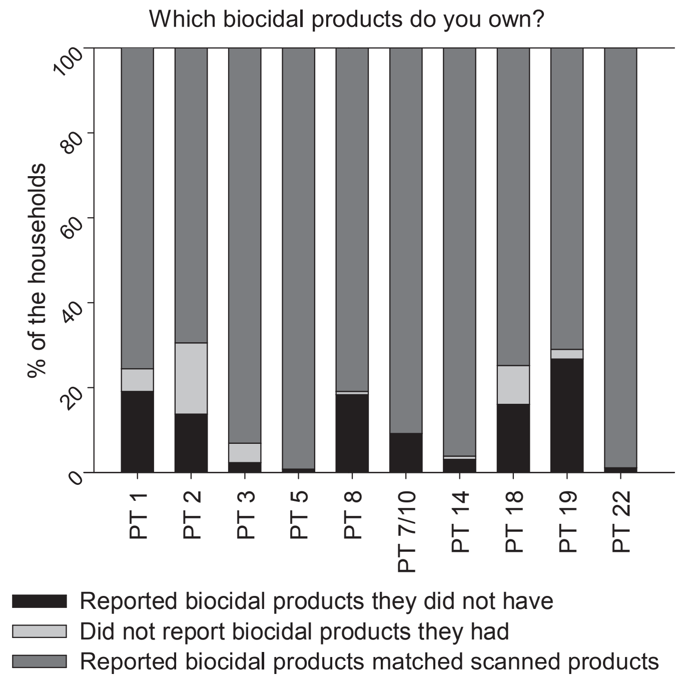

Fig. 2. Comparison of the answers to the question 'Which biocidal products do you own?' and the scanned products in the respective household after Wieck et al. (2016). PT 1: Human hygiene, PT 2: Disinfectants and algaecides not intended for direct application to humans or animals, PT 3: Veterinary hygiene, PT 5: Drinking water, PT 8: Wood preservatives, PT 7/10: Film preservatives/Construction material preservatives, PT 14: Rodenticides, PT 18: Insecticides, acaricides and products to control other arthropods, PT 19: Repellents and attractants, PT 22: Embalming and taxidermist fluids.

as the most dangerous product group in Neighbourhood A and only as the second dangerous product group in Neighbourhood C. For biocidal products, it was the other way around: The average rank in the rural Neighbourhood A was 2.0 and 1.6 in urban Neighbourhood C. In the intermediate Neighbourhood B, biocidal products and plant protection products were, on average, perceived as equally dangerous. These results might be explained by the fact that the risk perception has been shown to decrease for familiar products (European Chemicals Agency, 2012) and that in Neighbourhood A a higher percentage of the interviewees had heard of biocides before. However, this neighbourhood was also more familiar with plant protection products because they were the only ones owning them. What has to be noted is that the variability of the ranking is the highest for biocidal products followed by the variability of the ranking of plant protection products. This might implicate that people are not as familiar with these products as with personal care products and washing and cleaning agents and thus unsure how to rank them.

Interviewees were asked to rank the products according to the perceived risk for humans and the environment in one question. Therefore, it remains unclear whether the results would have been different if two questions had been posed. It is possible that the interviewees thought of risks for human health only.

3.3. Awareness of the biocidal products in households

To evaluate interviewees' awareness of biocidal products in their households, we asked what biocidal product types (PT) they owned. Interviewees claimed that they owned disinfectants (PT 1, 2, 3, 5), façade protection (PT 7, 10), wood preservatives (PT 8), rodenticides (PT 14), insecticides (PT 18), repellents (PT 19) and embalming fluids (PT 22). Using the inventories of our first study (Wieck et al., 2016), we compared the products indicated by the interviewees in the questionnaire with the data collected during our visits to their homes. In 80% of the households, their responses did not completely correspond to the products found in their household. Looking at the different products, we observed that 17% of the interviewees failed to mention disinfectants used for surfaces, e.g. disinfecting toilet cleaners, hygiene sprays for surfaces or products against mould (PT 2). In the case of the seasonally used wood preservatives, insecticides and repellents, interviewees reported that they owned products that were not found later during inventorying (Fig. 2). This might be due to the fact that inventorying took place in spring.

We assume that for disinfectants, the reason might be that people are not aware that some cleaning products they use do, in fact, have disinfecting properties. Bacteria and the effect of disinfectants on their growth are difficult for consumers to perceive. They might only see them as cleaning products. Our results show that cleaning products are perceived as less risky than biocidal products (see Section 3.2). This can result in an increased exposure of consumers to potentially harmful products, as instructions for use are less likely to be followed for cleaning products than for pesticides (European Commission, 2011). Furthermore, misapplication is also discussed to result in sub-lethal exposure of bacteria and thereby increase the risk of resistance (Levy, 2001; Pieper et al., 2014; SCENIHR, 2009). Indeed, it has been shown that the use of disinfectants by consumers did not result in a reduction of bacteria in their homes or a reduction of viral infections (Josephson et al., 1997; Larson et al., 2004). This use of potentially risky products by consumers without having a health benefit is considered problematic and has been criticised often (Food and Drug Administration, 2016; Kampf and Dettenkofer, 2011; Pieper et al., 2014). Moreover, it might give consumers a false sense of security and prevent them from using general hygiene measures (Schuster and Daschner, 2002). For these reasons, consumers need to have detailed information on risks and benefits.

3.4. Articles treated with biocidal active substances

During the interviews, interviewees were questioned regarding their use of biocidal products and articles treated with biocidal active substances ('treated articles'). Only 3% of all interviewees stated that they owned the latter, naming sports clothes and dishcloths as examples. All others denied having such articles or were not sure. This result indicates that there is a need for more information regarding those treated articles. For most consumers a basic introduction would most likely suffice, as the existence of biocidal active substances in products will seemingly be new for a large share of consumers.

3.5. Disposal

Concerning disposal habits, there is a clear difference between the product groups. 89% of the interviewees stated that washing and cleaning agents (n = 131) and personal care products (n = 130) were used up completely. In contrast, only 58% (n = 19) and 65% (n = 99) mentioned that they had done so when it came to plant protection products and biocidal products, respectively. Plant protection products and biocidal products, interviewees often disposed not being completely empty as hazardous waste. This pathway was especially used in the Neighbourhoods A and B. Here, 23% and 25% of the interviewees stated that they used the hazardous waste collection for the disposal of biocidal products, while not one used it in Neighbourhood C.

Only a few interviewees disposed products by pouring them down the drain. The disposal of human pharmaceuticals presented a different trend. Studies conducted in Germany and the United Kingdom show that these are often disposed via the toilette (Bound and Voulvoulis, 2005; Götz and Keil, 2007; Stemplewski et al., 2014). For this reason, information campaigns regarding the correct disposal of products as they have been proposed for pharmaceuticals (Dieter et al., 2010) will probably not be a promising measure to reduce emissions of biocidal active substances into wastewater.

3.6. Information offers

20% of the interviewees (n = 133) reported that they primarily controlled for ants, followed by mould (6%) and fruit flies (4%). Interviewees living in one-family houses mostly dealt with ants, those living in flats sought to contain mould and fruit flies. All respondents were asked where they would search for information on pest control (multiple answers possible). The most important information source was the internet (69%), followed by salespersons (39%) and family or friends (35%).

Specific information offers should focus on ants and other major pests. To minimise exposure to related biocidal product types, one could design information and communication materials for specific biocidal product applications with a focus on preventive or alternative measures against insects, mould or bacteria.

In our study, we specifically asked for general information sources in case of pest infestation because we also wanted to find out how to promote alternative and preventive measures. ‘Product label’ was not included as a possible answer in the questionnaire because consumers may only read a label once they have to deal with an infestation. By then, it is already too late to apply preventive measures, let alone to promote them. Also, manufacturers might be reluctant to promote alternative control measures on products labels because this might lead to decreased sales. Product labels are, however, a good way to communicate information on the risks and the correct use of those products (see Section 3.7). European studies that included ‘product label’ as information source for risks by products showed that this was the most commonly used source of information followed by the internet (Epp et al., 2010; European Commission, 2011).

Our results confirm that the internet is indeed an important source of information. In Germany, it seems to be more important than in other European countries (European Commission, 2016b), this should be kept in mind when designing information campaigns for other regions. When asked how they search for information, most interviewees used search engines instead of visiting specific websites by authorities, manufacturers or non-governmental organisations. This has also been shown by Epp et al. (2010) and suggests that it is very important that consumers can find reliable independent information offers conducting a basic online search. In Europe, all European member states are requested by law to provide information to the public on the benefits and risks associated with biocidal products and ways of minimising their use (European Union, 2013b). In Germany this includes an information platform on alternatives to biocidal products called ‘Biozid-Portal’ (www.biozid.info). It seems advisable to us to ensure that this platform can also be found with other search terms than ‘biocide’ because many consumers do not understand this term (see Section 3.1).

Concerning information provided by salespersons, one has to keep in mind that many preventive measures such as good kitchen hygiene are free and that this information can be communicated more effectively via other channels, e.g. the internet.

3.7. Instructions for use

In our study, 52.4% of the interviewees (n = 124) indicated that they always read the instructions for use for biocidal products; 42.7% did so sometimes. Interviewees included in the latter group (n = 52) were asked with an open question why they chose to read the instructions. The majority (55.8%) stated that they only read the instructions for use of products that were new to them. We also asked all interviewees who indicated that they had read the instructions for whether they also followed those. 57.4% stated that they were always following the instructions; 42.6% sometimes did. Interviewees who were sometimes following the instruction (n = 44) did so if they were able to either understand the instructions (29.5%) or put them into practice (20.5%).

The results correspond to the results of studies showing that risk perception is decreasing if products are used often (European Chemicals Agency, 2012). Our results are also in line with the literature, as a vast majority of people (79%) tend to follow the instructions for use (European Commission, 2011). Discussing these answers, it has to be kept in mind that the social desirability of the answers might play an important role here. It can be assumed that interviewees were reluctant to admit that they did not read instructions or that they read them but did not follow them. Several of our interviewees emphasised the problem of readability, e.g. due to a small font size, a problem that has already been discussed in previous studies (Glegg and Richards, 2007).

These results are closely linked to the importance of product labels as information sources because the instructions for use are often printed on the packaging. Further risk communication tools on labels, for example lists of ingredients (Klaschka and Rother, 2013) or hazard pictograms in accordance with the ‘Globally Harmonized System of Classification and Labelling of Chemicals’ (European Chemicals Agency, 2012; European Commission, 2016b), are often not understood. The design of the packaging (e.g. eco-labels, pictures of families) can adversely affect the risk perception of consumers (Bearth et al., 2017; European Chemicals Agency, 2012). Eco-labels specifically for biocidal products are not available in the EU and not deemed suitable for biocidal products due to their inherent properties and designated purpose of controlling organisms (European Commission, 2016a). Only biocide-free pest control products can receive an eco-label (RAL gGmbH, 2011). On the contrary, the US Environment Protection Agency allows the use of the ‘Designed for the Environment’ logo on antimicrobial products with favourable properties, stating at the same time that no ‘registered pesticide is safe under all circumstances’ (US EPA, 2017).

In the light of the importance of labels for risk communication, we think it is advisable to regulate their design and content in more detail than it is done until now. It seems clear that there should be minimum requirements regarding readability and comprehensibility. From our point of view, these need to go further than the actual implementation of Article 69 of the BPR, which prohibits misleading labels in respect of the risks posed by the product to human health, animal health or the environment or its efficacy (European Union, 2013b).

3.8. Further risk reduction measures

Interviewees were asked to evaluate the importance of the following measures to reduce chemicals in water bodies: (i) behavioural changes of consumers, (ii) technical upgrades of sewage water treatment plants and (iii) official restrictions for manufacturers. Behavioural changes and official restrictions were regarded to be of greater importance than technical upgrades by the interviewees.

These results imply a general understanding of the importance of reducing pollution at the source and not just using end-of-pipe technology. The same trend was observed by Stemplewski et al. (2014). Official restrictions could, for example, be a stronger regulation of information offers by manufacturers, which might lead to a reduction of the information asymmetry described by Stiglitz (2002). Further measures could be a regulation of labels, as explained above, and the regulation of advertisement could go beyond Article 72 of the BPR, which requires the sentence '*Use biocides safely. Always read the label and product information before use.*' According to Article 72, the word 'biocides' can be replaced with a clear reference to the product type being advertised. This seems clearly advisable to us, in light of our findings concerning the term 'biocide'.

Besides all these recommendations for a better information policy for biocidal products, we would like to emphasise that providing information to consumers only has a very limited effect (Howells, 2005). Even if consumers understand products and their possible impact, they do not necessarily make rational decisions based on this kind of knowledge (Howells, 2005). Knowledge is only one of many factors influencing pro-environmental decisions, and its impact is rather limited (Dembkowski and Hanmer-Lloyd, 1994; Kollmuss and Agyeman, 2002). These results are supported by findings by Glegg and Richards (2007), showing that cost and performance of chemical household products are the main drivers for purchasing decisions. These authors state that 'the expectation that individuals could interpret the significance of information and compare it with other factors in the decision-making process, such as price or performance, is unrealistic' (Glegg and Richards, 2007). Several studies conclude that consumer policy has to move beyond information campaigns to enhance consumer protection against potential risks of products (Best and Kneip, 2011; Howells, 2005; Mainieri et al., 1997).

Based on our findings, we can only second these recommendations. The existing on-going authorisation of biocidal products, which is supposed to evaluate the risks for humans and the environment, has been shown to have limits (Glegg and Richards, 2007; Wieck et al., 2016). A broader interpretation of the necessity to reduce the use of biocidal products to the 'minimum necessary,' as it is required in Article 17(5) of the BPR, could serve as the background for further regulations. The *Directive 2009/128/EC establishing a framework for Community action to achieve the sustainable use of pesticides* only discusses measures to reduce the use of plant protection products at the moment but could serve as a starting point (European Union, 2009). Table 3 summarises possible starting points to improve the risk communication to consumers and other possible measures.

3.9. Limitations

As described by Wieck et al. (2016), the demographic characteristics closely matched the characteristics of the respective regions. However, there were fewer households with children, and the average age of the interviewees was 53 years, while the average age in Germany in 2015 was 44 years (Statistisches Bundesamt, 2017b). The results might not be representative, as age has been shown to influence attitudes towards chemical products. Respondents below the age of 24 perceived chemicals as less negative than older Europeans (European Commission, 2011). Additionally, the interviewees in this study were predominantly female (69%), while in Germany only 50.7% of the population is female (Statistisches Bundesamt, 2017a). Men have more positive attitude towards chemical products than women (European Commission, 2011), and this may have also affected the results. As it has been discussed above in Section 3.7, we assume socially desirable answers to be a potential problem within the results.

Seasonally used products, for example wood preservatives, insecticides and repellents, might not yet have been stored in the households during the main inventorying period in spring. For this reason, follow-up investigations in other seasons would have been desirable. As discussed in Section 3.3, the results of product inventories by questionnaires were also not always correct because interviewees were not aware of using specific products, for example disinfectants. This points to potential limitations of questioning and inventorying and highlights the need to combine several methods. This need is confirmed by Eriksson et al. (2003), as they also showed that different methods might miss different aspects and complement each other for the combination of product inventories and chemical analyses of wastewater.

4. Conclusions

Our results show the limitations of collecting data on household products with only one method, as the results from products inventories of the households taken in our previous study differ from those of the interviews. We demonstrate that a combination of both can allow researchers to create more accurate inventories of biocidal products or other products stored in households.

This is the first study to provide comprehensive data on why risk communication regarding chemicals products, including biocidal products, can be so difficult. It clearly demonstrates that the term 'biocide' is often unknown and misunderstood. Risk communication using this term may therefore not lead to the intended outcome. To enhance consumer perception of potential risks associated with biocidal products, information campaigns should not only be based on the term 'biocide' but use language that is easy to understand. In the context of the European Union national linguistic and cultural differences would also have to be considered. If consumers own biocidal products, they often do not seem to be aware that they are dealing with pest control products and thus might not take appropriate precautions. The internet is the most important communication channel for general information regarding preventive and alternative measures against pests. Of special importance is information regarding insects, mould and the use of disinfectants because these were the most important topics for consumers regarding pest control in households.

Our results demonstrate that providing information and raising awareness can only protect consumers and the environment to some extent. It is difficult not only to reach consumers, but also to address their information needs because consumers are a very heterogeneous group and the effects of information and awareness raising are limited. For this reason, further measures that could lead to a sustainable use of biocidal products by consumers should be considered. These could be, for example, risk-based charges on biocidal products, regulations on sales to consumers, promotion of alternative measures or, as a last resort, prohibition of certain applications.

Conflict of interest

Stefanie Wieck is also working at the German Federal Environment Agency. This paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

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Table 3
Recommendations for enhanced consumer protection against biocidal products.

	General information on biocides	Information on alternative and preventive measures	Information on behaviour and safe use
Content	Explain the term 'biocide/biocidal product' to the public. Do not, however, base risk communication solely on it. Use easily understandable language adapted to national characteristics.	Focus on alternative and preventive measures against mould and insects and on information on general hygiene.	Formulate easily understandable instructions for use.
	Provide information specifically on disinfectants, insecticides and repellents.	Raise consumers' awareness concerning how to differentiate disinfectants and cleaning agents and in what situations general hygiene measures are sufficient.	Communicate the benefits of using the products correctly (e.g. saving money, less exposure to risky substances, less emissions to the environment).
	Provide basic information on articles treated with biocidal active substances to the public.		
Communication channels	Official internet pages	Official internet pages, eco-labels for biocide-free products	Product labels, sales persons
Further remarks	Ensure that official information offers on the internet, e.g. the 'Biozid-Portal' or 'Biocider er hverdagsgifter', are easily found via search engines with search terms consumers would use. Develop additional measures for risk reduction, such as risk-based charges on biocidal products, regulations on sales, support of alternative and preventive measures or prohibitions of certain applications.	Ensure that official information offers on the internet, e.g. the 'Biozid-Portal' or 'Biocider er hverdagsgifter', are easily found via search engines with search terms consumers would use.	Ensure readers can understand and easily read labels of biocidal products and especially instructions of use, e.g. by using an appropriate font size. Introduce mandatory EU-wide standards for labels

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijheh.2017.11.005.

References

ANSES, 2010. Exposition de la population generale aux residus de pesticides en France. (https://www.anses.fr/fr/content/exposition-de-la-population-g%C3%A9n%C3%A9rale-aux-pesticides Accessed 2 October 2017).
Adomßent, M., 2015. What do doctors and nursing staff know about pharmaceutical residues in the water cycle and how do they handle them? Int. J. Chem. Environ. Eng. 6 (3), 143–149.
Armes, M.N., Liew, Z., Wang, A., Wu, X., Bennett, D.H., Hertz-Picciotto, I., Ritz, B., 2011. Residential pesticide usage in older adults residing in Central California. Int. J. Environ. Res. Public Health 8 (8), 3114–3133. http://dx.doi.org/10.3390/ijerph8083114.
BBSR, 2009. Raumtypen 2010. (http://www.bbsr.bund.de/BBSR/DE/Raumbeobachtung/Raumabgrenzungen/Raumtypen2010_vbg/Download_RefTypenLageSied.xls?_blob=publicationFile&v=2. Accessed 28 February 2017).
Bearth, A., Miesler, L., Siegrist, M., 2017. Consumers' risk perception of household cleaning and washing products. Risk Anal. 37 (4), 647–660. http://dx.doi.org/10.1111/risa.12635.
Beck, U., 2017. Die Metamorphose der Welt. Suhrkamp, Berlin 266 pp.
Bennett, D.H., Wu, X.M., Teague, C.H., Lee, K., Cassady, D.L., Ritz, B., Hertz-Picciotto, I., 2012. Passive sampling methods to determine household and personal care product use. J. Expos. Sci. Environ. Epidemiol. 22 (2), 148–160. http://dx.doi.org/10.1038/jes.2011.40.
Best, H., Kneip, T., 2011. The impact of attitudes and behavioral costs on environmental behavior: a natural experiment on household waste recycling. Soc. Sci. Res. 40 (3), 917–930. http://dx.doi.org/10.1016/j.ssresearch.2010.12.001.
Bound, J.P., Voulvoulis, N., 2005. Household disposal of pharmaceuticals as a pathway for aquatic contamination in the United Kingdom. Environ. Health Perspect. 113 (12), 1705–1711. http://dx.doi.org/10.1289/ehp.8315.
Brausch, J.M., Rand, G.M., 2011. A review of personal care products in the aquatic environment: environmental concentrations and toxicity. Chemosphere 82 (11), 1518–1532. http://dx.doi.org/10.1016/j.chemosphere.2010.11.018.
Bruinen de Bruin, Y., Hakkinen, P.B., Lahaniatis, M., Papameletiou, D., del Pozo, C., Reina, V., van Engelen, J., Heinemeyer, G., Viso, A.C., Rodriguez, C., Jantunen, M., 2007. Risk management measures for chemicals in consumer products: documentation, assessment, and communication across the supply chain. J. Expos. Sci. Environ. Epidemiol. 17 (Suppl. 1), S55–66. http://dx.doi.org/10.1038/sj.jes.7500587.
Buergi, D., Knechtenhofer, L., Meier, I., Giger, W., 2007. Projekt BIOMIK: Biozide als Mikroverunreinigungen in Abwasser und Gewässern. In: Teilprojekt 1: Priorisierung von bioziden Wirkstoffen. Zürich. 189 pp.
Buffet-Bataillon, S., Tattevin, P., Maillard, J.-Y., Bonnaure-Mallet, M., Jolivet-Gougeon, A., 2016. Efflux pump induction by quaternary ammonium compounds and fluoroquinolone resistance in bacteria. Future Microbiol. 11 (1), 81–92. http://dx.doi.org/10.2217/fmb.15.131.
COWI, 2009. Assessment of Different Options to Adress Risks from the Use Phase of Biocides. Kongens Lyngby 131 pp.
Corcellas, C., Eljarrat, E., Barceló, D., 2015. First report of pyrethroid bioaccumulation in wild river fish: a case study in Iberian river basins (Spain). Environ. Int. 75, 110–116. http://dx.doi.org/10.1016/j.envint.2014.11.007.
Dembkowski, S., Hanmer-Lloyd, S., 1994. The environmental value-attitude-system model: a framework to guide the understanding of environmentally-conscious consumer behaviour. J. Market. Manage. 10 (7), 593–603. http://dx.doi.org/10.1080/0267257X.1994.9964307.
Dieter, H., Götz, K., Kümmerer, K., Rechenberg, B., Keil, F., 2010. Handlungsmöglichkeiten zur Minderung des Eintrags von Humanarzneimitteln und ihren Rückständen in das Roh- und Trinkwasser. Umweltbundesamt, Berlin/Frankfurt am Main.
Epp, A., Hertel, R.F., Böl, G.-F., 2010. Chemie im Alltag. In: BfR-Wissenschaft. Bundesinstitut für Risikobewertung, Berlin. 156 pp.
Eriksson, E., Auffahrt, K., Eilersen, A.-M., Henze, M., Ledin, A., 2003. Household chemicals and personal care products as sources for xenobiotic organic compounds in grey wastewater. Water SA 29 (2), 135–146.
European Chemicals Agency, 2012. Communication on the Safe Use of Chemicals. ECHA, Helsinki 23 pp.
European Commission, 2011. Special Eurobarometer 360 Consumer Understanding of Labels and the Safe Use of Chemicals. Brussels, 195 pp.
European Commission, 2016a. Report on the Sustainable Use of Biocides Pursuant to Article 18 of Regulation (EU) No 528/2012 of the European Parliament and of the Council Concerning the Making Available on the Market and Use of Biocidal Products COM(2016) 151. Brussels.
European Commission, 2016b. Special Eurobarometer 456 Chemical Safety. Brussels.
European Court of Justice, 1998. Gut Springenheide and Tusky v Oberkreisdirektor des Kreises Steinfurt. CURIA.
European Union, 2009. Directive 2009/128/EC of the European Parliament and of the Council of 21October 2009 Establishing a Framework for Community Action to Achieve the Sustainable Use of Pesticides.
European Union, 2013a. Decision No 1386/2013/EU of the European Parliament and of the Council of 20 November 2013 on a General Union Environment Action Programme to 2020 'Living Well, Within the Limits of Our Planet'.
European Union, 2013b. Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 Concerning the Making Available on the Market and Use of Biocidal Products: BPR.
Eurostat, 2017. Urban-rural Typology. (http://ec.europa.eu/eurostat/statistics-explained/index.php/Urban-rural_typology. Accessed 2 October 2017).
Food and Drug Administration, 2016. Safety and Effectiveness of Consumer Antiseptics; Topical Antimicrobial Drug Products for Over-the-Counter Human Use Docket No. FDA-1975-N-0012.
Götz, K., Keil, F., 2007. Medikamentenentsorgung in privaten Haushalten: Ein Faktor bei der Gewässerbelastung mit Arzneimittelwirkstoffen? UWSF – Z Umweltchem Ökotox 19 (3), 180–188. http://dx.doi.org/10.1065/uwsf2007.07.201.
Geier, J., Lessmann, H., Schnuch, A., Uter, W., 2012. Recent increase in allergic reactions

to methylchloroisothiazolinone/methylisothiazolinone: is methylisothiazolinone the culprit? Contact Dermat. 67 (6), 334–341. http://dx.doi.org/10.1111/j.1600-0536.2012.02157.
Glegg, G.A., Richards, J.P., 2007. Chemicals in household products: problems with solutions. Environ. Manage. 40 (6), 889–901. http://dx.doi.org/10.1007/s00267-007-9022-1.
Hahn, S., Schneider, K., Gartiser, S., Heger, W., Mangelsdorf, I., 2010. Consumer exposure to biocides–identification of relevant sources and evaluation of possible health effects. Environ. Health 9, 7. http://dx.doi.org/10.1186/1476-069X-9-7.
Hertz-Picciotto, I., Cassady, D., Lee, K., Bennett, D.H., Ritz, B., Vogt, R., 2010. Study of Use of Products and Exposure-Related Behaviors (SUPERB): study design, methods, and demographic characteristics of cohorts. Environ. Health 9, 54. http://dx.doi.org/10.1186/1476-069X-9-54.
Horton, M.K., Rundle, A., Camann, D.E., Boyd Barr, D., Rauh, V.A., Whyatt, R.M., 2011. Impact of prenatal exposure to piperonyl butoxide and permethrin on 36-month neurodevelopment. Pediatrics 127 (3), e699–e706. http://dx.doi.org/10.1542/peds.2010-0133.
Howells, G., 2005. The potential and limits of consumer empowerment by information. J. Law Soc. 32 (3), 349–370. http://dx.doi.org/10.1111/j.1467-6478.2005.00328.x.
Josephson, K.L., Rubino, J.R., Pepper, I.L., 1997. Characterization and quantification of bacterial pathogens and indicator organisms in household kitchens with and without the use of a disinfectant cleaner. J. Appl. Microbiol. 83 (6), 737–750. http://dx.doi.org/10.1046/j.1365-2672.1997.00308.x.
Kampf, G., Dettenkofer, M., 2011. Disinfection in the domestic area ?what is really meaningful? Hygiene Medizin 36 (1), 8–11.
Kim, S.A., Moon, H., Lee, K., Rhee, M.S., 2015. Bactericidal effects of triclosan in soap both in vitro and in vivo. J. Antimicrob. Chemother. 70, 3345–3352. http://dx.doi.org/10.1093/jac/dkv275.
Klaschka, U., Rother, H.-A., 2013. 'Read this and be safe!' Comparison of regulatory processes for communicating risks of personal care products to European and South African consumers. Environ. Sci. Eur. 25 (1), 30. http://dx.doi.org/10.1186/2190-4715-25-30.
Kollmuss, A., Agyeman, J., 2002. Mind the gap: why do people act environmentally and what are the barriers to pro-environmental behavior? Environ. Educ. Res. 8 (3), 239–260. http://dx.doi.org/10.1080/13504620220145401.
Kosma, C.I., Lambropoulou, D.A., Albanis, T.A., 2014. Investigation of PPCPs in wastewater treatment plants in Greece: occurrence, removal and environmental risk assessment. Sci. Total Environ. 466–467, 421–438. http://dx.doi.org/10.1016/j.scitotenv.2013.07.044.
Kraus, N., Malmfors, T., Slovic, P., 1992. Intuitive toxicology: expert and lay judgments of chemical risks. Risk Anal. 12 (2), 215–232. http://dx.doi.org/10.1111/j.1539-6924.1992.tb00669.x.
Lakoff, G., Johnson, M., 2014. Leben in Metaphern: Konstruktion und Gebrauch von Sprachbildern, 8th ed. Carl-Auer-Verl., Heidelberg 272 pp.
Larson, E.L., Lin, S.X., Gomez-Pichardo, C., Della-Latta, P., 2004. Effect of antibacterial home cleaning and handwashing products on infectious disease symptoms: a randomized, double-blind trial. Ann. Intern. Med. 140 (5), 321–329.
Levy, S., 2001. Antibacterial household products: cause for concern. Emerg. Infect. Dis. 7 (3 Suppl), 512–515.
Llop, S., Julvez, J., Fernandez-Somoano, A., Santa Marina, L., Vizcaino, E., Iniguez, C., Lertxundi, N., Gascon, M., Rebagliato, F., Ballester, M., 2013. Prenatal and postnatal insecticide use and infant neuropsychological development in a multicenter birth cohort study. Environ. Int. 59, 175–182. http://dx.doi.org/10.1016/j.envint.2013.06.010.
Mainieri, T., Barnett, E.G., Valdero, T.R., Unipan, J.B., Oskamp, S., 1997. Green buying: the influence of environmental concern on consumer behavior. J. Social Psychol. 137 (2), 189–204. http://dx.doi.org/10.1080/00224549709595430.
Midden, C., del Pozo, C., Poumadère, M., Wiedemann, P., 2011. In-depth Study of Hazard Perception of Household Chemical Products: Consequences for the Communication of Information on Safe Use to the General Public. Helsinki.
Moran, R.E., Bennett, D.H., Tancredi, D.J., Wu, X., Ritz, B., Hertz-Picciotto, I., 2012. Frequency and longitudinal trends of household care product use. Atmos. Environ. 55, 417–424. http://dx.doi.org/10.1016/j.atmosenv.2012.03.021.
OECD, 2002. OECD Guidance Document on risk communication for chemical risk management. In: Series on Risk Management 16. Paris.
Pieper, C., Schwebke, I., Noeh, I., Uhlenbrock, K., Hübner, N.-O., Solecki, R., 2014. Antimicrobial products in the domestic area – a consideration of the effects on human health and the environment as well as on the benefit for consumers. Hygiene Medizin 39 (3), 68–76.
Presgrave, R.d.F., Alves, E.N., Camacho, L.A.B., Bôas, M.H.S.V., 2008. Labelling of household products and prevention of unintentional poisoning. Ciênc. saúde coletiva 13, 683–688. http://dx.doi.org/10.1590/S1413-81232008000700017.
Rüdel, H., Böhmer, W., Müller, M., Fliedner, A., Ricking, M., Teubner, D., Schröter-Kermani, C., 2013. Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: results from the German Environmental Specimen Bank. Chemosphere 91 (11), 1517–1524. http://dx.doi.org/10.1016/j.chemosphere.2012.12.030.
RAL gGmbH, 2011. Basic Criteria for Award of the Environmental Label Non-Tocic Indoor Pest Control and Prevention RAL-UZ 34. (https://www.blauer-engel.de/en/products/home-living/indoor-pest-control/indoor-pest-control-and-prevention. Accessed 2 June 2017).
Ruckart, P.Z., Orr, M.F., Kaye, W.E., 2004. Hazardous-chemical releases in the home. J. Environ. Health 67 (5), 14–19 (32; quiz 35-6).
SCENIHR, 2009. Assessment of the Antibiotic Resistance Effects of Biocides. Brussels.
Scheer, D., Gold, S., Benighaus, C., Benighaus, L., Ortleb, J., Renn, O., 2010. Kommunikation von risiko und gefährdungspotenzial aus sicht verschiedener stakeholder. In: BfR Wissenschaft 01/2010. Bundesinstitut für Risikobewertung, Berlin.
Schuster, A., Daschner, F., 2002. Antibakterielle produkte im haushalt: chance oder risiko? Dtsch. Med. Wochenschr. 127 (44), 2340–2344. http://dx.doi.org/10.1055/s-2002-35198. (1946).
Statistisches Bundesamt, 2010. Statistik und Wissenschaft 17. In: Demographische Standards: Ausgabe 2010. Wiesbaden.
Statistisches Bundesamt, 2017a. Bevölkerung auf Grundlage des Zensus 2011: Bevölkerung nach Geschlecht und Staatsangehörigkeit. (https://www.destatis.de/DE/ZahlenFakten/GesellschaftStaat/Bevoelkerung/Bevoelkerungsstand/Tabellen/Zensus_Geschlecht_Staatsangehoerigkeit.html;jsessionid=BC838266A9A68CB69DA9E9F1C1B3A3E4. cae3. Accessed 26 January 2017).
Statistisches Bundesamt, 2017b. Bevölkerung auf Grundlage des Zensus 2011: Durchschnittsalter nach Geschlecht und Staatsangehörigkeit. (https://www.destatis.de/DE/ZahlenFakten/GesellschaftStaat/Bevoelkerung/Bevoelkerungsstand/Tabellen/Durchschnittsalter_Zensus.html;jsessionid=BC838266A9A68CB69DA9E9F1C1B3A3E4. cae3. Accessed 26 January 2017).
Stemplewski, J., Pfeiffer, E., Nafo, I., Liesenfeld, J., Müller, R., Stachowiak, J., 2014. Herausforderung spurenstoffe im wasser: empirische befunde zum umgang mit medikamenten. KA – Korrespondenz Abwasser Abfall 10, 886–893. http://dx.doi.org/10.3242/kae2014.10.003.
Stiglitz, J.E., 2002. Information and the Change in the Paradigm in Economics. Am. Econ. Rev. 92 (3), 460–501.
Ternes, T.A., Joss, A., Siegrist, H., 2004. Scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environ. Sci. Technol. 38 (20), 392A–399A. http://dx.doi.org/10.1021/es040639t.
US EPA, 2017. Design for the Environment Antimicrobial Pesticide Pilot Project: Moving Toward the Green End of the Pesticide Spectrum. (https://www.epa.gov/pesticide-labels/design-environment-antimicrobial-pesticide-pilot-project-moving-toward-green-end. Accessed 14 May 2017).
Webber, M.A., Buckner, M.M.C., Redgrave, L.S., Ifill, G., Mitchenall, L.A., Webb, C., Iddles, R., Maxwell, A., Piddock, L.J.V., 2017. Quinolone-resistant gyrase mutants demonstrate decreased susceptibility to triclosan. J. Antimicrob. Chemother. 72 (10), 2755–2763. http://dx.doi.org/10.1093/jac/dkx201.
Weigel, S., Kuhlmann, J., Hühnerfuss, H., 2002. Drugs and personal care products as ubiquitous pollutants: occurrence and distribution of clofibric acid, caffeine and DEET in the North Sea. Sci. Total Environ. 295 (1-3), 131–141. http://dx.doi.org/10.1016/S0048-9697(02)00064-5.
Wieck, S., Olsson, O., Kümmerer, K., 2016. Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater. Environ. Int. 94, 695–705. http://dx.doi.org/10.1016/j.envint.2016.07.007.
Wieck, S., 2015. The necessity of disinfected toilet brushes – information policy of companies on disinfectants in private homes. Environ. Sci. Eur. 27 (1), 3. http://dx.doi.org/10.1186/s12302-015-0038-5.
Wu, X.M., Bennett, D.H., Ritz, B., Frost, J., Cassady, D., Lee, K., Hertz-Picciotto, I., 2011. Residential insecticide usage in northern California homes with young children. J. Expos. Sci. Environ. Epidemiol. 21 (4), 427–436. http://dx.doi.org/10.1038/jes.2010.36.

Supplementary information to:

Consumers' perception of biocidal products in households

Stefanie Wieck. Oliver Olsson, Klaus Kümmerer

On the following pages, an English translation of the questions and the original questions in German can be found.

EvaSys	Chemicals in wastewater	Electric Paper

Leuphana University of Lüneburg Stefanie Wieck
Institute for Sustainable and Environmental

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Korrektur: ☐ ■ ☐ ☒ ☐ Bitte beachten Sie im Interesse einer optimalen Datenerfassung die links gegebenen Hinweise beim Ausfüllen.

1. Pest control

First of all, I would like to talk about the different products and their ingredients, theoretically entering the wastewater after use. First, I will ask some questions on pest control products. These are products to control different pests, for example insects, rodent or bacteria.

1.1 In your household, has anyone controlled pests in the last 12 months to protect plants? ☐ Yes ☐ No ☐ Not specified

1.2 In your household, has anyone controlled pests for other reasons than for the protection of plants in the last 12 months? ☐ Yes ☐ No ☐ Not specified

1.3 **If yes in 1.2:** Which pests were controlled?

[ ]

1.4 If pests inside of your household are concerned: Where would you inform yourself regarding pest organisms and their control?

☐ Local newspaper ☐ Radio ☐ TV
☐ Internet ☐ Weekly newspaper ☐ Salespersons in stores
☐ Familie/friends ☐ Other ☐ Not specified

1.5 **If "other":** Where?

[ ]

1.6 **If "internet":** Which pages?

☐ Producer ☐ Authorities ☐ Consumer/Environment protection organisations
☐ Forum ☐ Search engines ☐ Other

1.7 **If "other":** Where?

[ ]

1.8 Have you ever heard of the term "biocide"? ☐ Yes ☐ No

1.9 If you would hear the term “biocides”, what would you think that it means?

[ ]

Products used for the control of pests are seperated into plant protection products and biocides by law. Plant rotection products are all products that are used for the protection of plants. Biocides are all other products used for the protection of materials or health. Now, I would like to ask you some more questions on biocides - pest control products that are not used for the protection of plants.

1. Pest control [Fortsetzung]

1.10 Which biocidal product types do you own in your household?
- ☐ Disinfectants for the disinfection of skin
- ☐ Disinfectants for surfaces or objects
- ☐ Disinfectants for pets
- ☐ Drinking water disinfectants
- ☐ Wood preservatives
- ☐ Preservatives for building materials, e.g. facades
- ☐ Products for the control of rodents
- ☐ Products for the control of insects
- ☐ Repellents, e.g. against mosquitos
- ☐ Embalming fluids
- ☐ None

1.11 Have you or other household members used biocides in your household in the last 12 months? ☐ Yes ☐ No ☐ Not specified

1.12 Has someone else been using biocides in your household in the last 12 months?
- ☐ Professional pest controller
- ☐ Cleaner
- ☐ Other
- ☐ None

1.13 **If "other":** Who?

1.14 On your property, do you sometimes use a pool during the year? ☐ Yes ☐ No

1.15 **If "yes" in 1.14:** How often do you empty the pool into the sewage system during the year? 1er ☐ x0 ☐ x1 ☐ x2 ☐ x3 ☐ x4 ☐ x5 ☐ x6 ☐ x7 ☐ x8 ☐ x9

1.16 **If "yes" in 1.14:** In which season do you empty the pool into the sewage system?
- ☐ Spring
- ☐ Summer
- ☐ Autumn
- ☐ Winter

1.17 **If "yes" in 1.14:** How big is your pool (surface or volume)?

1.18 **If "yes" in 1.14:** Do you use products for the purification of the pool water? ☐ Yes ☐ No ☐ Not specified

1.19 Do you read the instructions for use of biocides? ☐ Yes ☐ No ☐ Sometimes

1.20 **If "sometimes" in 1.19:** Depending on what do you read the intructions for use?

1.21 **If "yes" or "sometimes" in 1.19**: Do you consider the information in the instructions for use usually helpful? ☐ Yes ☐ No

1.22 **If "yes" or "sometimes" in 1.19:** Do you follow the instructions for use (e.g. use frequency, dosage? ☐ Yes ☐ No ☐ Sometimes

1.23 **If "sometimes" in 1.22:** Depending on what do you follow the instructions for use?

1.24 Do you have articles treated with biocidal active substances in your household (e.g. antibacterial kitchenware, textiles with mosquito protection)? ☐ Yes ☐ No ☐ Don't know

1.25 **If "yes":** What articles do you have?

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2. Comparison of the product groups

Within the following questions, we will compare the different product groups biocides, plant protection products, washing and cleaning agents and personal care products.

		Yes	Rather yes	Rather no	No	Not specified
2.1	Do you always buy the same biocidal products?	☐	☐	☐	☐	☐
2.2	Do you always buy the same plant protection products?	☐	☐	☐	☐	☐
2.3	Do you always buy the same washing and cleaning agents?	☐	☐	☐	☐	☐
2.4	Do you always buy the same personal care products?	☐	☐	☐	☐	☐

If rank 1 represents the the product group with the highest risk for humans and the environment and rank 4 represents the lowest risk, how would you rank the following product groups?

		1 - Highest risk	2	3	4 - Lowest risk	Not specified
2.5	Biocides	☐	☐	☐	☐	☐
2.6	Plant protection products	☐	☐	☐	☐	☐
2.7	Washing and cleaning agents	☐	☐	☐	☐	☐
2.8	Personal care products	☐	☐	☐	☐	☐

3. Use

		Interviewee	Partner	Both	Other	Not specified
3.1	In this household, who is in charge of the choice of biocidal products?	☐	☐	☐	☐	☐
3.2	In this household, who is in charge of the application of biocidal products?	☐	☐	☐	☐	☐
3.3	In this household, who is in charge of the choice of plant protection products?	☐	☐	☐	☐	☐
3.4	In this household, who is in charge of the application of plant protection products?	☐	☐	☐	☐	☐
3.5	In this household, who is in charge of the choice of washing and cleaning agents?	☐	☐	☐	☐	☐
3.6	In this household, who is in charge of the application of washing and cleaning agents?	☐	☐	☐	☐	☐
3.7	In this household, who is in charge of the choice of personal care products?	☐	☐	☐	☐	☐

3.8 Do you have a specific day of the week for cleaning activities? ☐ Yes ☐ No

3.9 **If "yes":** What day?

4. Disposal

Now I would like to talk to you about the disposal of products that were not completely emptied. How do you do that normally?

		Sink/toilet	Normal waste	Hazard waste collection	Has never been disposed	Is always used up	Not specified
4.1	When you want to dispose biocides, that are not completely empty, where would you do that normally?	☐	☐	☐	☐	☐	☐
4.2	When you want to dispose plant protection products, that are not completely empty, where would you do that normally?	☐	☐	☐	☐	☐	☐
4.3	When you want to dispose washing and cleaning agents, that are not completely empty, where would you do that normally?	☐	☐	☐	☐	☐	☐
4.4	When you want to dispose personal care products, that are not completely empty, where would you do that normally?	☐	☐	☐	☐	☐	☐

Following questions on disposal only if "sink/toilet" was chosen: Now I would like to talk to you on how often products are disposed via the sink or the toilet.

		App. monthly	App. every 6 months	App. annually	More seldomly	On special occasions	After best before date	Never	Not specified
4.5	How often do you dispose biocides, that are not completely empty?	☐	☐	☐	☐	☐	☐	☐	☐
4.6	How often do you dispose plant protection products, that are not completely empty?	☐	☐	☐	☐	☐	☐	☐	☐
4.7	How often do you dispose washing and cleaning agents, that are not completely empty?	☐	☐	☐	☐	☐	☐	☐	☐
4.8	How often do you dispose personal care products, that are not completely empty?	☐	☐	☐	☐	☐	☐	☐	☐

4.9 What would you say, was ususally the fill level of the disposed products?

☐ Full ☐ Almost full ☐ Half full
☐ Almost empty ☐ Not specified

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5. Measures

Different measures can be used to minimise chemicals in surface waters. The technology of sewage treatment plants could be upgraded with financial investments to enhance the removal of chemicals from the wastewater. Also, behaviour of users has an influence on the amount of chemicals discharged into wastewater. Another possibility could be official restrictions for manufacturers to reduce the emission of chemicals into wastewater. In your opinion, how important are the following measures to reduce chemicals in the water system?

		Not important	Less important	Important	Very important	Not specified
5.1	Behavioural changes of users	☐	☐	☐	☐	☐
5.2	Upgrade of sewage treatment plants	☐	☐	☐	☐	☐
5.3	Restrictions for manufacturers concerning products	☐	☐	☐	☐	☐

6. Household

Now I would like to ask you some questions regarding your household.

6.1 Where do you live? ☐ House ☐ Flat ☐ Shared flat

6.2 How large is the living space approximately in square meters?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
100er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.3 How many persons between 0 and 3 years are living in your household?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.4 How many persons between 3 and 6 years are living in your household?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.5 How many persons between 6 and 18 years are living in your household?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.6 How many persons between 18 and 65 years are living in your household?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.7 How many persons above 65 years are living in your household?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.8 How many persons living in your household have a weakened immune system?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.9 How many people living in this household are in need of special care?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.10 Are people living in your household with:

☐ Asthma ☐ Contact allergy ☐ Skin diseases

6.11 Are furry pets living in your household? ☐ Yes ☐ No

6.12 **If "yes": Which ones and how many?**

6.13 Do you have an aquarium in your household? ☐ Yes ☐ No

7. Demographics

The following questions will help us to evaluate the results of this questionaire. It is important for us to be able to discuss the results for different demographic groups seperatly. For this reason, we need some information about your household and you. With these information, your answers will anonymously be attributed to specific groups. We won't evaluate your person, but only certain groups as a whole, for example of certain ages, sexes or education.

7.1 Sex of the interviewee ☐ Female ☐ Male

7.2 The results will be evaluated for different age groups. Please tell me the year you were born.

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
1000er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
100er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

7.3 The main income earner in this household, what is his or her highest school education?*

*As the answers to this question are very specific for the German educational system, the school-levels were not translated.

- ☐ Von der Schule abgegangen ohne Hauptschulabschluss (Volksschulabschluss)
- ☐ Hauptschulabschluss (Volksschulabschluss)
- ☐ Realschulabschluss (Mittlere Reife)
- ☐ Polytechnische Oberschule der DDR mit Abschluss der 8. oder 9. Klasse
- ☐ Polytechnische Oberschule der DDR mit Abschluss der 10. Klasse
- ☐ Fachhochschulreife, Abschluss einer Fachoberschule
- ☐ Allgemeine oder fachgebundene Hochschulreife/ Abitur (Gymnasium bzw. EOS, auch EOS mit Lehre)
- ☐ Abitur über zweiten Bildungsweg nachgeholt
- ☐ Einen anderen Schulabschluss

7.4 **If "other":** Which one?

[ ]

7.5 The main income earner in this household, what professional trainings did she or he complete?*

* As the answers to this question are very specific for the German system for professional training, the answers were not translated.

- ☐ Noch in beruflicher Ausbildung (Berufsvorbereitungsjahr, Auszubildende(r), Praktikant/-in, Student/-in)
- ☐ Schüler/-in und besucht eine berufsorientierte Aufbau-, Fachschule o. Ä.
- ☐ Keinen beruflichen Abschluss und nicht in beruflicher Ausbildung
- ☐ Beruflich-betriebliche Berufsausbildung (Lehre) abgeschlossen
- ☐ Beruflich-schulische Ausbildung (Berufsfachschule, Handelsschule, Vorbereitungsdienst für den mittleren Dienst in der öffentlichen Verwaltung) abgeschlossen
- ☐ Ausbildung an einer Fachschule der DDR abgeschlossen
- ☐ Ausbildung an einer Fach-, Meister-, Technikerschule, Berufs- oder Fachakademie abgeschlossen
- ☐ Bachelor an (Fach-) Hochschule abgeschlossen
- ☐ Fachhochschulabschluss (z. B. Diplom, Master)
- ☐ Universitätsabschluss (z. B. Diplom, Magister, Staatsexamen, Master)
- ☐ Promotion
- ☐ Einen anderen beruflichen Abschluss

7.6 **If "other":** Which one?

[ ]

7. Demographics [Fortsetzung]

7.7 With this question, we would like to evaluate the results seperately for different income groups. For this reason, we would like to know: How high is the monthly net income of your household on average? With net income, we mean the income minus taxes and social contributions. Please name the according letter from this list. **(Hand over list with income groups.)** Please be assured, that your response will never be evaluated in combination with your name.

If questions arise: The monthly net income of your household is the sum of the incomes of employment and self-employment or pension. Also, please add income from public aid, from the letting of properties, assets, housing benefit, child benefit and other incomes. Then subtract all taxes and social contributions.

For self-employed persons: Please state the average net income, subtracting business expenses and taxes.

- ☐ M Up to 450 €
- ☐ N 451 to 850 €
- ☐ B 851 to 1500 €
- ☐ V 1501 to 2000 €
- ☐ C 2001 to 3000 €
- ☐ Y 3001 to 4000 €
- ☐ S 4001 to 5000 €
- ☐ X 5001 to 6000 €
- ☐ F More than 6000 €
- ☐ Not specified

8. End

8.1 This was the last question. Would you like to tell me anything else?

Thank you very much!

EvaSys	Chemikalien im Abwasser [Copy] [Copy]	Electric Paper

Leuphana Universität Lüneburg   Stefanie Wieck
Institut für Nachhaltige Chemie und Umweltchemie

Bitte so markieren: ☐ ☒ ☐ ☐ ☐ Bitte verwenden Sie einen Kugelschreiber oder nicht zu starken Filzstift. Dieser Fragebogen wird maschinell erfasst.
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1. Schädlingsbekämpfung

Zunächst geht es im Fragebogen um die verschiedenen Produkte bzw. ihre Inhaltsstoffe, die als Folge der Anwendung theoretisch ins Abwasser gelangen können. Zuerst möchte ich Ihnen einige Fragen zu Schädlingsbekämpfungsmitteln stellen. Das können Mittel gegen verschiedene Schädlinge sein, z.B. Insekten, Nagetiere oder auch Bakterien.

1.1 Wurden in den letzten 12 Monaten in Ihrem Haushalt Schädlinge zum Schutz von Pflanzen bekämpft? ☐ Ja ☐ Nein ☐ Keine Angabe

1.2 Wurden in den letzten 12 Monaten in Ihrem Haushalt Schädlinge aus anderen Gründen bekämpft (nicht zum Schutz von Pflanzen)? ☐ Ja ☐ Nein ☐ Keine Angabe

1.3 **Wenn ja bei 1.2:** Welche waren das?

1.4 Wenn es um Schädlinge im Haus geht: Wo informieren Sie sich über mögliche Schädlinge und Bekämpfungsmaßnahmen?

☐ Lokale Tageszeitung ☐ Radio ☐ Fernsehen
☐ Internet ☐ Wochenzeitung ☐ Verkäufer im Geschäft
☐ Familie / Freundeskreis ☐ Andere ☐ Keine Angabe

1.5 **Wenn "Andere":** Wo?

1.6 **Wenn "Internet":** Auf welchen Seiten?

☐ Hersteller ☐ Behörden ☐ Verbraucher-/ Umweltschutzorganisationen
☐ Foren ☐ Suchmaschinen ☐ Andere

1.7 **Wenn "Andere":** Wo?

1.8 Haben Sie den Begriff „Biozid“ schon einmal gehört? ☐ Ja ☐ Nein

1.9 Was bezeichnet der Begriff Ihrer Meinung nach?

In der Gesetzgebung wird bei Produkten, die zur Schädlingsbekämpfung eingesetzt werden, zwischen Pflanzenschutzmitteln und Bioziden unterschieden. Pflanzenschutzmittel sind alle Schädlingsbekämpfungsmittel, die zum Schutz der Pflanzen genutzt werden. Biozide sind alle anderen Schädlingsbekämpfungsmittel, die zum Beispiel zum Schutz von Materialien oder der Gesundheit eingesetzt werden. Ich möchte Ihnen nun noch einige Fragen zu Bioziden stellen, also zu Schädlingsbekämpfungsmitteln, die nicht zum Schutz von Pflanzen eingesetzt werden.

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1. Schädlingsbekämpfung [Fortsetzung]

1.10 Welche Biozide haben Sie in Ihrem Haushalt?

- ☐ Desinfektionsmittel zur Desinfektion der Haut
- ☐ Desinfektionsmittel für Oberflächen und Gegenstände
- ☐ Desinfektionsmittel im Haustierbereich
- ☐ Trinkwasserdesinfektionsmittel
- ☐ Holzschutzmittel
- ☐ Schutzmittel für Baumaterialien, z.B. Fassaden
- ☐ Nagetierbekämpfungsmittel
- ☐ Insektenbekämpfungsmittel
- ☐ Repellentien, z.B. gegen Mücken
- ☐ Einbalsamierungsmittel
- ☐ Keine

1.11 Haben Sie oder andere Haushaltsmitglieder in den letzten 12 Monaten in Ihrem Haushalt Biozide angewendet? ☐ Ja ☐ Nein ☐ k.A.

1.12 Hat in den letzten 12 Monaten jemand anderes in Ihrem Haushalt Biozide angewendet?

- ☐ Schädlingsbekämpfer
- ☐ Putzhilfe
- ☐ Andere
- ☐ Keiner

1.13 **Wenn "Andere":** Wer?

1.14 Nutzen Sie auf Ihrem Grundstück im Laufe des Jahres einen Pool/Schwimmbecken? ☐ Ja ☐ Nein

1.15 **Wenn "ja" in 1.14:** Wie häufig in einem Jahr entleeren Sie den Pool in die Kanalisation?

10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9

1.16 **Wenn "ja" in 1.14:** Zu welcher Jahreszeit entleeren Sie den Pool in die Kanalisation?

- ☐ Frühling
- ☐ Sommer
- ☐ Herbst
- ☐ Winter

1.17 **Wenn "ja" in 1.14:** Wie groß ist Ihr Pool (Oberfläche oder Volumen)?

1.18 **Wenn "ja" in 1.14:** Fügen Sie dem Poolwasser Produkte zur Wasseraufbereitung zu? ☐ Ja ☐ Nein ☐ Keine Angabe

1.19 Lesen Sie vor Gebrauch die Gebrauchsanweisung von Bioziden? ☐ Ja ☐ Nein ☐ Teils/teils

1.20 **Wenn "teils/teils" in 1.19:** Wovon machen Sie es abhängig, ob Sie die Gebrauchsanweisung lesen?

1.21 **Wenn "immer" oder "teils/teils" in 1.19**: Finden Sie die Angaben in der Gebrauchsanweisung in der Regel hilfreich? ☐ Ja ☐ Nein

1.22 **Wenn "immer" oder "teils/teils" in 1.19:** Befolgen Sie die Gebrauchsanweisung (z. B. Anwendungshäufigkeit, Dosierung)? ☐ Ja ☐ Nein ☐ Teils/teils

1.23 **Wenn "teils/teils" in 1.22:** Wovon machen Sie es abhängig, ob Sie die Gebrauchsanweisung befolgen?

1.24 Haben Sie mit Bioziden ausgerüstete Gegenstände im Haus (z.B. antibakterielle Küchengeräte oder Kleidung, Outdoor-Textilien mit Mückenschutzfunktion)? ☐ Ja ☐ Nein ☐ Weiß nicht

1.25 **Wenn "ja":** Um welche Gegenstände handelt es sich?

2. Vergleich der Produktgruppen

Im Folgenden schauen wir uns die einzelnen Produktgruppen Wasch- und Reinigungsmittel, Körperpflegeprodukte, Biozide und Pflanzenschutzmittel kurz im Vergleich an.

		Ja	Eher ja	Eher nein	Nein	K.A.
2.1	Kaufen Sie bei Bioziden immer die gleichen Produkte?	☐	☐	☐	☐	☐
2.2	Kaufen Sie bei Pflanzenschutzmitteln immer die gleichen Produkte?	☐	☐	☐	☐	☐
2.3	Kaufen Sie bei Wasch- und Reinigungsmitteln immer die gleichen Produkte?	☐	☐	☐	☐	☐
2.4	Kaufen Sie bei Körperpflegeprodukten immer die gleichen Produkte?	☐	☐	☐	☐	☐

Bitte nennen Sie mir nun die Reihenfolge, in der Sie die Gefährlichkeit der Produktgruppen für Mensch und Umwelt sehen. Beginnen Sie mit der gefährlichsten und enden mit der ungefährlichsten.

		1 - Am gefährlichsten	2	3	4 - Am ungefährlichsten	k.A.
2.5	Biozide	☐	☐	☐	☐	☐
2.6	Pflanzenschutzmittel	☐	☐	☐	☐	☐
2.7	Wasch- und Reinigungsmittel	☐	☐	☐	☐	☐
2.8	Körperpflegeprodukte	☐	☐	☐	☐	☐

MUSTER

EvaSys	Chemikalien im Abwasser [Copy] [Copy]	Electric Paper

3. Nutzung

		Befragte/r	Lebensgefährte/in	Beide	Andere	k.A.
3.1	Wer ist im Haushalt für die Auswahl von Bioziden verantwortlich?	☐	☐	☐	☐	☐
3.2	Wer nutzt Biozide im Haushalt hauptsächlich?	☐	☐	☐	☐	☐
3.3	Wer ist im Haushalt für die Auswahl von Pflanzenschutzmitteln verantwortlich?	☐	☐	☐	☐	☐
3.4	Wer nutzt Pflanzenschutzmittel im Haushalt hauptsächlich?	☐	☐	☐	☐	☐
3.5	Wer ist im Haushalt für die Auswahl von Wasch- und Reinigungsmitteln verantwortlich?	☐	☐	☐	☐	☐
3.6	Wer nutzt Wasch- und Reinigungsmittel im Haushalt hauptsächlich?	☐	☐	☐	☐	☐
3.7	Wer ist im Haushalt für die Auswahl von Körperpflegeprodukten verantwortlich?	☐	☐	☐	☐	☐

3.8 Gibt es in Ihrem Haushalt einen bestimmten Tag, an dem Sie putzen? ☐ Ja ☐ Nein

3.9 **Wenn "ja":** Welcher?

MUSTER

4. Entsorgung

Im nächsten Abschnitt geht es um die Entsorgung von nicht vollständig geleerten Behältern der einzelnen Produktarten. Wie ist das bei Ihnen in der Regel?

		Waschbecken/Toilette	Normaler Abfall	Schadstoffsammlung/-mobil	Wurde noch nie entsorgt	Inhalt wird aufgebraucht	k.A.
4.1	Wenn Sie Biozide entsorgen möchten, die nicht komplett aufgebraucht wurden, wie entsorgen Sie diese in der Regel?	☐	☐	☐	☐	☐	☐
4.2	Wenn Sie Pflanzenschutzmittel entsorgen möchten, die nicht komplett aufgebraucht wurden, wie entsorgen Sie diese in der Regel?	☐	☐	☐	☐	☐	☐
4.3	Wenn Sie Wasch- und Reinigungsmittel entsorgen möchten, die nicht komplett aufgebraucht wurden, wie entsorgen Sie diese in der Regel?	☐	☐	☐	☐	☐	☐
4.4	Wenn Sie Körperpflegeprodukte entsorgen möchten, die nicht komplett aufgebraucht wurden, wie entsorgen Sie diese in der Regel?	☐	☐	☐	☐	☐	☐

Restliche Fragen aus diesem Abschnitt: "Nur wenn Entsorgung über Waschbecken/Toilette": Jetzt geht es darum, wie häufig Sie nicht entleerte Behältnisse über Waschbecken oder die Toilette entleeren.

		etwa monatlich	etwa halbjährlich	etwa jährlich	größere zeitl. Abstände	bei besonderen Anlässen	nach Ablauf des MHD	nie	k.A.
4.5	Wie häufig entsorgen Sie Biozidbehälter, die nicht vollständig leer sind?	☐	☐	☐	☐	☐	☐	☐	☐
4.6	Wie häufig entsorgen Sie Pflanzenschutzmittelbehälter, die nicht vollständig leer sind?	☐	☐	☐	☐	☐	☐	☐	☐
4.7	Wie häufig entsorgen Sie Wasch- und Reinigungsmittelbehälter, die nicht vollständig leer sind?	☐	☐	☐	☐	☐	☐	☐	☐
4.8	Wie häufig entsorgen Sie Behälter von Körperpflegeprodukten, die nicht vollständig leer sind?	☐	☐	☐	☐	☐	☐	☐	☐

4.9 Was würden Sie sagen, wie voll waren die Behälter im Durchschnitt, als Sie diese entsorgt haben?

☐ Voll ☐ Fast voll ☐ Halbvoll
☐ Fast leer ☐ Keine Angabe

5. Maßnahmen

5. Maßnahmen [Fortsetzung]

Chemikalienresten in Gewässern kann in unterschiedlicher Weise begegnet werden. Durch umfangreiche Investitionen könnten die Kläranlagen in Deutschland so nachgerüstet werden, dass die Reste größtenteils aus dem Abwasser gefiltert werden. Wirksam wäre auch, wenn durch ein verändertes Nutzerverhalten von vornherein deutlich weniger Chemikalienreste ins Abwasser gelangen würden. Möglich wäre auch, dass bestimmte Auflagen an die Hersteller der Produkte den Eintrag von Chemikalien ins Abwasser verringern. Wie wichtig sind Ihres Erachtens die im Folgenden genannten Maßnahmen, mit denen das Vorkommen von Chemikalien in Gewässern verringert werden könnte?

		Unwichtig	Weniger wichtig	Wichtig	Sehr wichtig	k.A.
5.1	Menschliche Verhaltensänderungen	☐	☐	☐	☐	☐
5.2	Technische Nachrüstung der Kläranlagen	☐	☐	☐	☐	☐
5.3	Auflagen für Hersteller hinsichtlich Produkte	☐	☐	☐	☐	☐

6. Haushalt

Nun folgen einige Fragen zu Ihrem Haushalt.

6.1 Wie wohnen Sie? ☐ Haus ☐ Wohnung ☐ Wohngemeinschaft

6.2 Wie groß ist die Wohnfläche ungefähr in Quadratmetern?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
100er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.3 Wieviele Personen in Ihrem Haushalt sind zwischen 0 und 3 Jahren?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.4 Wieviele Personen in Ihrem Haushalt sind zwischen 3 und 6 Jahren?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.5 Wieviele Personen in Ihrem Haushalt sind zwischen 6 und 18 Jahren?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.6 Wieviele Personen in Ihrem Haushalt sind zwischen 18 und 65 Jahren?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.7 Wieviele Personen in Ihrem Haushalt sind über 65 Jahren?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.8 Wieviele Personen in diesem Haushalt haben ein geschwächtes Immunsystem?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.9 Wieviele Personen in diesem Haushalt sind pflegebedürftig?

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

6.10 Leben in Ihrem Haushalt Personen mit:

☐ Asthma ☐ Kontaktallergien ☐ Hautkrankheiten (allg.)

6.11 Werden Haustiere mit Fell in Ihrem Haushalt gehalten? ☐ Ja ☐ Nein

6. Haushalt [Fortsetzung]

6.12 **Wenn ja:** Welche und wieviele?

6.13 Haben Sie ein Aquarium in Ihrem Haushalt? ☐ Ja ☐ Nein ☐ K.A.

7. Statistische Angaben

Die folgenden Fragen helfen, die Ergebnisse dieser Umfrage auszuwerten. Dabei ist es wichtig, dass ich die Antworten auf die bisher beantworteten Fragen nach Merkmalen auswerten kann, die gesellschaftliche Gruppen beschreiben. Hierfür benötige ich Angaben zu Ihrem Haushalt und Ihrer Person, damit ich Sie anonym einer entsprechenden Gruppe zuordnen kann. Ich werte die Daten nicht für Ihre Person aus, sondern für solche Gruppen, zu denen man Sie zum Beispiel entsprechend Ihrer Altersgruppe, Ihrem Geschlecht oder Ihrem Schulabschluss zuordnen kann.

7.1 Geschlecht des Befragten ☐ Weiblich ☐ Männlich

7.2 Die Ergebnisse dieser Befragung werden auch für unterschiedliche Altersgruppen ausgewertet. Bitte nennen Sie mir dazu das Jahr Ihrer Geburt.

	x0	x1	x2	x3	x4	x5	x6	x7	x8	x9
1000er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
100er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
10er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
1er	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

7.3 Die Person in diesem Haushalt, die das höchste Einkommen bezieht: Welchen höchsten allgemeinbildenden Schulabschluss hat sie?
Sagen Sie es mir bitte anhand der **Liste 5**.

- ☐ Von der Schule abgegangen ohne Hauptschulabschluss (Volksschulabschluss)
- ☐ Hauptschulabschluss (Volksschulabschluss)
- ☐ Realschulabschluss (Mittlere Reife)
- ☐ Polytechnische Oberschule der DDR mit Abschluss der 8. oder 9. Klasse
- ☐ Polytechnische Oberschule der DDR mit Abschluss der 10. Klasse
- ☐ Fachhochschulreife, Abschluss einer Fachoberschule
- ☐ Allgemeine oder fachgebundene Hochschulreife/ Abitur (Gymnasium bzw. EOS, auch EOS mit Lehre)
- ☐ Abitur über zweiten Bildungsweg nachgeholt
- ☐ Einen anderen Schulabschluss

7.4 **Wenn "anderer Schulabschluss":** Welchen anderen Schulabschluss?

7. Statistische Angaben [Fortsetzung]

7.5 Die Person in diesem Haushalt, die das höchste Einkommen bezieht: Welche beruflichen Ausbildungsabschlüsse hat sie?

- ☐ Noch in beruflicher Ausbildung (Berufsvorbereitungsjahr, Auszubildende(r), Praktikant/-in, Student/-in)
- ☐ Schüler/-in und besucht eine berufsorientierte Aufbau-, Fachschule o. Ä.
- ☐ Keinen beruflichen Abschluss und nicht in beruflicher Ausbildung
- ☐ Beruflich-betriebliche Berufsausbildung (Lehre) abgeschlossen
- ☐ Beruflich-schulische Ausbildung (Berufsfachschule, Handelsschule, Vorbereitungsdienst für den mittleren Dienst in der öffentlichen Verwaltung) abgeschlossen
- ☐ Ausbildung an einer Fachschule der DDR abgeschlossen
- ☐ Ausbildung an einer Fach-, Meister-, Technikerschule, Berufs- oder Fachakademie abgeschlossen
- ☐ Bachelor an (Fach-) Hochschule abgeschlossen
- ☐ Fachhochschulabschluss (z. B. Diplom, Master)
- ☐ Universitätsabschluss (z. B. Diplom, Magister, Staatsexamen, Master)
- ☐ Promotion
- ☐ Einen anderen beruflichen Abschluss

7.6 **Wenn "anderer beruflicher Abschluss":** Welcher andere berufliche Abschluss?

7.7 Bei dieser Frage geht es darum, Gruppen in der Bevölkerung mit unterschiedlichem Einkommen auswerten zu können. Daher möchte ich gerne wissen: Wie hoch ist das durchschnittliche monatliche Nettoeinkommen Ihres Haushalts insgesamt, also das Einkommen nach Abzug der Steuern und Sozialabgaben? Geben Sie bitte den entsprechenden Buchstaben auf dieser Liste an **(Liste überreichen)**. Sie können sicher sein, dass Ihre Antwort nicht in Verbindung mit Ihrem Namen ausgewertet wird.

Bei Fragen: Unter durchschnittlichem monatlichem Nettoeinkommen Ihres Haushalts ist die Summe zu verstehen, die sich aus Lohn, Gehalt, Einkommen aus selbstständiger Tätigkeit, Rente oder Pension ergibt. Rechnen Sie bitte auch die Einkünfte aus öffentlichen Beihilfen, Einkommen aus Vermietung und Verpachtung, Vermögen, Wohngeld, Kindergeld und sonstige Einkünfte hinzu und ziehen Sie dann Steuern und Sozialversicherungsbeiträge ab.

Bei Selbstständigen: Bitte nennen Sie die durchschnittlichen Nettobezügen, d. h. abzüglich der Betriebsausgaben und der Steuern.

- ☐ M Bis 450 €
- ☐ N 451 bis 850 €
- ☐ B 851 bis 1500 €
- ☐ V 1501 bis 2000 €
- ☐ C 2001 bis 3000 €
- ☐ Y 3001 bis 4000 €
- ☐ S 4001 bis 5000 €
- ☐ X 5001 bis 6000 €
- ☐ F Über 6000 €
- ☐ Keine Angabe

8. Abschluss

8.1 So, das war unsere letzte Frage. Gibt es von Ihrer Seite noch etwas, das Sie mir zu unserer Umfrage sagen möchten?

Vielen Dank!

Artikel 3

Stefanie Wieck, Oliver Olsson, Klaus Kümmerer (2018).

Not only biocidal products: Washing and cleaning agents and personal care products can act as further sources of biocidal active substances in wastewater.

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Not only biocidal products: Washing and cleaning agents and personal care products can act as further sources of biocidal active substances in wastewater

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ABSTRACT

The emission sources of biocidal active substances in households have been under discussion since these substances have been detected frequently in municipal wastewater and receiving surface water bodies. Therefore, the goal of this study was to investigate the products responsible for the emission of these substances to wastewater.

We analysed the wastewater of two streets for a set of biocidal active substances. Time-proportional sampling was conducted for one week of each season during one year in each street. The 14 substances analysed with liquid chromatography coupled with tandem mass spectrometry were 1,2-benzisothiazol-3(2H)-one (BIT), C_{12}-benzalkonium chloride, carbendazim, 5-chloro-2-methyl-2H-isothiazol-3-one (CMIT), dichlorooctylisothiazolinone (DCOIT), N,N-diethyl-meta-toluamide (DEET), diuron, icaridine, 2-octyl-2H-isothiazol-3-one (OIT), piperonyl butoxide (PBO), triclosan, tebuconazole, terbutryn and tetramethrin. Using data available from household product inventories of the two streets, we searched the lists of ingredients for the products possibly being responsible for the emissions.

Except for four substances, all substances have been detected in at least 10% of the samples. Highest concentrations were measured for C_{12}-benzalkonium chloride with an average concentration in the daily samples of 7.7 μg/L in one of the streets. Next to C_{12}-benzalkonium chloride, BIT, DEET and icaridine were detected in all samples in average concentrations above 1 μg/L in at least one street. The results show that washing and cleaning agents were important sources for preservatives such as BIT and OIT, while triclosan was apparently mainly emitted through personal care products. The mosquito repelling substances DEET and icaridine were found throughout the year, with highest emissions in summer and autumn.

In conclusion, the results demonstrate that the sources of biocidal active substances in municipal wastewater are complex and that measures for the prevention of the emission of biocidal active substances into the aquatic environment have to be carried out under different legislations. This has to be taken into account discussing emission reduction at the source.

1. Introduction

Discussions on solving the problem of micropollutants in wastewater falter between end-of-pipe technologies, such as the improvement of removal technologies at sewage treatment plants, or proactive pollution prevention at the source (Kümmerer et al., 2015; Ternes et al., 2004). One possible source for chemicals that might enter the sewage system and end up as micropollutants are products in households. They can contain pest controlling substances, so-called biocidal active substances according to the Biocidal Products Regulation 528/2012 (Bollmann et al., 2014; European Union, 2013; Launay et al., 2016; Merel and Snyder, 2016). Until now, when biocidal active substances have been detected during monitoring studies, the specific products or materials releasing the substances within households remained unclear (Bollmann et al., 2014; Launay et al., 2016; Singer et al., 2010; Wittmer et al., 2011). It has already been shown by Wieck et al. (2016) based on

Abbreviations: BIT, 1,2-benzisothiazol-3(2H)-one; BKC, alkyl (C_{12}) dimethylbenzyl ammonium chloride; CAR, carbendazim; CMIT, 5-chloro-2-methyl-2H-isothiazol-3-one; DCOIT, dichlorooctylisothiazolinone; DEET, N,N-diethyl-meta-toluamide; DIU, diuron; ESI, electrospray ionisation; ICA, icaridine; LC-MS/MS, liquid chromatography coupled with tandem mass spectrometry; LOQ, limit of quantification; MIT, 2-methylisothiazol-3(2H)-one; MWWC, measured average wastewater concentration; OIT, 2-octyl-2H-isothiazol-3-one; PBO, piperonyl butoxide; PWWC, predicted wastewater concentration; TCS, triclosan; TEB, tebuconazole; TER, terbutryn; TET, tetramethrin

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product inventories that personal care products and washing and cleaning agents could be important potential sources for biocidal active substances in wastewater. In contrast to most biocidal products, the ingredients of many washing and cleaning agents and personal care products, such as shampoo or washing agents, are directly emitted into the wastewater during use (Ternes et al., 2004). Studies that link product inventories to analytical results, enabling a better understanding on products potentially emitting the substances within one study site, are rare and urgently needed. The selection of analytes only based on the substances that have been already identified in prior studies, instead on the substances actually emitted in a study site, i.e. based on product inventories, has already been criticised by Daughton (2014). To the best of our knowledge, such studies are only available for other product categories such as pharmaceuticals (Herrmann et al., 2015), or wastewater types such as grey water (Eriksson et al., 2003).

Sampling for biocidal active substances in municipal wastewater requires a thorough selection of the sampling location and sampling strategy. To differentiate between emissions from the outside of houses, such as leaching of material preservatives from facades, and substances used within households, samples should be taken in sewer systems with separate stormwater sewers. To get hold of single pulses of biocidal active substances, grab samples would not provide sufficiently high resolution in time. Time-proportional sampling with a sampling frequency of at least 15 min should at least be applied (Ort et al., 2010a). For the detection of micropollutants in wastewater, e.g. biocidal active substances, several sample preparation and analytical methods are available that cover a range of biocidal active substances. In the majority of studies, these methods are using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) (Chen et al., 2012; Singer et al., 2010; Wick et al., 2010). Electrospray ionisation (ESI) should be applied if a broad spectrum of substances is to be analysed and the use of labelled surrogate standards is important to account for ion suppression or enhancement (Wick et al., 2010). With these methods, biocidal active substances have been detected frequently in wastewater, which is the main exposure pathway for urban-use biocidal active substances to surface water (Singer et al., 2010). N,N-diethyl-meta-toluamide (DEET), an active substance repelling mosquitos, was for example detected in 100% of effluent samples of 90 sewage treatment plants across Europe; diuron (DIU), a herbicidal material preservative, in 77% of the samples and triclosan (TCS), a disinfectant and preservative, in 41% (Loos et al., 2013). 2-octyl-2H-isothiazol-3-one (OIT), 1,2-benzisothiazol-3(2H)-one (BIT), dichlorooctylisothiazolinone (DCOIT), icaridine (ICA), triclosan and carbendazim (CAR) were also frequently found in wastewater influent in China (Liu et al., 2017). Quaternary ammonium compounds, such as benzalkonium chloride (BKC), are discussed to promote resistance development against antibiotics and have been detected in influent of sewage treatment plants in concentrations of 170 µg/L and bind in high amounts to particles (Östman et al., 2017; Sütterlin et al., 2007; Zhang et al., 2015). This highlights the importance to monitor both, the aqueous phase and suspended particulate matter (Barco-Bonilla et al., 2010; Ort et al., 2010a).

In view of the considerations above, the main objective of this study was to allocate detections of biocidal active substances in municipal wastewater to possible emission sources within households. For the first time, this was possible for biocidal active substances in municipal wastewater because of existing product inventories of the households in the sampling area. This area was deliberately chosen as study site because the existing infrastructure allowed the assumption that all analysed biocidal active substances resulted from a use within households. The possible sources discussed in this study are, besides biocidal products, personal care products and washing and cleaning agents. Furthermore, we wanted to investigate whether product inventories suffice to characterise the emission of biocidal active substances from households to wastewater. Time-proportional sampling of wastewater of one neighbourhood was conducted during one year and 14 biocidal active substances were chosen for analysis using LC-MS/MS.

2. Methods

2.1. Sampling site and sampling strategy

2.1.1. Sampling site

As sampling site, we selected a neighbourhood in Schleswig-Holstein in the north of Germany. The neighbourhood consisted of 132 single-family houses mainly built between 1970 and 1980, with two wastewater streams (supplementary material S1) connecting 49 houses (street A) and 89 houses (street B) with the municipal sewer system. Based on information collected during interviews with the inhabitants of the streets, 113 inhabitants live in street A and 223 inhabitants in street B (Wieck et al., 2018). This neighbourhood was selected because (i) no professional users of biocides were discharging wastewater to the sewage system, (ii) no agricultural holdings were present and (iii) it had a separate sewer system for stormwater and the households' wastewater, thus ensuring that all analysed biocidal active substances resulted from a use within households. Due to the separate sewer system no runoff from facades and thereto related emission of biocidal active substances or emissions from the professional use of plant protection products should be present in the sampled wastewater.

Additional to the optimal infrastructure for a representative sampling of biocidal active substances in municipal wastewater, this sampling site was selected because recent product inventories of household products connected to the sampled sewers were available (Wieck et al., 2016; sampling area is "neighbourhood A"). These inventories contained data on biocidal products, personal care products and washing and cleaning agents. Product inventories of 29 households in street A (59% of the households) and 60 households in street B (67%) were obtained. Demographic data showed no significant differences between the inhabitants of street A and B. The only exception was that significantly more children of age 3 and 6 years (95% CI = −0.181 to −0.022; p = 0.013) lived in street B. Wieck et al. (2016) reported that with 53 years, the average age of the interviewees was higher than the German average age (44 years). The products that were inventoried also did not contain significantly different numbers of biocidal active substances except for TCS which was only used in toothpastes inventoried in street B.

2.1.2. Sampling procedure

Composite samples were taken daily for 14 h during approximately one week in each season to catch possible daily input variations and to reflect the differing use of products in the different seasons (Table 1). In spring, samples were taken only in street B due to technical reasons, in summer the sampling period in both streets was extended to 10 days due to problems during sampling. Teledyne Isco 6712 Portable Samplers (Teledyne Isco, Lincoln, USA) placed into manholes in the two streets were used for sampling. Each sampler contained 24 polypropylene bottles with a volume of 500 mL each. Automated sampling

Table 1
Description of the sampling campaign.

Season	Sampling locations	Sampling dates	Number of 14 h-samples	Number of days 1 h-samples were analysed separately
Spring	Street B	07.–13.04.2016	7	1
Summer	Street A	04.–14.08.2016	8	2
	Street B	04.–14.08.2016	5	1
Autumn	Street A	06.–12.10.2016	6	1
	Street B	06.–12.10.2016	7	2
Winter	Street A	12.–18.01.2017	5	2
	Street B	12.–18.01.2017	6	3

took place from 6 am to 8 pm as during the night hours the volume of the wastewater was not sufficient to allow for sampling. During the sampling period, samples of 125 mL were taken every 15 min to account for the variation of the substance pulses (Ort et al., 2010b). Every bottle contained a composite sample of 1 h. Every evening, samples were picked up, transported to the laboratory and stored at 4 °C. Samples were filtrated on the following day and frozen at −20 °C until further processing.

2.1.3. Sample types

Out of the 14 sampling bottles representing 1 h-samples each, two kinds of time-proportional composite samples were established to evaluate the concentrations of biocidal active substances during the day, week or seasons (Table 1):

For the comparison between weekdays or seasons, composite samples (100 mL) of the whole day were established in duplicates by taking shares from each hourly composite sample (14 h-samples).

To evaluate the change in concentrations during the day, a limited number of hourly composite samples (100 mL) was taken from morning (6–7 am), noon (12–13 pm) and evening (19–20 pm) separately (1 h-samples).

2.2. Selection of analytes

To select biocidal active substances that could actually be emitted through products in the households, we used the product inventories established for this neighbourhood (Wieck et al., 2016). Of the 74 biocidal active substances inventoried in this neighbourhood, which is called "neighbourhood A" in the study of Wieck et al. (2016), those substances were rejected that fulfilled at least one of the following criteria:

- listed on less than 10 products (rejection of 48 substances),
- inorganic substance (rejection of 4 substances),
- readily biodegradable (rejection of 4 substances),
- analytically not accessible to analysis by LC-MS/MS or other analytical problems (rejection of 4 substances),
- further reasons for non-inclusion (such as natural occurrence in food or human metabolism, frequent use in pharmaceuticals not inventoried or being a releaser of formaldehyde; rejection of 12 substances).

Additionally, recent literature of biocidal active substances in wastewater was reviewed for other biocidal actives substances that were detected in municipal wastewater, but not present in the inventoried products (Bollmann et al., 2014; Chen et al., 2012; Loos et al., 2013; Singer et al., 2010; Wick et al., 2010). Those substances were included to investigate whether product inventories were sufficient to characterise household emissions of biocidal active substances. In total, a set of 14 substances was chosen (Table 2). The structural formulae can be found in the supplementary material S4. Some of the substances are also used in products regulated in other European laws than the Biocidal Products Regulation 528/2012. For example, BKC is also used in eye drops, PBO in products against head lice and TCS in medical skin cream. In general, biocidal active substances are considered as registered under REACH if they are evaluated under the Biocidal Products Regulation 58/2012 (European Union, 2007, Article 15). However, additional registrations have been submitted under REACH for some of the substances indicating further uses of the substances for different purposes.

2.3. Sample preparation and analytical method

2.3.1. Chemicals

Details on the chemicals used can be found in the supplementary material S5. All substances were stored in accordance with the supplier's instructions.

2.3.2. Sample preparation

All samples were filtered using VWR 691 glass fibre filters (particle retention: 1.6 µm, VWR International GmbH, Hannover, Germany). Filter residues were left to dry and stored together with the filtrate at −20 °C until further processing. Filtrate was extracted with an SPE procedure and filter residue was extracted using ultrasound. During SPE, Macherey-Nagel Chromabond HR-X SPE cartridges (3 mL/200 mg) were washed and conditioned using 3 × 2 mL acetone, 3 × 2 mL methanol and 3 × 2 mL Ultrapure water adjusted to pH 3 with formic acid (supplementary material S6a). For the filter extraction, acetonitrile was used as a solvent (supplementary material S6b). For interpretation of data, the results of the analyses of filtrate (c_f) and filter residue (c_r) were summed up to gain an overall picture over the total concentration of biocidal active substances present in the wastewater (c_{total}).

2.3.3. LC-MS/MS method

The samples were analysed using the LC-MS/MS method specified in the supplementary material S7 using an Agilent 1200 LC and Agilent Triple-Quad mass spectrometer 6430 (Agilent Technologies, Santa Clara, USA). This method was based on existing multi-methods for biocidal active substances (Chen et al., 2012; Wick et al., 2010). 13 of 14 biocidal active substances were detected using positive ionisation mode in an ESI source, only for TCS negative ionisation was used. If possible, two MRM transitions were monitored for each substance serving as a quantifier and qualifier (supplementary material S8).

2.4. QA/QC

For quality control, limits of quantification (LOQ), matrix effects, recoveries, inter- and intraday precisions and carry-over were determined for the extraction procedures and analytical methods (supplementary material S9 to S12). The LOQ was derived according to DIN 32645, which is comparable to ISO 11843 (Brüggemann et al., 2010) with the calibration curve method. It ranged from 1 to 10 ng/L for most of the substances and was highest for TCS in filtrate and filter residue (117 ng/L and 36 ng/L), the only substance measured in ESI negative mode. Most substances showed ion suppression due to matrix effect. An exemption was CAR that showed strong ion enhancement in the filter residue. Surrogate standards were used to compensate for the matrix effect.

Relative recovery in filtrate was good for most of the substances (70% to 115%), with the exemptions of BIT, CMIT and PBO (21% to 32%). In filter residue, recovery was 71% to 103% for most of the substances, with the exemptions of BIT, BKC, CMIT and PBO (16% to 56%). Similar ranges of relative recoveries have been reported for substances included in other multi-methods (Gago-Ferrero et al., 2017; Östman et al., 2017; Rodil et al., 2009). All measured concentrations in this study were corrected for the respective recoveries.

Samples of drinking water (1000 mL) from the neighbourhood were analysed in each season as field blanks. Laboratory blanks (1000 mL Ultrapure water) were extracted and analysed together with all sample batches. The field blank showed traces of BKC (up to 61 ng/L) in the filtrates, no substances above LOQ were detected in the filter residues. In the laboratory blanks, traces of BKC (up to 29 ng/L) were also detected in the filtrates and no substances were detected above LOQ in the filter residues. These blank values were subtracted from the results of the samples.

2.5. Prediction of wastewater concentrations

Product inventories by Wieck et al. (2016) were used to estimate the predicted wastewater concentrations (PWWC) of the substances that were both detected in the samples and in the household products inventoried. These were BIT, BKC, DEET, ICA, OIT and TCS. The

Table 2
Selected biocidal active substances.

Biocidal active substance	Abbreviation	CAS	Number of products	Uses				
				Consumer-relevant biocidal product type[a]	Plant protection products[b]	Preservative in personal care products[c]	REACH[d]	Human pharmaceuticals[e]
Included due to more than 10 products inventoried								
1,2-benzisothiazol-3(2H)-one	BIT	2634-33-5	261	2, 6, 9, 10	No	No	No	No
2-octyl-2H-isothiazol-3-one	OIT	26530-20-1	31	6, 7, 8, 9, 10	No	No	No	No
5-chloro-2-methyl-2H-isothiazol-3-one	CMIT	26172-55-4	102	2, 4, 6	No	Yes	No	No
Alkyl (C_{12}) dimethylbenzyl ammonium chloride	BKC	68424-85-1	23	1, 2, 3, 4, 8, 10, 22	No	Yes	Yes (intermediate)	Yes[f]
Icaridine	ICA	119515-38-7	15	19	No	No	Yes	No
Piperonyl butoxide	PBO	51-03-6	21	18	Yes[g]	No	Yes	Yes[f]
Tetramethrin	TET	7696-12-0	12	18	No	No	No	No
Not more than 10 products inventoried, but included due to recent detections in wastewater								
Carbendazim	CAR	10605-21-7	0	7, 9, 10	No	No	No	No
Dichlorooctylisothiazolinone	DCOIT	64359-81-5	0	7, 8, 9, 10	No	No	No	No
Diuron	DIU	330-54-1	0	7, 10	Yes[h]	No	Yes	No
Tebuconazole	TEB	107534-96-3	0	7, 8, 10	Yes[f]	No	No	No
Terbutryn	TER	886-50-0	0	7, 9, 10	No	No	No	No
N,N-diethyl-meta-toluamide	DEET	134-62-3	2	19	No	No	No	No
Triclosan	TCS	3380-34-5	4	Prohibited[i]	No	Yes	Yes	Yes[f]

[a] European Chemicals Agency (2017b).
[b] European Commission (2017) and Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (2017).
[c] European Union (2009), Annex V.
[d] European Chemicals Agency (2017a).
[e] Medizinische Medien Informations GmbH (2017).
[f] Products permitted in Germany.
[g] Synergist (European Commission, 2017).
[h] No products permitted in Germany.
[i] During inventorying period allowed in biocidal product type 1 (European Chemicals Agency, 2017b).

calculations were conducted separately for street A and B. Due to the different emission patterns of the products, different emission scenarios had to be applied (supplementary material 14). The formulas and default values were adapted to our study site and the available knowledge based on the product inventories.

- BIT and OIT were only inventoried as preservatives in washing and cleaning agents. Until now, no Emission Scenario Document (ESD) is available for this use. For this reason, the ESD for human hygiene disinfectants was used as proposed by van der Aa et al. (2004). Other than for the use of biocidal active substances in biocidal products, the concentrations of biocidal preservatives in washing and cleaning agents do not need to be declared. For this reason we had to use available data on concentrations from a study on isothiazolinones in cleaning products (Alvarez-Rivera et al., 2012). The calculations were done separately for fabric detergents, dishwashing liquids and surface cleaners and were then summed up for the total emission of the two substances to wastewater (supplementary material 14a). Use data was based on available guidance for the risk assessment of household cleaning products (HERA, 2005).
- TCS was only inventoried in toothpaste. No specific ESD is available for the use of preservatives in toothpaste. For this reason, own formulas were used (supplementary material 14b). Use data of toothpaste was based on Hall et al. (2007). The concentration of TCS in toothpaste is not declared. For this reason, we used the maximum allowed concentration of TCS in toothpaste based on Annex V of the EU Regulation 1223/2009 on cosmetic products (European Union, 2009).
- BKC was present in inventoried surface disinfectants. An ESD is available for surface disinfectants (van der Poel, 2001). This ESD has been adapted for the data available in this study (supplementary material 14c). The concentration of BKC in disinfectants has to be declared. For this reason, we were able to use the specific BKC concentration in the products inventoried for the calculation.
- DEET and ICA were listed on mosquito repellents. An ESD is available for those products (European Chemicals Agency, 2015). This ESD has been adapted for the data available in this study (supplementary material 14d). The concentration of DEET and ICA in mosquito repellents has to be declared. For this reason, we were able to use the specific concentrations in the products inventoried for the calculation.

The ratios between street A and B were calculated for the average measured (MWWC) and the predicted wastewater concentrations (PWWC) as percentages using Eq. (1).

Calculation of the ratio between street A and B

$$\text{Ratio}\ [\%] = \left(\frac{(\text{PWW/MWW})C_{\text{street A}}}{(\text{PWW/MWW})C_{\text{street B}}} - 1\right) * 100 \quad (1)$$

2.6. Data analysis

Statistical tests were conducted using IBM SPSS Statistics 24.0.0.0 (IBM, Armonk, USA). As the data was not normally distributed, Mann-Whitney *U* test was used to detect differences between two independent samples and Kruskal-Wallis test was used to detect differences between more than two independent samples. Correlations were analysed with Spearmans rank correlation. The uncertainty of the sampling and the method was calculated according to previous studies (Kovalova et al., 2012; Ort et al., 2010a; Verlicchi et al., 2014). The equation and the parameters used can be found in the supplementary material S13.

Table 3
Total concentrations and detection frequencies of the biocidal active substances in all 14 h-samples (n = 44).

	BIT	BKC	CAR	CMIT	DCOIT	DEET	DIU	ICA	OIT	PBO	TCS	TEB	TER	TET
Street A														
Detection frequency [n = 19; %]	100	100	15	0	0	100	0	100	5	0	95	0	11	0
Maximum C_{total} [ng/L]	6,261	15,340	47	0	0	12,808	0	436	16	0	319	0	2	0
Average C_{total} [ng/L, MWWC]	1,750	4,740	4	0	0	2,121	0	180	1	0	139	0	0.17	0
Standard deviation C_{total} [ng/L]	1,624	3,985	13	0	0	3,649	0	141	4	0	118	0	0.6	0
PWWC [ng/L]	100,278	179,631	–	–	–	243,517	–	394,265	33	–	0	–	–	–
Street B														
Detection frequency [n = 25; %]	100	100	56	0	0	100	60	100	20	0	100	64	100	0
Maximum C_{total} [ng/L]	2,885	19,090	268	0	0	4,401	119	6,452	133	0	928	20	465	0
Average C_{total} [ng/L, MWWC]	980	7,756	38	0	0	718	30	1,517	7	0	386	7	85	0
Standard deviation C_{total} [ng/L]	623	4,909	71	0	0	1,218	37	2,068	28	0	207	6	123	0
PWWC [ng/L]	104,201	195,348	–	–	–	0	–	915,369	95	–	870	–	–	–

3. Results

3.1. Daily composite samples

Of the 14 biocidal active substances analysed, 10 were found in at least 10% of the 14 h-samples of the wastewater (Table 3; n = 44). BIT, BKC, ICA and DEET were measured in all samples in average concentrations above 1 µg/L in at least one street. Highest concentrations were measured for BKC in street B, with an average of 7756 ng/L. CMIT, DCOIT, PBO and TET were not measured in any of the samples. Possible reasons for this are discussed in section 4.6. The standard deviations given in Table 3 were calculated for all samples taken over the course of the year.

Significantly higher concentrations of TCS were measured in the 14 h-samples of street B compared to street A ($median_{street\ A}$ = 159 ng/L, $median_{street\ B}$ = 323 ng/L; p = 0.001). Also, the measured concentrations of ICA ($median_{street\ A}$ = 111 ng/L, $median_{street\ B}$ = 563 ng/L; p = 0.014) and BKC ($median_{street\ A}$ = 3345 ng/L, $median_{street\ B}$ = 6653 ng/L; p = 0.022) were significantly higher in street B. CAR, DIU, TEB and TER were mainly measured in street B, but only rarely in street A.

To discuss the relationship between the average measured wastewater concentrations (MWWC) and the available information on the products possibly responsible for the emissions, predicted wastewater concentrations (PWWC) are given in Table 3 for the two streets.

3.2. Temporal variation

No significant differences of the concentrations were observed between the days of the week and only two substances showed significant concentration differences during the day (n = 12 samples (morning and noon), n = 10 samples (evening)). These were DEET ((Chi-square (2) = 7.0; p = 0.030): morning-noon: z = −2.6; p = 0.026) and BKC ((Chi-square(2) = 10.7; p = 0.003): morning-noon: z = −3.3; p = 0.003). Looking at the graphs (Fig. 1), however, more tendencies can be seen, even though not being statistically significant ($p > 0.05$). While TER (a) and TCS (b) seem to be emitted constantly over the sampled hours, BIT (c) and BKC (d) show lowest concentrations in the morning and the highest at noon. ICA (e) and DEET (f), both being insect repellents, show different emission patterns. While DEET is found in the highest concentrations during noon, ICA shows the highest concentrations during the evening hours. CAR, DIU, OIT and TEB do not show specific emission patterns during the day.

During the seasons, the concentrations of DEET, ICA and TER have been varying significantly (Fig. 2; n = 7 (spring), n = 13 (summer), n = 13 (autumn), n = 11 (winter)). The results for BIT, BKC, CAR, DIU, OIT, TCS and TEB did not show statistically significant differences between the seasons ($p > 0.05$).

1. ICA (Chi-square(3) = 12.1; p = 0.007): ICA concentrations were highest in summer, followed by autumn compared to winter and spring (spring-summer: z = −2.7; p = 0.039; winter-autumn: z = 3.0; p = 0.016; winter-summer: z = 3.4; p = 0.004).
2. DEET (Chi-square(3) = 17.0; p = 0.018): The same applies to DEET, that was measured in higher concentrations in summer (spring-summer: z = −2.9; p = 0.024).
3. TER (Chi-square(3) = 11.5; p = 0.009): The highest concentrations were also measured in summer and autumn (winter-summer: z = 3.2; p = 0.009; winter-autumn, z = 2.9; p = 0.026).

3.3. Analyses of the filter residues

Sorption to particles was of high relevance for BKC and TCS. On average, 84% of the amount of TCS was detected in the filter residues. While TCS was only detected in 59% of all filtrate samples, it was measured in 98% of all filter residue samples. Also, 50% of the total amount of BKC was measured in the filter residues on average. BIT (on average 23% of c_{total}) and ICA (on average 8% of c_{total}) were also measured frequently in the filter residue. All other substances were not measured above LOQ in the filter residues (supplementary material S15).

4. Discussion

4.1. Linking product inventories and measured wastewater concentrations

Links between product inventories and analytical measurements can be discussed for the biocidal active substances BIT, BKC, DEET, ICA, OIT and TCS because these substances were both measured and inventoried in the neighbourhood. Table 3 clearly shows that the predicted wastewater concentrations (PWWC) calculated based on the product inventories overestimate the emission of the six substances into wastewater. This is due to the fact that the Emission Scenario Documents (ESD) mainly used for the calculations are developed for regulatory risk assessment and are supposed to depict worst-case scenarios. They cannot be used to model the emissions of such a small sampling area as the one studied by us in a quantitative manner. Furthermore, the uncertainties associated with the analytical measurements are another reason why the average measured wastewater concentrations (MWWC) and PWWC might deviate.

The PWWC can, however, be used to compare the results qualitatively. For this reason, we calculated the ratios between the two streets for the PWWC and MWWC using Eq. (1) (Fig. 3). These ratios show that the tendencies of the MWWC are in good agreement with the PWWC. If we predicted a higher emission of a substance in street A, we generally also measured a higher concentration of this substance in street A. The only exemption is BIT, which had a higher MWWC in street A but a slightly higher PWWC in street B. This might be due to analytical

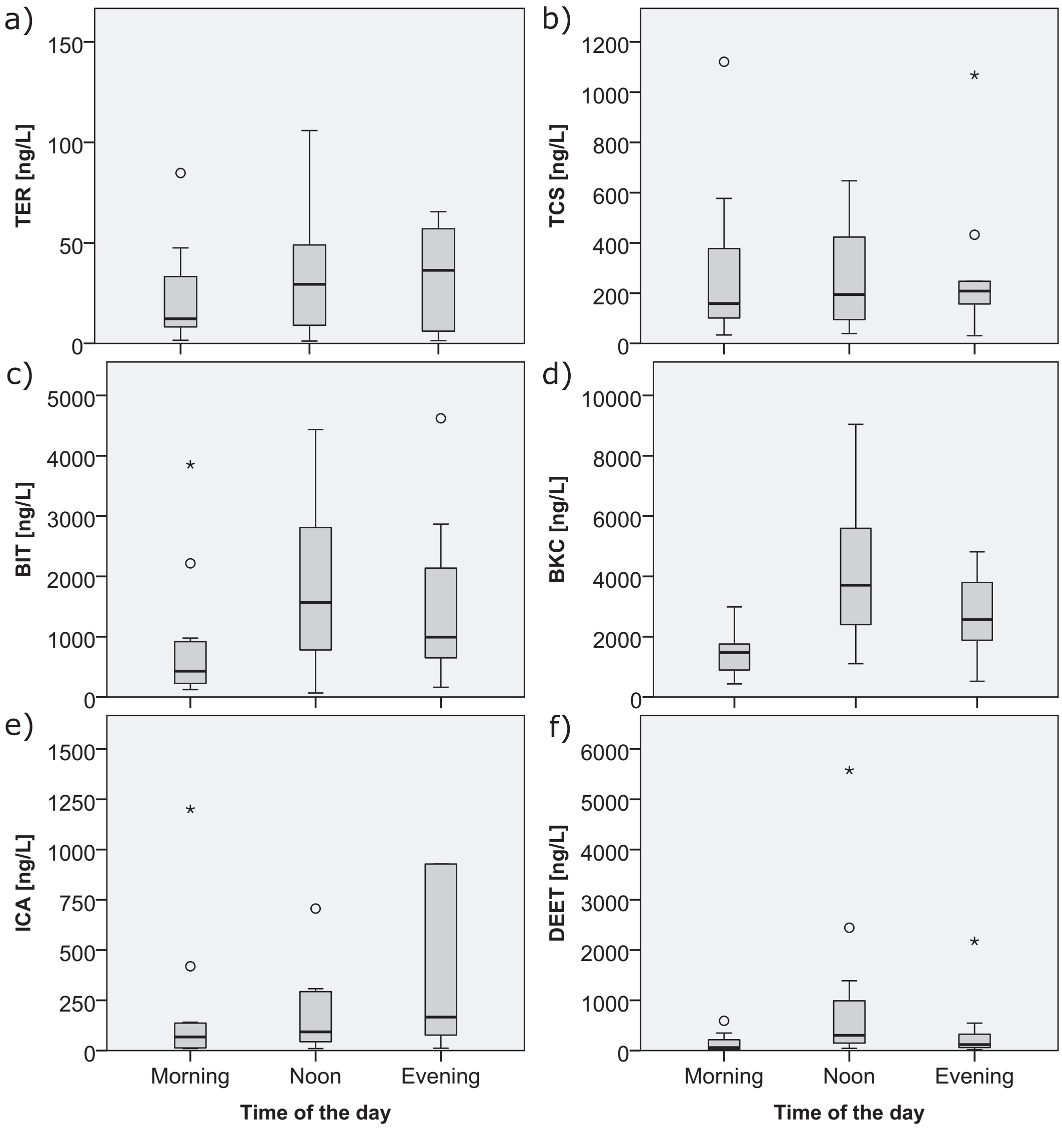

Fig. 1. Temporal variation during the day of TER (a), TCS (b), BIT (c), BKC (d), ICA (e) and DEET (f) in 1 h-samples of all seasons in ng/L (morning and noon: n = 12; evening: n = 10). Values considered as outliers are marked with "o" and far outliers with "*".

uncertainties that are further discussed in section 4.3.1. Potential sources of the biocidal active substances are discussed in detail in the following chapters based on the product inventories.

4.2. Repellents: N,N-diethyl-meta-toluamide (DEET) and icaridine (ICA)

DEET and ICA have been detected in all samples of the seasons (Table 3). While DEET was detected in higher concentrations in street A, ICA was detected in higher concentrations in street B. This reflects the PWWC based on the product inventories (Fig. 3). Both substances showed highest average concentrations in summer. Seasonal variance of DEET with peaks in summer has also been seen in previous studies (Engelmann, 2016; Gago-Ferrero et al., 2017; Launay et al., 2016; Merel et al., 2015) and can be explained by the seasonal use of mosquito repellents in Germany. However, both repelling substances were also measured in all winter samples despite this seasonal use. Merel and Snyder (2016) have assumed that the ubiquitous occurrence of DEET might be due to analytical interferences. Another suggestion for the continuous emission of ICA and DEET in autumn and winter could be derived from the results of an explorative study showing the discharge of ICA and DEET through washing of clothes worn during the application of mosquito repellent (supplementary material S2). This study shows indications that both substances are still emitted three washing cycles after wearing the clothes during repellent application. Even in washing cycles without clothes slightly elevated concentrations of ICA and DEET were measured in washing machine effluent. This is an emission pathway that has not been considered before in the discussion of DEET emissions (Merel and Snyder, 2016) and which should be investigated further. The ubiquitous presence of the repellents is further supported by the fact that we measured both substances in wastewater in winter. Interfering compounds for both, ICA and DEET, at the same time are unlikely. Another emission route of DEET in wastewater could be the excretion via urine. Behniwal and She (2017) found up to 0.4 μg/L DEET in US urine samples. However, we are not aware of studies linking the DEET concentration in urine to the time between DEET application and sampling. For this reason, it is not possible at the moment to draw conclusions whether delayed excretion of DEET via urine could also explain the detections of DEET in winterly samples.

The results of the 1 h-samples for morning, noon and evening show different emission patterns for the two substances. Considering, that both substances are in general used in products with the same purpose, mosquito and tick control, this is surprising. However, the number of

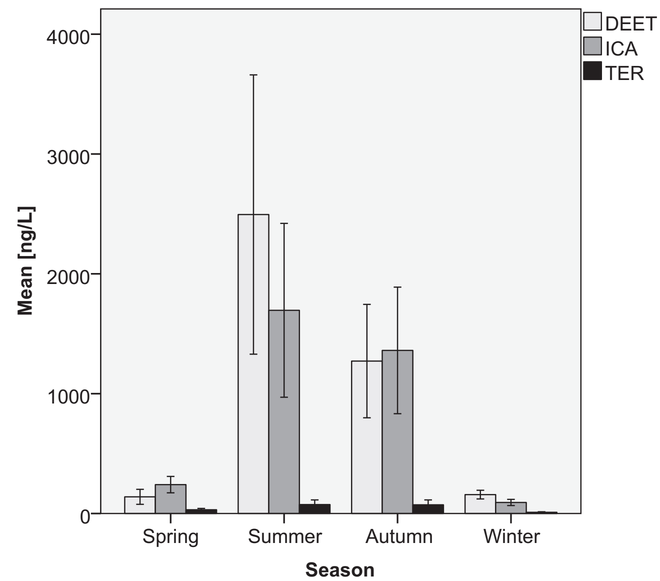

Fig. 2. Seasonal variance of the MWWC of DEET, ICA and TER in the 14 h-samples (spring: n = 7; summer: n = 13; autumn: n = 13; winter: n = 11).

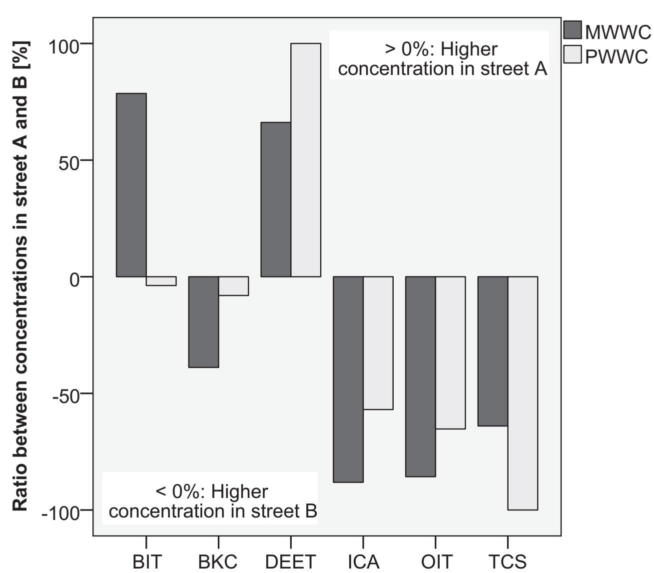

Fig. 3. Ratios between street A and B for MWWC (n = 44) and PWWC.

samples is too low to draw conclusions from this pattern. Further investigations are necessary.

The good qualitative agreement with the PWWC based on the product inventories show that the main sources probably are mosquito repellents. For this reason, to reduce concentrations of DEET and ICA in municipal wastewater, measures under the Biocidal Products Regulation 528/2012 could be applied because the potential emission sources fall under this regulation.

4.3. Preservatives

4.3.1. 1,2-benzisothiazol-3(2H)-one (BIT) and 2-octyl-2H-isothiazol-3-one (OIT)

BIT has been found in all of the wastewater samples (Table 3). This fits to the high number of inventoried washing and cleaning agents containing this preservative and previous studies on isothiazolinones in detergents (Garcia-Hidalgo et al., 2017). The results are also in line with a previous study that showed that BIT was detected in wastewater samples on all sampling days, whereas OIT was not detected in that study (Rafoth et al., 2007). In our study, OIT was measured in 14% of the daily samples fitting to the considerable lower numbers of the inventoried washing and cleaning agents containing OIT in Wieck et al. (2016). Looking at the quantitative results of the two isothiazolinones, it has to be taken into account that, especially for BIT, the relatives recoveries have been low (31% in filtrate, 16% in filter residue). This is probably due to its instability and missing surrogate standards. These methodological uncertainties might be the reason, why the PWWC does not predict the MWWC of BIT well. Another reason could be that further emission sources of BIT, which have not been inventoried, are present in the households. The recovery of OIT is higher, as it has been in previous studies (Rafoth et al., 2007).

Emission reduction measures for BIT and OIT could be applied through the Biocidal Products Regulation 528/2012 because this regulates the use of preservatives in washing and cleaning agents. It is, however, possible that there are further sources of BIT that have not been inventoried and might not fall under the Biocidal Product Regulation. It has to be kept in mind that OIT has already been found in personal care products without being declared on the labels (Alvarez-Rivera et al., 2012) even though it is not allowed to be used in personal care products. This leads to additional sources that were not possible to inventory and discuss.

4.3.2. Triclosan (TCS)

A high proportion of TCS was detected in the filter residues. Due to its high octanol-water partition coefficient (K_{OW}) of log K_{OW} = 4.66 it is likely to be sorbed to particles and found in the filter residue instead of the filtrate (Bester, 2003). The average total concentration of TCS measured in all 14 h-samples was 303 ng/L, being in the same range as previous studies on TCS in wastewater (Wick et al., 2010). The uncertainty for the analyses of TCS in the filtrate was relatively high (83%, supplementary material S13).

In our study area, we detected significantly higher results in street B. This fits to the product inventories because TCS containing products were only inventoried in street B (Table 3). Toothpastes as relevant emission source of TCS are supported by the fact that TCS concentrations in urine are correlated to the use of TCS containing Colgate® toothpaste (Philippat et al., 2015).

As TCS is no longer allowed to be used in biocidal products, emission reduction measures could not be applied through the Biocidal Products Regulation 528/2012. The uses that are to be further regulated to minimise the emissions to the environment are the uses in personal care products, e.g. toothpaste, regulated in the EU Regulation 1223/2009 on cosmetic products (European Union, 2009). Other possible TCS sources falling under this regulation are deodorants. TCS is allowed to be used in non-spray deodorants according to annex V of the regulation and was also found to be used illegally in spray deodorants by a Danish consumer protection organisation (Forbrugerrådet Tænk Kemi, 2016). Further sources of TCS in wastewater could be pharmaceutical lotions containing TCS (Medizinische Medien Informations GmbH, 2017).

4.4. Disinfectant: C_{12}-benzalkonium chloride (BKC)

On average, 50% of the total amount of BKC was measured in the filter residues. This is due to its hydrophobic part of the molecule, other studies found even higher shares of BKC in the particular phase (Butkovskyi et al., 2016; Östman et al., 2017).

High concentrations of BKC, with an average of 7.7 µg/L in street B, were measured in all of the 14 h-samples (Table 3). It was also detected previously in 100% of incoming water samples in sewage treatment plants in Sweden (Östman et al., 2017). The average in the samples of Östman et al. (2017) was 6.9 µg/L, being in the same range as the concentrations found in our study. However, it has to be kept in mind that our samples were undiluted wastewater, while the influent of the

Swedish study was not separated into stormwater and wastewater.

In the inventoried products, BKC was present in surface disinfectants, soaps or washing agents. Based on the product inventories, higher PWWC were predicted for street B, a tendency that is also reflected in the MWWC. The differences between the MWWC in the two streets is, however, higher than we would assume from the product inventories. It is possible that further sources of BKC have been present in street B that were not inventoried. It has been assumed previously that a high proportion of BKC emissions result from unspecified non-biocidal uses (Buser and Morf, 2009). A study in Austria showed BKC concentrations of up to 2100 μg/L in the wastewater of a laundry. The authors assumed that detergents might be an important source of BKC, besides its use as disinfectant in hospitals (Kreuzinger et al., 2007; Kümmerer et al., 1997). We cannot confirm this for our sampling area as cationic surfactants have been listed rarely on the labels. Further uses of BKC are in eyedrops or nasal spray, however, the emission from these uses to wastewater seems negligible. Thus, we assume that the emissions of BKC could probably be regulated by applying emission mitigation measures via the Biocidal Products Regulation 528/2012 as surface disinfectants seem to be the main source.

4.5. Material preservatives: Carbendazim (CAR), diuron (DIU), tebuconazole (TEB) and terbutryn (TER)

CAR, DIU, TEB and TER were mainly measured in the sewer system of street B (Table 3). All of these substances are material preservatives that have not been inventoried but might have been present in materials used in the households. While TER was detected in 100% of the samples in an average concentration of 85 ng/L, DIU and TEB were measured in 60% of the samples in street B in average concentrations of 30 ng/L and 7 ng/L, respectively. CAR was detected in 56% of the samples of street B with an average concentration of 38 ng/L. These concentrations are in the range of measured influent concentrations during dry weather conditions in mixed sewers (Bollmann et al., 2014) and concentrations in stormwater (Wicke et al., 2017). TER concentrations varied significantly between the seasons with highest concentrations in summer (Fig. 2). This has been reported previously for effluent of sewage treatment plants (Engelmann, 2016).

Emission via outdoor surface runoff has been assumed before to be a source of material preservatives in wastewater (Launay et al., 2016; Wittmer et al., 2011). Additionally, it was assumed previously that indoor applications of the preservatives could also be an important source (Bollmann et al., 2014; Launay et al., 2016; Singer et al., 2010; Wittmer et al., 2011). To be able to analyse solely indoor sources of the material preservatives, a sampling site with a separated sewer system was chosen in this study (section 2.1.1). However, in March 2018, after the sampling campaign, the local company responsible for the sewer system detected a faulty connection of a stormwater to a wastewater sewer in street B. This is a plausible explanation for the concentrations of material preservatives that were mainly measured in street B. An indoor source could be the use of the substances as material preservatives, e.g. for films, coatings, construction materials and also for fibre, leather, rubber and polymerised materials (Table 2). Due to the recently detected faulty connection it is, however, not possible to draw any conclusions on the indoor sources of these substances.

4.6. Other substances

CMIT, DCOIT, PBO and TET were not found in any of the samples. Quantifier ions of PBO and DCOIT were frequently detected in the samples at the respective retention times, however, qualifier ratios were much higher than expected and we deemed only 20% tolerance as acceptable for the ratio between quantifier and qualifier. For this reason, our conclusion was that the signals probably also resulted from other, co-eluting substances and we did not include the results for these substances in the further discussion. An additional problem analysing PBO in the samples could have been its low relative recovery. Even though we tested all available surrogate standards, only 56% and 32% relative recovery were achieved in filter residue and filtrate.

The reason TET was not found could be low concentrations of this substance in products and the low number of products (12 products) inventoried. The same could hold true for PBO that was only listed on 21 products. Furthermore, both substances are incorporated in products that are only used in acute pest infestations with insects. This makes it more difficult to catch emissions of these substances during one sampling campaign compared to emissions from substances used in personal care products used on a daily basis.

CMIT might also not have been detected because of the low concentrations in the products. There is no information on concentrations of CMIT in washing and cleaning agents but in accordance with Annex V of the EU Regulation 1223/2009 on cosmetic products, CMIT in a mixture with 2-methylisothiazol-3(2H)-one (MIT) is only allowed to be used in concentrations up to 0.0015% in personal care products (European Union, 2009). Another possible explanation for not detecting CMIT is its instability. It has been reported previously that this results in low recoveries (Rafoth et al., 2007; Speksnijder et al., 2010), something we experienced as well. Even though the study of Rafoth et al. (2007) led us to the assumption that CMIT was stable enough to be stored at 4 °C over night until filtration and freezing at −20 °C without the addition of a stabilising agent, it is possible that it degraded more rapidly in our sewage samples.

4.7. Limitations

The product inventories by Wieck et al. (2016) were established one year prior to the start of the sampling campaign. It might thus be possible that they no longer exactly reflect current use practices. However, Wieck et al. (2016) asked the interviewees in the questionnaires whether they were tending to always buy the same products. In general, the household members were loyal to the brands with > 80% stating to always or mostly buying the same products. For this reason, we conclude that the product inventories in general are still valid for the discussion of possible emissions from household products. Brand loyalty in our neighbourhood was probably comparatively strong because the average age of the residents was high (Wieck et al., 2016). Wu et al. (2010) showed that older users tend to have a stronger brand loyalty than younger. Limiting the explanatory power of the product inventories is the possibly wrong declaration of ingredients on the product labels that has been shown for isothiazolinones (Alvarez-Rivera et al., 2012; Speksnijder et al., 2010).

The results of the sampling campaigns would have been more robust if flow-proportional sampling had been conducted. Without flow-proportional sampling, the calculation of loads of the substances was not possible. As the samples consist of several types of wastewater (e.g. toilet, shower, washing machine) it is possible, that high emissions of a substance in one type of wastewater were diluted by another time-dependent type of wastewater not containing the same substance. For this reason, lower concentrations of substances at specific sampling times also could be due to dilution rather that lower emission of the respective substance. Samples were taken at the ends of the two streets. As the maximal distances of the houses to the sampling points was 600 m, bias due to different emission times at the households within hourly samples are considered negligible.

It might have increased the absolute recovery of isothiazolinones, especially CMIT, if we would have added a stabilising agent to the samples (Speksnijder et al., 2010). Low absolute recoveries can be corrected through the use of surrogate standards. Ideally, a corresponding labelled standard would be used for every substance. This was, however, not possible as labelled standards were not available for all substances. For this reason, we corrected low recoveries of substances without corresponding surrogate standards with the surrogate standards available for us that fitted best. For some substances well-fitting surrogate standards were not available, leading to low relative recoveries. Even though a surrogate standard of the same chemical class, D17-OIT, was tested, low relative recoveries for CMIT and BIT had to be accepted. For this reason, we conducted an uncertainty analysis for the sampling and analytical method (supplementary material S13). The uncertainty for the results of the filtrate analyses ranged from 12 to 83% and was highest for TCS. Uncertainty for the results of the filter residues was generally higher and covered a range from 13 to 88%. This is mainly associated with the higher variation in the recovery of the substances in this matrix. These uncertainties are in the same range as in other studies (Kovalova et al., 2012; Verlicchi et al., 2014) and we assume that the results are still valuable to discuss the trends and possible sources of the biocidal active substances.

5. Conclusion

Our study is the first investigation trying to allocate the emission of biocidal active substances into municipal wastewater to household products. The results show that washing and cleaning agents, personal care products and biocidal products in households are important sources of biocidal active substances in the environment.

The combination of wastewater analysis and product inventories proofed to be a useful instrument to identify the household products responsible for the emissions of biocidal active substances. The comparison of inventories and measured concentrations shows that biocidal products are not necessarily the main source but that washing and cleaning agents and personal care products also play an important role, depending on the specific substances and use patterns as well as application modes. The applied combined approach, however, has its limits when it comes to the emission from building materials used indoors that cannot be included in product inventories. These materials could be an important source for material preservatives such as CAR, DIU, TEB and TER next to outdoor applications. All of these substances have been detected in our samples. However, a faulty connection of a stormwater to the wastewater sewer did not allow to draw further conclusions.

The results show the complexity of the emission sources of biocidal active substances in households making it difficult for the consumers to understand and follow recommendations to minimise the emissions of the substances from their households. When it comes to building materials, consumers' influence and knowledge is even more limited. Regulatory approaches should therefore start even further up the chain, i.e. at the very beginning as a measure of source control and aim to minimise the use of the substances in the products at first. This cannot all be done under the Biocidal Products Regulation as some uses of the substances do not fall under its scope. For example, the EU Regulation 1223/2009 on cosmetic products is of importance too when it comes to the emission reduction of certain substances.

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Conflict of interest

Stefanie Wieck is also working at the German Federal Environment Agency. This paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2018.03.040.

References

van der Aa, E., Kuppen, I., Balk, F., 2004. Environmental Emission Scenarios for Biocides Used as In-can Preservatives (Product type 6). Nijmegen (4L1 78 4.A0/R0 18/FBA/TL/Nijm).
Alvarez-Rivera, G., Dagnac, T., Lores, M., Garcia-Jares, C., Sanchez-Prado, L., Lamas, J.P., et al., 2012. Determination of isothiazolinone preservatives in cosmetics and household products by matrix solid-phase dispersion followed by high-performance liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1270, 41–50.
Barco-Bonilla, N., Romero-González, R., Plaza-Bolaños, P., Garrido Frenich, A., Vidal, Martínez, Luis, José, 2010. Analysis and study of the distribution of polar and non-polar pesticides in wastewater effluents from modern and conventional treatments. J. Chromatogr. A 1217 (50), 7817–7825.
Behniwal, P.K., She, J., 2017. Development of HPLC-MS/MS method for the simultaneous determination of metabolites of organophosphate pesticides, synthetic pyrethroids, herbicides and DEET in human urine. Int. J. Environ. Anal. Chem. 97 (6), 548–562.
Bester, K., 2003. Triclosan in a sewage treatment process—balances and monitoring data. Water Res. 37 (16), 3891–3896.
Bollmann, U.E., Tang, C., Eriksson, E., Jönsson, K., Vollertsen, J., Bester, K., 2014. Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources. Water Res. 60, 64–74.
Brüggemann, L., Morgenstern, P., Wennrich, R., 2010. Comparison of international standards concerning the capability of detection for analytical methods. Accred. Qual. Assur. 15 (2), 99–104.
Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, 2017. Register of Approved Plant Protection Products (Verzeichnis zugelassener Pflanzenschutzmittel). https://apps2.bvl.bund.de/psm/jsp/index.jsp (accessed October 26, 2017).
Buser, A.M., Morf, L.S., 2009. Substance flow analysis of quartery ammonium compounds in Switzerland (Stoffflussanalyse von quartären Ammoniumverbindungen für die Schweiz). UWSF - Z Umweltchem Ökotox 21 (1), 27–35.
Butkovskyi, A., Rijnaarts, H.H.M., Zeeman, G., Hernandez Leal, L., 2016. Fate of personal care and household products in source separated sanitation. J. Hazard. Mater. 320, 427–434.
Chen, Z.-F., Ying, G.-G., Lai, H.-J., Chen, F., Su, H.-C., Liu, Y.-S., et al., 2012. Determination of biocides in different environmental matrices by use of ultra-high-performance liquid chromatography-tandem mass spectrometry. Anal. Bioanal. Chem. 404 (10), 3175–3188.
Daughton, C.G., 2014. The Matthew Effect and widely prescribed pharmaceuticals lacking environmental monitoring: case study of an exposure-assessment vulnerability. Sci. Total Environ. 466–467, 315–325.
Engelmann, U., 2016. Biozid-Wirkstoffe in kommunalen Abwassereinleitungen in Sachsen. In: KA - Korrespondenz Abwasser, Abfall. vol. 5. pp. 388–402.
Eriksson, E., Auffahrt, K., Eilersen, A.-M., Henze, M., Ledin, A., 2003. Household chemicals and personal care products as sources for xenobiotic organic compounds in grey wastewater. Water SA 29 (2), 135–146.
European Chemicals Agency, 2015. Emission Scenario Document for Product Type 19 – Repellents and Attractants. ECHA, Helsinki.
European Chemicals Agency, 2017a. Registered Substances. https://echa.europa.eu/web/guest/information-on-chemicals/registered-substances (accessed July 24, 2017).
European Chemicals Agency, 2017b. Biocidal Active Substances. https://echa.europa.eu/information-on-chemicals/biocidal-active-substances (accessed July 24, 2017).
European Commission, 2017. EU pesticides database. http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN (accessed August 11, 2017).
European Union, 2007. Regulation (EC) No 1907/2006 of the European parliament and of the council of 18 December 2006 concerning the registration, evaluation, authorisation and restriction of chemicals (REACH). In: Establishing a European Chemicals Agency, Amending Directive 1999/45/EC and Repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.
European Union, 2009. Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on Cosmetic Products.
European Union, 2013. Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 Concerning The Making Available on the Market and Use of Biocidal Products. BPR.
Forbrugerrådet Tænk Kemi, 2016. Spray Deodorants Containing Illegal Triclosan Found in Many Shops. http://kemi.taenk.dk/bliv-groennere/spray-deodorants-containing-illegal-triclosan-found-many-shops (accessed August 09, 2017).
Gago-Ferrero, P., Gros, M., Ahrens, L., Wiberg, K., 2017. Impact of on-site, small and large

scale wastewater treatment facilities on levels and fate of pharmaceuticals, personal care products, artificial sweeteners, pesticides, and perfluoroalkyl substances in recipient waters. Sci. Total Environ. 601-602, 1289–1297.
Garcia-Hidalgo, E., Sottas, V., von, Goetz N., Hauri, U., Bogdal, C., Hungerbühler, K., 2017. Occurrence and concentrations of isothiazolinones in detergents and cosmetics in Switzerland. Contact Dermatitis 76 (2), 96–106.
Hall, B., Tozer, S., Safford, B., Coroama, M., Steiling, W., Leneveu-Duchemin, M.C., et al., 2007. European consumer exposure to cosmetic products, a framework for conducting population exposure assessments. Food Chem. Toxicol. 45 (11), 2097–2108.
HERA, 2005. Human & Environmental Risk Assessment on Ingredients of Household Cleaning Products Guidance Document Methodology.
Herrmann, M., Olsson, O., Fiehn, R., Herrel, M., Kümmerer, K., 2015. The significance of different health institutions and their respective contributions of active pharmaceutical ingredients to wastewater. Environ. Int. 85, 61–76.
Kovalova, L., Siegrist, H., Singer, H., Wittmer, A., McArdell, C.S., 2012. Hospital wastewater treatment by membrane bioreactor: performance and efficiency for organic micropollutant elimination. Environ. Sci. Technol. 46 (3), 1536–1545.
Kreuzinger, N., Fuerhacker, M., Scharf, S., Uhl, M., Gans, O., Grillitsch, B., 2007. Methodological approach towards the environmental significance of uncharacterized substances — quaternary ammonium compounds as an example. Desalination 215 (1–3), 209–222.
Kümmerer, K., Eitel, A., Braun, U., Hubner, P., Daschner, F., Mascart, G., et al., 1997. Analysis of benzalkonium chloride in the effluent from European hospitals by solid-phase extraction and high-performance liquid chromatography with post-column ion-pairing and fluorescence detection. J. Chromatogr. A 774 (1–2), 281–286.
Kümmerer, K., Dionysiou, D.D., Fatta-Kassinos, D., 2015. Long-Term Strategies for Tackling Micropollutants. Springer, Berlin, Heidelberg.
Launay, M.A., Dittmer, U., Steinmetz, H., 2016. Organic micropollutants discharged by combined sewer overflows - characterisation of pollutant sources and stormwater-related processes. Water Res. 104, 82–92.
Liu, W.-R., Yang, Y.-Y., Liu, Y.-S., Zhang, L.-J., Zhao, J.-L., Zhang, Q.-Q., et al., 2017. Biocides in wastewater treatment plants: mass balance analysis and pollution load estimation. J. Hazard. Mater. 329, 310–320.
Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., et al., 2013. EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Res. 47 (17), 6475–6487.
Medizinische Medien Informations GmbH, 2017. Gelbe Liste Online. https://www.gelbe-liste.de/ (accessed July 24, 2017).
Merel, S., Snyder, S.A., 2016. Critical assessment of the ubiquitous occurrence and fate of the insect repellent N,N-diethyl-m-toluamide in water. Environ. Int. 96, 98–117.
Merel, S., Nikiforov, A.I., Snyder, S.A., 2015. Potential analytical interferences and seasonal variability in diethyltoluamide environmental monitoring programs. Chemosphere 127, 238–245.
Ort, C., Lawrence, M.G., Reungoat, J., Mueller, J.F., 2010a. Sampling for PPCPs in wastewater systems: comparison of different sampling modes and optimization strategies. Environ. Sci. Technol. 44 (16), 6289–6296.
Ort, C., Lawrence, M.G., Rieckermann, J., Joss, A., 2010b. Sampling for pharmaceuticals and personal care products (PPCPs) and illicit drugs in wastewater systems: are your conclusions valid? A critical review. Environ. Sci. Technol. 44 (16), 6024–6035.
Östman, M., Lindberg, R.H., Fick, J., Bjorn, E., Tysklind, M., 2017. Screening of biocides, metals and antibiotics in Swedish sewage sludge and wastewater. Water Res. 115, 318–328.
Philippat, C., Bennett, D., Calafat, A.M., Picciotto, I.H., 2015. Exposure to select phthalates and phenols through use of personal care products among Californian adults and their children. Environ. Res. 140, 369–376.
van der Poel, P., 2001. Emission scenarios document for product type 2: private and public health area disinfectants and other biocidal products (sanitary and medical sector). In: RIVM Report 601450 008. RIVM, Bilthoven.
Rafoth, A., Gabriel, S., Sacher, F., Brauch, H.-J., 2007. Analysis of isothiazolinones in environmental waters by gas chromatography-mass spectrometry. J. Chromatogr. A 1164 (1–2), 74–81.
Rodil, R., Quintana, J.B., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2009. Multi-residue analytical method for the determination of emerging pollutants in water by solid-phase extraction and liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1216 (14), 2958–2969.
Singer, H., Jaus, S., Hanke, I., Lück, A., Hollender, J., Alder, A.C., 2010. Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water. Environ. Pollut. 158 (10), 3054–3064.
Speksnijder, P., van Ravestijn, J., de, Voogt P., 2010. Trace analysis of isothiazolinones in water samples by large-volume direct injection liquid chromatography tandem mass spectrometry. J. Chromatogr. A 1217 (32), 5184–5189.
Sütterlin, H., Trittler, R., Bojanowski, S., Stadlbauer, E.A., Kümmerer, K., 2007. Fate of benzalkonium chloride in a sewage sludge low temperature conversion process investigated by LC-LC/ESI-MS/MS. Clean: Soil, Air, Water 35 (1), 81–87.
Ternes, T.A., Joss, A., Siegrist, H., 2004. Scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environ. Sci. Technol. 38 (20), 392A–399A.
Verlicchi, P., Al Aukidy, M., Jelic, A., Petrović, M., Barceló, D., 2014. Comparison of measured and predicted concentrations of selected pharmaceuticals in wastewater and surface water: a case study of a catchment area in the Po Valley (Italy). Sci. Total Environ. 470-471, 844–854.
Wick, A., Fink, G., Ternes, T.A., 2010. Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1217 (14), 2088–2103.
Wicke, D., Matzinger, A., Sonnenberg, H., Caradot, N., Schubert, R.-L., Rouault, P., et al., 2017. Micropollutants in stormwater in Berlin (Spurenstoffe im Regenwasserabfluss Berlins). KA - Korrespondenz Abwasser, Abfall 64 (5), 394–404.
Wieck, S., Olsson, O., Kümmerer, K., 2016. Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater. Environ. Int. 94, 695–705.
Wieck, S., Olsson, O., Kümmerer, K., 2018. Consumers' perceptions of biocidal products in households. Int. J. Hyg. Environ. Health 221 (2), 260–268.
Wittmer, I.K., Scheidegger, R., Bader, H.-P., Singer, H., Stamm, C., 2011. Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409 (5), 920–932.
Wu, X.M., Bennett, D.H., Ritz, B., Cassady, D.L., Lee, K., Hertz-Picciotto, I., 2010. Usage pattern of personal care products in California households. Food Chem. Toxicol. 48 (11), 3109–3119.
Zhang, C., Cui, F., Zeng, G.-M., Jiang, M., Yang, Z.-Z., Yu, Z.-G., et al., 2015. Quaternary ammonium compounds (QACs): a review on occurrence, fate and toxicity in the environment. Sci. Total Environ. 518-519, 352–362.

Supplementary information to:

Not only biocidal products: Washing and cleaning agents and personal care products can act as further sources of biocidal active substances in wastewater

Stefanie Wieck, Oliver Olsson, Klaus Kümmerer

Content

S1. Sketch of the sampling area

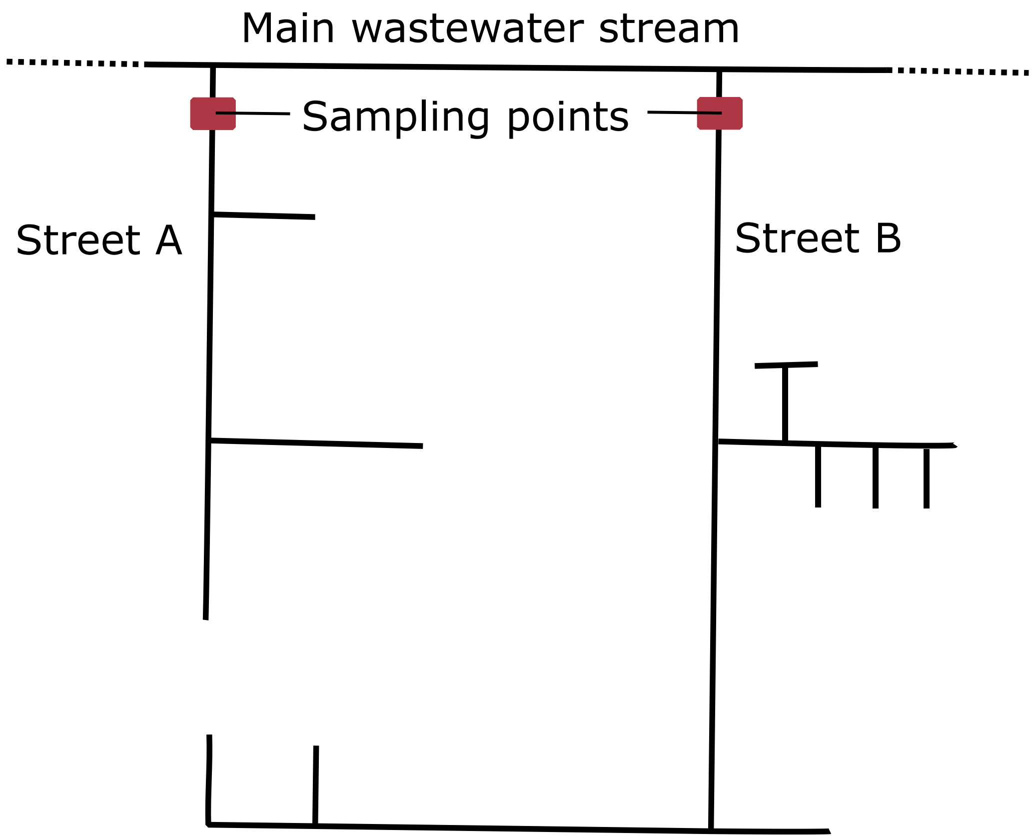


Figure 1 Sketch of the sampling area

S2. Sampling of washing machine effluent

To explore the origin of the repellents ICA and DEET in wastewater in more detail, effluent of a washing machine was sampled and analysed. The clothes to be washed (in total 4.6 kg) were worn while repellents containing ICA and DEET were sprayed on the skin (arms, legs, neck) during daily use according to the instruction on the products. To evaluate the duration of the emission of the two biocidal active substances, 100 mL of the effluent were sampled during three washing cycles. After each washing cycle with clothes, the machine was run without clothes but with washing agent once (see below). Clothes were not worn between the washing cycles. This explorative study is supposed to give an idea on the constant detection of repelling active substances in wastewater, but should be considered as indicative only due to the small sample size.

Effluent of a washing machine was sampled in the following order:

Washing cycle with washing agent, but without clothes (empty prior to study)

↓

Washing cycle with washing agent and clothes (1st cycle)

↓

Washing cycle with washing agent, but without clothes (2nd cycle)

↓

Washing cycle with washing agent and clothes (3rd cycle)

↓

Washing cycle with washing agent, but without clothes (4th cycle)

↓

Washing cycle with washing agent and clothes (5th cycle)

The explorative study showed emissions of ICA and DEET through the washing machine. Compared to the first washing cycle without clothes, ICA peak areas were almost 40 times bigger when clothes worn during repellent application were washed for the first time. DEET peak areas were almost 230 times bigger. Even in the third washing cycle of the clothes, areas were still almost 10 times bigger compared to the first empty washing cycle. Even in washing cycles without clothes slightly elevated concentrations of ICA and DEET were measured in washing machine effluent. TEB and DIU were also detected in the water of all washing cycles, whether or not clothes were washed. Further investigations are necessary to further elaborate this emission route.

S3. Selection of analytes

The selection of analytes was based on the biocidal active substances listed on products inventoried in neighbourhood A (Wieck et al., 2016).

a) Non-inclusion due to less than 10 products inventoried:

Table 1 Non-inclusion due to less than 10 products containing the substance

Substance	CAS number	Number of products inventoried
Alkyldimethylbenzylammoniumsaccharinate	68989-01-5	1
Ammonium sulphate	7783-20-2	1
Chlorphenapyr	122453-73-0	1
Chrysanthemum cinerariaefolium, extract	89997-63-7	1
Cyphenothrin	39515-40-7	1
d-Allethrin	231937-89-6	1
Difethialone	104653-34-1	1
Esbiothrin	260359-57-7	1
Imidacloprid	138261-41-3	1
Copper sulphate pentahydrate	7758-98-7	1
Methyl nonyl ketone	112-12-9	1
Monolinuron	1746-81-2	1
Potassium caroate	70693-62-8	1
Pyriproxifen	95737-68-1	1
Trichloro-s-triazinetrione	87-90-1	1
Amines, C10-16-alkyldimethyl, N-oxides	70592-80-2	2
Biphenyl-2-ol	90-43-7	2
DEET	134-62-3	2
d-Tetramethrin	1166-46-7	2
Ethylbutylacetoaminopropionate	52304-36-6	2
Etofenprox	80844-07-1	2
Glycolic acid	79-14-1	2
Imiprothrin	72963-72-5	2
Nonanoic acid	112-05-0	2
Cypermethrin	52315-07-8	3
Fipronil	120068-37-3	3
Glyoxal	107-22-2	3
Lavandin oil	91722-69-9	3
Mecetronium ethyl sulphate	3006-10-8	3
Lauric acid	143-07-7	4
Margosa extract	-	4
S-Methopren	65733-16-6	4
Triclosan	3380-34-5	4
d-Phenothrin	26046-85-5	5
Thiacloprid	111988-49-9	5
Cetylpyridinium chloride	123-03-5	6
Caprylic acid	124-07-2	6
Sodium borate	1330-43-4/1303-96-4	6
IPBC	55406-53-6	7
CHDG	18472-51-0	8
DDAC	7173-51-5	8
Permethrin	52645-53-1	9
1-Propanol	71-23-8	9

b) Non-inclusion due to inorganic structure

Table 2 Non-inclusion due to inorganic structure

Substance	CAS number
Boric acid	10043-35-3
Sodium hypochlorite	7681-52-9
Hydrogen peroxide	7722-84-1
Hydrochloric acid	7647-01-0

c) Non-inclusion due to readily biodegradability

Table 3 Non-inclusion due to readily biodegradability

Substance	CAS number	Source
Glutaraldehyde	111-30-8	Assessment report for biocidal active substances (http://dissemination.echa.europa.eu/Biocides/factsheet?id=1310-03)
Propan-2-ol	67-63-0	Assessment report for biocidal active substances (http://dissemination.echa.europa.eu/Biocides/factsheet?id=1355-01)
Geraniol	106-24-1	REACH registration dossier (https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15160/5/3/2)
2-Phenoxyethanol	122-99-6	REACH registration dossier (https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15160/5/3/2)

d) Non-inclusion due to analytical problems

Table 4 Non-inclusion due to analytical problems

Substance	CAS number
Zinc pyrithione	13463-41-7
PHMB	27083-27-8
Pyrethrins and pyrethroids	8003-34-7
Methylisothiazolinone (MIT)	2682-20-4

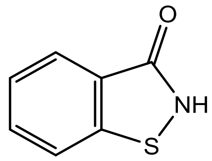
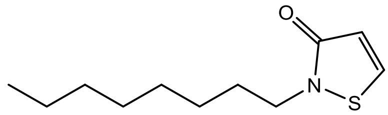
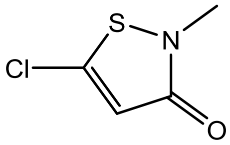
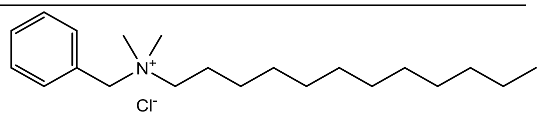
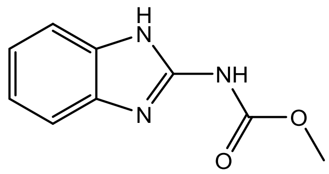
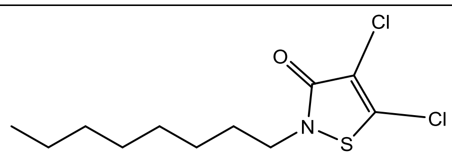
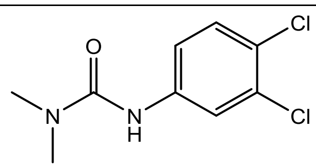
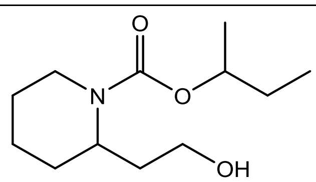
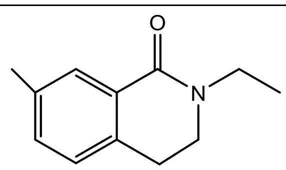
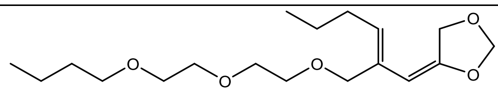
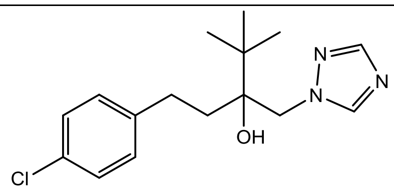
e) Non-inclusion due to other reasons

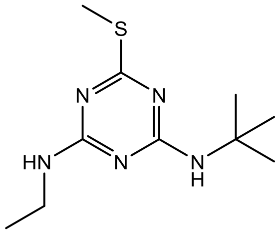
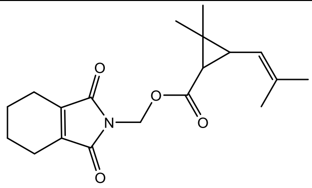
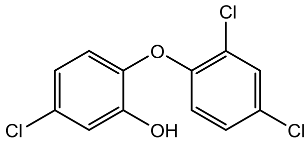
Table 5 Non-inclusion due to other reasons

Substance	CAS number	Comment
Salicylic acid	69-72-7	Frequent use in pharmaceuticals that have not been inventoried
Sorbic acid	110-44-1	Natural occurence
Benzoic acid	65-85-0	Natural occurence
Lactic acid	79-33-4	Natural occurence
Potassium sorbate	24634-61-5	Natural occurence
Ethanol	64-17-5	Natural occurence
Citric acid	77-92-9	Natural occurence
Formic acid	64-18-6	Natural occurence
TMAD	5395-50-6	Releaser of formaldehyde
(Ethylenedioxy)dimethanol	3586-55-8	Releaser of formaldehyde
DMDMH	6440-58-0	Releaser of formaldehyde
Bronopol	52-51-7	Releaser of formaldehyde

S4. Structural formulae

Table 6 Structural formulae of the biocidal active substances

Biocidal active substance	Abbreviation	CAS	
1,2-benzisothiazol-3(2H)-one	BIT	2634-33-5	
2-octyl-2H-isothiazol-3-one	OIT	26530-20-1	
5-chloro-2-methyl-2h-isothiazol-3-one	CMIT	26172-55-4	
Alkyl (C_{12}) dimethylbenzyl ammonium chloride	BKC	68424-85-1	
Carbendazim	CAR	10605-21-7	
Dichlorooctylisothiazolinone	DCOIT	64359-81-5	
Diuron	DIU	330-54-1	
Icaridine	ICA	119515-38-7	
N,N-diethyl-meta-toluamide	DEET	134-62-3	
Piperonyl butoxide	PBO	51-03-6	
Tebuconazole	TEB	107534-96-3	

Terbutryn	TER	886-50-0	
Tetramethrin	TET	7696-12-0	
Triclosan	TCS	3380-34-5	

S5. Chemicals

Ultrapure water was used from an Ultra Clear UV TM system (Evoqua Water Technologies, Barsbüttel, Germany). The following chemicals were used during analyses:

Table 7 Suppliers and purity of the chemicals used

	Supplier	Purity
BIT	TCI Deutschland GmbH, Eschborn, Germany	>98%
BKC	Alfa Aesar, Karlsruhe, Germany	98.0%
CAR	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	99.5%
CAR-D4	LGC Standards GmbH, Wesel, Germany	99.5%
CMIT	LGC Standards GmbH, Wesel, Germany	99.0%
DCOIT	TCI Deutschland GmbH, Eschborn, Germany	>98%
DEET	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	98.1%
DEET-D6	LGC Standards GmbH, Wesel, Germany	98.0%
DEET-D7	LGC Standards GmbH, Wesel, Germany	98.8%
DIU	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	>96%
DIU-D6	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	>96%
ICA	Biomol GmbH, Hamburg, Germany	>95%
OIT	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	>96%
PBO	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	99.0%
TCS	Alfa Aesar, Karlsruhe, Germany	>99%
TCS-D3	LGC Standards GmbH, Wesel, Germany	98.1%
TEB	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	99.6%
TEB-D6	LGC Standards GmbH, Wesel, Germany	97.0%
TER	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	>96%
TER-D5	Neochema GmbH, Bodenheim, Germany	98.5%
TET	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	98.3%
Acetone	Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany	>99.9%
Acetonitrile	VWR International GmbH, Hannover, Germany	>99.9%
Formic acid	Merck KGaA, Darmstadt, Germany	98-100%
Methanol	VWR International GmbH, Hannover, Germany	>99.9%

S6. Extraction procedure

The samples were filtered using VWR 691 glass fibre filters (particle retention: 1.6 µm, VWR International GmbH, Hannover, Germany) and underwent the following extraction procedure:

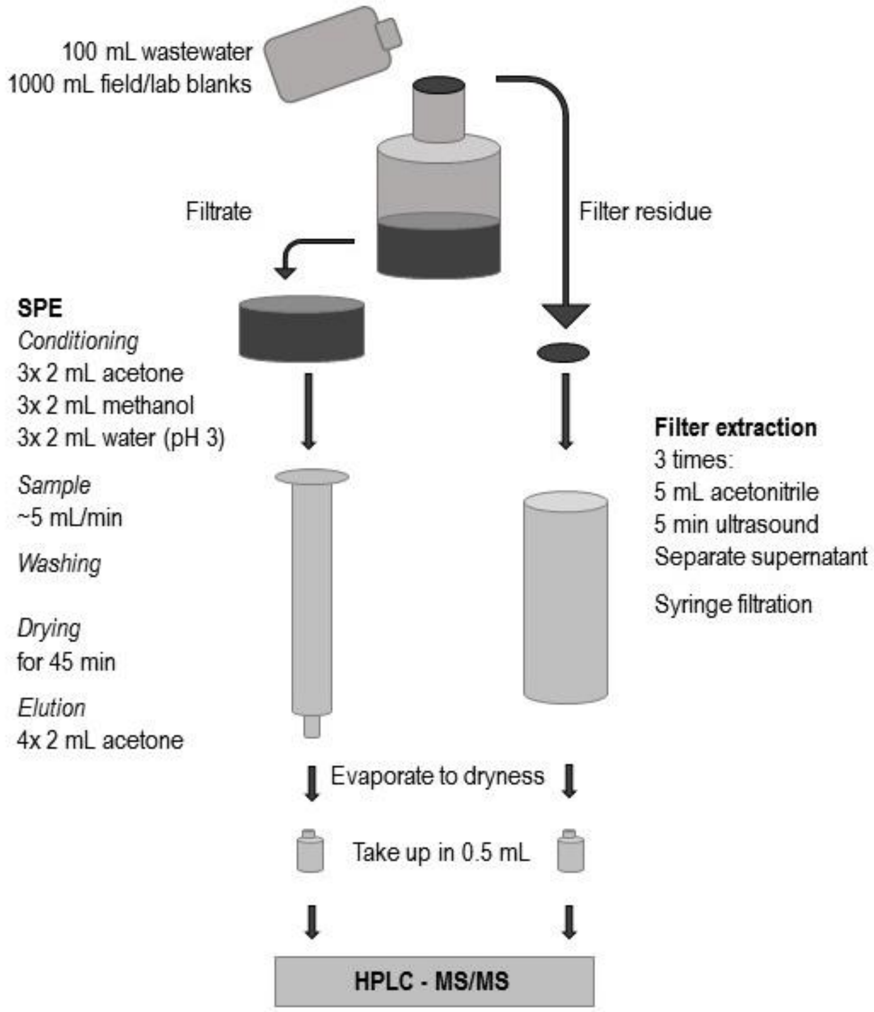


Figure 2 Workflow of the extraction procedure

a) Water phase

Filtrate of 100 mL wastewater and of 1000 mL laboratory and field blanks underwent the following extraction procedure:

1. pH was adjusted to pH 3 using 100% formic acid
2. Samples were spiked with 0.25 mL IS (1 mg/L)
3. Macherey-Nagel Chromabond HR-X SPE cartridges (3 mL/ 200 mg) were washed and conditioned with 3x 2 mL acetone, 3x 2 mL methanol and 3x 2 mL Ultrapure water adjusted to pH 3 with formic acid.
4. Samples were then passed through the cartridges with an approximate speed of 5 mL/min.
5. Cartridges were then washed with 3 mL Ultrapure water adjusted to pH 3 and then left to dry for 45 minutes. Afterwards, samples were eluted with 4x 2 mL acetone.
6. Samples were evaporated to dryness with a Büchi Syncore Polyvap (BÜCHI Labortechnik GmbH, Essen, Germany) and taken up in 0.25 mL 0.1% formic acid and 0.25 mL acetone.

b) Filter

Filter residue of 100 mL wastewater and 1000 mL drinking water underwent the following procedure for extraction:

7. Filters with filter residue were spiked with 0.25 mL IS (0.5 mg/L)
8. Filters were cut into pieces and placed in tubes
9. 5 mL acetonitrile were added
10. Tubes were placed in ultrasonic bath for 5 min at room temperature
11. Supernatant was taken off
12. Acetonitrile was added two more times, followed by 5 min in ultrasonic bath and taking off supernatant which was pooled.
13. Samples was filtrated with syringe filter (Macherey Nagel Chromafil Xtra PES-45/25) and then evaporated until dryness in the Büchi Syncore Poyvap.
14. Samples were then taken up in 0.25 mL 0.1% formic acid and 0.25 mL acetonitrile.

S7. Analytical method

An Agilent 1200 LC consisting of a degasser, a binary pump, a thermostatted column (temperature set at 20 °C) compartment and an autosampler was used for LC. A Macherey-Nagel Nucleoshell RP 18plus column (150 mm x 3 mm, 2.7 µm) was used for separation together with a Macherey-Nagel Nucleoshell RP 18plus pre-column (4 mm x 3 mm, 2.7 µm; Macherey-Nagel, Düren, Germany). The flow was set at 0.2 mL/min and injection volume was 10 µL.

13 of 14 biocidal active substances were detected using positive ionisation mode in an ESI source, only for TCS negative ionisation was used. The following gradient was applied for the LC method in combination with the positive ESI mode. For the detection of TCS in negative mode, isocratic conditions of 90% acetonitrile and 10% formic acid (0.1%) were used.

Table 8 Gradient of the HPLC method

Time [min]	0.1% Formic acid in H_2O [%]	Acetonitrile [%]
0	100	0
2	80	20
13	20	80
23	20	80
25	100	0

Substances were analysed using an Agilent Triple-Quad mass spectrometer 6430 using multiple reaction monitoring (MRM). Dwell time for each substance was 100 ms and cell accelerator voltage was 7 V. Compound specific parameters were optimised prior to sample analyses using direct injection.

S8. MS/MS transitions

Table 9 Transitions used as quantifiers and qualifiers

	Retention time [min]	Quantifier transition [m/z]	Fragmentor voltage [V]	Collison energy [V]	Qualifier transition [m/z]	Fragmentor voltage [V]	Collison energy [V]
BIT	14.032	152.0 -> 77.1	104	32	152.0 -> 134.0	104	24
BKC	19.239	305.3 -> 91.1	144	32	305.3 -> 213.3	144	20
CAR	12.052	192.1 -> 160.1	114	16	192.1 -> 132.1	114	32
CMIT	13.082	150.0 -> 87.0	104	48	150.0 -> 58.1	104	32
DCOIT	27.500	282.1 -> 169.9	106	12	282.1 -> 57.2	106	16
DEET	18.399	192.1 -> 119.1	104	16	192.1 -> 91.1	104	32
DIU	18.548	233.0 -> 72.1	96	17	233.0 -> 56.0	96	57
ICA	18.265	230.2 -> 130.2	86	8	230.2 -> 174.2	86	4
OIT	20.175	214.1 -> 102.1	96	12	214.1 -> 57.2	96	16
PBO	26.980	358.4 -> 178.1	76	4	358.4 -> 177.1	76	4
TCS	5.122	286.9 -> 35.0	83	0	289.0 -> 35.0	73	4
TEB	20.770	308.2 -> 70.1	134	20	308.2 -> 125.1	134	44
TER	17.753	242.1 -> 186.1	116	16	242.1 -> 68.1	116	52
TET	27.181	332.2 -> 164.1	96	20	332.2 -> 135.2	96	12
CAR-D4	12.021	196.1 -> 164.1	114	16	196.1 -> 136.1	114	32
DEET-D6	18.313	198.2 -> 119.0	122	16	198.2 -> 91.0	122	32
DEET-D7	18.188	199.2 -> 126.1	117	16	199.2 -> 98.1	117	32
DIU-D6	18.462	239.1 -> 78.2	106	20	239.1 -> 52.2	106	16
TCS-D3	5.084	290.0 -> 35.0	83	0	292.0 -> 35.1	73	0
TEB-D6	20.725	314.2 -> 72.1	134	20	314.2 -> 73.1	134	20
TER-D5	17.625	247.2 -> 191.2	104	16	247.2 -> 69.1	104	48

S9. Limit of quantification (LOQ)

The limit of quantification (LOQ) was derived according to the calibration curve method described in DIN 32645. It was derived separately for the analysis of filtrate and filter residue samples as these analyses were done at different points of time. The German DIN 32645 is comparable to the international ISO 11843 (Brüggemann et al., 2010). As no blank matrix samples are available for wastewater it was not possible to determine the LOQ by spiking blank matrix samples, instead Ultrapure water was used. The confidence range *k* was set to 3, the likelihood of error *α* was 1 % and 10 calibration samples ranging from 125 to 0.24 µg/L were analysed.

The different LOQs for the samples and blanks are due to the different enrichment of the samples. Wastewater samples were concentrated by the factor 200 while field and laboratory blanks were concentrated by the factor 1000.

Table 10 Limits of quantification for the substances in filtrate and filter residue

	LOQ filtrate [ng/L]		LOQ filter residue [ng/L]	
	Wastewater	**Blanks**	**Wastewater**	**Blanks**
BIT	15	3	24	5
BKC	7	1	7	1
CAR	14	3	8	2
CMIT	37	7	10	2
DCOIT	10	2	11	2
DEET	5	1	4	1
DIU	8	2	9	2
ICA	9	2	6	1
OIT	6	1	6	1
PBO	21	4	22	4
TCS	117	23	36	7
TEB	5	1	4	1
TER	4	1	4	1
TET	10	2	9	2

S10. Matrix effect and recovery

Matrix effect and recovery were determined using wastewater from the sampled neighbourhood.

To estimate the recovery for the extraction of the filtrate, 100 mL of the filtrate were placed in two tubes. One of them was spiked with the standards (incl. surrogate standards) to a final concentration of 500 µg/L (S_1). Both were extracted according to the extraction procedure. After drying and taking up, the sample from the second vessel was split in two parts. One was spiked to the same concentration as the first sample (S_2). To the second half, the corresponding volume of acetonitrile was added

(S_3). This was done in triplicates. Afterwards, samples were analysed with LC-MS/MS. Absolute recovery was calculated using the peak areas:

Absolute recovery [%] = $S_1/(S_2-S_3)$

To estimate the recovery for the extraction of the filter residue, filters carrying the solids of 100 mL wastewater were used. One of them was spiked with the standards to a final concentration of 500 µg/L. Surrogate standards were spiked to a final concentration of 250 µg/L (S_1). Both filters were extracted according to the extraction procedure. After drying and taking up, the sample from the second filter was split in two parts. One was spiked to the same concentration as the first sample (S_2). To the second half, the corresponding volume of acetonitrile was added (S_3). This was done in triplicates. Afterwards, samples were analysed with LC-MS/MS. Absolute recovery was calculated using the peak areas (see formula above).

To calculate the matrix effect, peak areas of S_2 and S_3 were compared to the peak areas of a sample of acetonitrile spiked to the same concentrations as S_2 (S_{ACN}). This was also done in triplicates for filtrates and filter residues.

Matrix effect [%] = $((S_2-S_3)/ S_{ACN}) \times 100$

Table 11 Recoveries and matrix effects in filtrate and filter residue

	Filtrate			Filter residue		
	Absolute recovery [%]	**Relative recovery [%]**	**Matrix effect [%]**	**Absolute recovery [%]**	**Relative recovery [%]**	**Matrix effect [%]**
BIT	6	31	11	9	16	87
BKC	30	90	31	173	34	46
CAR	104	91	31	481	96	122
CMIT	4	21	10	14	24	86
DCOIT	18	91	25	60	102	48
DEET	23	115	32	55	93	78
DIU	31	92	35	50	84	67
ICA	105	92	27	69	102	79
OIT	79	70	22	42	71	59
PBO	6	32	11	33	56	1
TCS	65	99	51	107	93	93
TEB	34	100	34	75	102	50
TER	32	106	34	80	103	73
TET	17	86	22	58	98	42
CAR-D4	114		31	503		125
DEET-D6	20		30	-		-
DEET-D7	-		-	59		79
DIU-D6	33		38	67		73
TCS-D3	65		51	114		101
TEB-D6	34		34	73		50
TER-D5	30		35	77		73

The following surrogate standards were used to calculate the relative recovery:

Table 12 Surrogate standards

	Surrogate standard - Filtrate	Surrogate standard – Filter residue
BIT	DEET-D6	DEET-D7
BKC	DIU-D6	CAR-D4
CAR	CAR-D4	CAR-D4
CMIT	DEET-D6	DEET-D7
DCOIT	DEET-D6	DEET-D7
DEET	DEET-D6	DEET-D7
DIU	DIU-D6	DIU-D6
ICA	CAR-D4	DIU-D6
OIT	CAR-D4	DEET-D7
PBO	DEET-D6	DEET-D7
TCS	TCS-D3	TCS-D3
TEB	TEB-D6	TEB-D6
TER	TER-D5	TER-D5
TET	DEET-D6	DEET-D7

S11. Intra- and interday precision

To evaluate the precision of the analytical method, a sample with a concentration of 0.08 mg/L was injected three times during one day (intraday precision) and during three days (interday precision).

Table 13 Intraday and interday precision

	Intraday precision [%] (n=3)	Interday precision [%] (n=3)
BIT	3.2	3.2
BKC	1.0	3.4
CAR	2.7	1.5
CMIT	4.4	7.5
DCOIT	4.2	6.1
DEET	2.6	3.4
DIU	3.0	2.1
ICA	1.9	1.4
OIT	2.4	4.8
PBO	4.8	15.2
TCS	3.0	4.1
TEB	2.1	3.2
TER	1.2	6.1
TET	4.9	8.3

S12. Carry-over

To evaluate carry-over between analyses, a standard mixture with a concentration of 2.5 mg/L was injected followed by two injections of Ultrapure water. Most of the compounds showed less than 0.1 % carry-over comparing the peak areas. Highest carry-over of 0.21 % was seen for TCS. For this reason, carry-over was not regarded as problematic.

Table 14 Carry-over between samples

	Ultrapure 1 [%]	Ultrapure 2 [%]
BIT	0.00	0.00
BKC	0.08	0.03
CAR	0.19	0.06
CMIT	0.00	0.00
DCOIT	0.07	0.03
DEET	0.11	0.02
DIU	0.08	0.02
ICA	0.08	0.03
OIT	0.15	0.04
PBO	0.02	0.01
TCS	0.21	0.00
TEB	0.07	0.03
TER	0.06	0.01
TET	0.06	0.04

S13. Uncertainty

The uncertainty of the results was calculated with Equation 1 using the approaches of Kovalova et al. (2012) and Verlicchi et al. (2014). The calculations were done for the matrices filtrate and filter residue.

Equation 1 Calculation of the uncertainty

$U_{total} = \sqrt{(U_{sampling}^2 + U_{recocery}^2 + U_{precision}^2)}$

$U_{sampling}$ was set to 12% based on the results of Ort et al. (2010), because time-proportional sampling with an interval of 15 min was used.

$U_{recovery}$ was the respective relative standard deviation for the recovery of the different substances in the two matrices, filtrate and filter residue.

$U_{precision}$ was the respective relative standard deviation of the interday-variability (see section S11).

Table 15 Calculated uncertainties

			$U_{recovery}$		U_{total}	
	$U_{sampling}$	$U_{precision}$	Filtrate	Filter residue	Filtrate	Filter residue
BIT	12	3	11	2	17	13
BKC	12	3	47	24	49	27
CAR	12	2	2	2	12	12
CMIT	12	8	5	3	15	14
DCOIT	12	6	3	69	14	70
DEET	12	3	2	11	13	17
DIU	12	2	11	8	16	15
ICA	12	1	6	23	13	26
OIT	12	5	35	11	37	17
PBO	12	15	59	86	62	88
TCS	12	4	82	44	83	46
TEB	12	3	37	53	39	54
TER	12	6	18	15	22	20
TET	12	8	5	60	15	62

S14. Calculation of PWWC

a) Emission via washing and cleaning agents

Until now, no specific Emission Scenario Document (ESD) is available for the use of preservatives in washing and cleaning agents (PT 6). It is recommended to use the available ESD for disinfectants for human hygiene (PT1) (van der Aa et al., 2004). This ESD has been adapted for the data available in this study. The formulas were used to calculate the predicted wastewater concentrations (PWWC) of BIT and OIT for the two streets. This was based on the inventoried products containing the two substances. The products were divided in fabric detergents, dish-washing liquids and surface cleaners.

i) Calculation of the PWWC of BIT in street A

Release of preservatives used in fabric detergents				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.00026	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	150	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.57	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.55	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ fabric}$	1.4	[g/d]	$\mathbf{Elocal_{water,fabric}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Release of preservatives used in dish-washing liquids				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.00004	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	40	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.71	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.41	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ dish\text{-}washing}$	0.05	[g/d]	$\mathbf{Elocal_{water,dish\text{-}washing}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Release of preservatives used in surface cleaners				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.000038	[g/L]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	60	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.29	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.69	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ surface\ cleaner}$	0.05	[g/d]	$\mathbf{Elocal_{water,surface\ cleaner}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Predicted wastewater concentration				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of BIT in street A	$\mathbf{PWWC_{BIT,\ street\ A}}$	0.0001	[g/L]	$\mathbf{PWWC} = (Elocal_{water,\ fabric} + Elocal_{water,\ dish\text{-}washing} + Elocal_{water,\ surface\ cleaner}) / (N_{household\ members} * V_{water})$
		100 278	[ng/L]	

ii) Calculation of the PWWC of BIT in street B

Release of preservatives used in fabric detergents				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.00026	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	150	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.57	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.58	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ fabric}$	2.8	[g/d]	$\mathbf{Elocal_{water,fabric}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Release of preservatives used in dish-washing liquids				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.00004	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	40	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.71	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.33	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ dish\text{-}washing}$	0.08	[g/d]	$\mathbf{Elocal_{water,dish\text{-}washing}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Release of preservatives used in surface cleaners				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.000038	[g/L]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	60	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.29	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.6	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ surface\ cleaner}$	0.09	[g/d]	$\mathbf{Elocal_{water,surface\ cleaner}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Predicted wastewater concentration				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of BIT in street B	$\mathbf{PWWC_{BIT,\ street\ B}}$	0.0001	[g/L]	$\mathbf{PWWC} = (Elocal_{water,\ fabric} + Elocal_{water,\ dish\text{-}washing} + Elocal_{water,\ surface\ cleaner}) / (N_{household\ members} * V_{water})$
		104 201	[ng/L]	

iii) Calculation of the PWWC of OIT in street A

Release of preservatives used in fabric detergents				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.0000007	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	150	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.57	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ fabric}$	0.0	[g/d]	$\mathbf{Elocal_{water,fabric}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Release of preservatives used in dish-washing liquids				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.0000007	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	40	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.71	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.17	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ dish\text{-}washing}$	0.0004	[g/d]	$\mathbf{Elocal_{water,dish\text{-}washing}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Release of preservatives used in surface cleaners				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.0000007	[g/L]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	60	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.29	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.07	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ surface\ cleaner}$	0.0001	[g/d]	$\mathbf{Elocal_{water,surface\ cleaner}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * T_{task}$

Predicted wastewater concentration				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of OIT in street A	$\mathbf{PWWC_{OIT,\ street\ A}}$	3.3E-08	[g/L]	$\mathbf{PWWC} = (Elocal_{water,\ fabric} + Elocal_{water,\ dish\text{-}washing} + Elocal_{water,\ surface\ cleaner}) / (N_{household\ members} * V_{water})$
		33	[ng/L]	

iv) Calculation of the PWWC of OIT in street B

Release of preservatives used in fabric detergents				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.0000007	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	150	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.57	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.15	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ fabric}$	0.002	[g/d]	**$Elocal_{water,fabric}$** = $N_{household\ members}$ * $Q_{product}$ * $C_{product}$ * $F_{households}$ * F_{water} * T_{task}

Release of preservatives used in dish-washing liquids				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.0000007	[g/g]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	40	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.71	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.12	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ dish-washing}$	0.0005	[g/d]	**$Elocal_{water,dish-washing}$** = $N_{household\ members}$ * $Q_{product}$ * $C_{product}$ * $F_{households}$ * F_{water} * T_{task}

Release of preservatives used in surface cleaners				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	0.0000007	[g/L]	Alvarez-Rivera et al. (2012)
Consumption per task	$Q_{product}$	60	[g/task]	HERA (2005)
Tasks per day	T_{task}	0.29	[tasks/d]	HERA (2005)
Fraction of households	$F_{households}$	0.07	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ surface\ cleaner}$	0.0002	[g/d]	**$Elocal_{water,surface\ cleaner}$** = $N_{household\ members}$ * $Q_{product}$ * $C_{product}$ * $F_{households}$ * F_{water} * T_{task}

Predicted wastewater concentration				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of OIT in street B	**$PWWC_{OIT,\ street\ B}$**	9.5E-08	[g/L]	**PWWC** = ($Elocal_{water,\ fabric}$ + $Elocal_{water,\ dish-washing}$ + $Elocal_{water,\ surface\ cleaner}$) / ($N_{household\ members}$ * V_{water})
		95	[ng/L]	

b) Emission via toothpaste

No specific Emission Scenario Document (ESD) is available for the use of preservatives in toothpaste. For this reason, own formulas were used. As toothpastes containing TCS were only inventoried in street B, no calculations for street A are presented. $PWWC_{TCS,\ street\ A}$ is 0 ng/L.

Release of TCS used in toothpaste				
			Unit	**Comment**
Number of TCS toothpaste users per household	$N_{toothpaste\ users}$	1	[-]	Default
Use of toothpaste	$Q_{toothpaste}$	2	[g/d]	Hall et al. (2007)
Toothpastes containing TCS	$N_{toothpaste;TCS}$	4	[-]	Based on own product inventories
Fraction released to wastewater	F_{water}	1	[-]	Default
Fraction of active substance in product	$C_{product}$	0.003	[-]	European Union (2009, Annex V)
Emission rate to wastewater	$Elocal_{water,\ toothpaste}$	0.02	[g/d]	$\mathbf{Elocal_{water,toothpaste}} = N_{toothpaste\ users} * Q_{toothpaste} * C_{product} * N_{toothpaste;TCS} * F_{water}$

Predicted wastewater concentration				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of TCS in street B	$\mathbf{PWWC_{TCS,\ street\ B}}$	8.7E-07	[g/L]	$\mathbf{PWWC} = (Elocal_{water,\ toothpaste} / (N_{household\ members} * V_{water})$
		870	[ng/L]	

c) **Emission via surface disinfectants**

An ESD is available for surface disinfectants (van der Poel, 2001). This ESD has been adapted for the data available in this study. The formulas were used to calculate the PWWC of BKC for the two streets. BKC was only used in surface disinfectants in the products inventoried.

i) Calculation of the PWWC of BKC in street A

Release of BKC from surface disinfectants				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	12	g/L	Highest product concentration in products inventoried
Consumption per capita (General purpose (tiles, floors, sinks) + Lavatory)	$Q_{product}$	0.007	L/d	Default
Fraction of households	$F_{households}$	0.28	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ surface\ disinfection}$	2.62	[g/d]	$\mathbf{Elocal_{water,surface\ disinfection}}$ = $N_{household\ members}$ * $Q_{product}$ * $C_{product}$ * $F_{households}$ * F_{water}

Predicted wastewater concentration				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of BKC in street A	$\mathbf{PWWC_{BKC,\ street\ A}}$	0.00017	[g/L]	**PWWC** = $Elocal_{water,\ surface\ disinfection}$ / ($N_{household\ members}$ * V_{water})
		179 631	[ng/L]	

ii) Calculation of the PWWC of BKC in street B

Release of BKC from surface disinfectants				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	12	g/L	Highest product concentration in products inventoried
Consumption per capita (General purpose (tiles, floors, sinks) + Lavatory)	$Q_{product}$	0.007	L/d	Default
Fraction of households	$F_{households}$	0.3	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ surface\ disinfection}$	5.62	[g/d]	$\mathbf{Elocal_{water,surface\ disinfection}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water}$

Predicted wastewater concentration				
			Unit	**Comment**
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of BKC in street B	$\mathbf{PWWC_{BKC,\ street\ B}}$	0.0002	[g/L]	$\mathbf{PWWC} = Elocal_{water,\ surface\ disinfection} / (N_{household\ members} * V_{water})$
		195 348	[ng/L]	

d) Emission via repellents

An ESD is available for mosquito repellents (European Chemicals Agency, 2015). This ESD has been adapted for the data available in this study. The formulas were used to calculate the PWWC of DEET and ICA. Both substances were only used in repellents in the products inventoried. As products containing DEET were only inventoried in street A, no calculations for street B are presented. $PWWC_{DEET,\ street\ B}$ is 0 ng/L.

i) Calculation of the PWWC of DEET in street A

Release of DEET from insect repellents				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	300	[g/kg]	Maximum concentration in the products inventoried
Consumption per capita	$Q_{product}$	0.006	[kg/d]	European Chemicals Agency (2015)
Fraction of days of product use	$F_{product\ use}$	0.25	[-]	European Chemicals Agency (2015)
Fraction of households	$F_{households}$	0.07	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ insect\ repellent}$	3.55	[g/d]	$\mathbf{Elocal_{water,insect\ repellent}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * F_{product\ use}$

Predicted wastewater concentration				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of DEET in street A	$\mathbf{PWWC_{DEET,\ street\ A}}$	2.4E-04	[g/L]	$\mathbf{PWWC} = Elocal_{water,\ insect\ repellent} / (N_{household\ members} * V_{water})$
		243 517	[ng/L]	

ii) Calculation of the PWWC of ICA in street A

Release of ICA from insect repellents

			Unit	Comment
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	200	[g/kg]	Maximum concentration in the products inventoried
Consumption per capita	$Q_{product}$	0.006	[kg/d]	European Chemicals Agency (2015)
Fraction of days of product use	$F_{product\ use}$	0.25	[-]	European Chemicals Agency (2015)
Fraction of households	$F_{households}$	0.17	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ insect\ repellent}$	5.75	[g/d]	$\mathbf{Elocal_{water,insect\ repellent}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * F_{product\ use}$

Predicted wastewater concentration

			Unit	Comment
Number of inhabitants	$N_{household\ members}$	113	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of ICA in street A	$\mathbf{PWWC_{ICA,\ street\ A}}$	3.9E-04	[g/L]	$\mathbf{PWWC} = Elocal_{water,\ insect\ repellent} / (N_{household\ members} * V_{water})$
		394 265	[ng/L]	

iii) Calculation of the PWWC of ICA in street B

Release of ICA from insect repellents				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Fraction released to wastewater	F_{water}	1	[-]	Default
Active substance in product	$C_{product}$	200	[g/kg]	Maximum concentration in the products inventoried
Consumption per capita	$Q_{product}$	0.006	[kg/d]	European Chemicals Agency (2015)
Fraction of days of product use	$F_{product\ use}$	0.25	[-]	European Chemicals Agency (2015)
Fraction of households	$F_{households}$	0.20	[-]	Based on own product inventories
Emission rate to wastewater	$Elocal_{water,\ insect\ repellent}$	13.34	[g/d]	$\mathbf{Elocal_{water,insect\ repellent}} = N_{household\ members} * Q_{product} * C_{product} * F_{households} * F_{water} * F_{product\ use}$

Predicted wastewater concentration				
			Unit	Comment
Number of inhabitants	$N_{household\ members}$	223	[-]	Based on own questionnaire
Water consumption per inhabitant	V_{water}	129	[L/d]	Statistisches Bundesamt (2013)
Predicted wastewater concentration of ICA in street B	$\mathbf{PWWC_{ICA,\ street\ B}}$	9.2E-04	[g/L]	$\mathbf{PWWC} = Elocal_{water,\ insect\ repellent} / (N_{household\ members} * V_{water})$
		915 369	[ng/L]	

S15. Distribution between filtrate and filter residue

The distribution of the total detected amount of substance in a sample (c_{total}) between filtrate and filter residue is presented in the following table as percentages.

	BIT	BKC	CAR	DEET	DIU	ICA	OIT	TCS	TEB	TER
Share of c_{total} detected in filter residue [%]	23	50	0	0	0	8	0	84	0	0
Share of c_{total} detected in filtrate [%]	77	50	100	100	100	92	100	16	100	100

S16. References

Alvarez-Rivera G, Dagnac T, Lores M, Garcia-Jares C, Sanchez-Prado L, Lamas JP, et al. Determination of isothiazolinone preservatives in cosmetics and household products by matrix solid-phase dispersion followed by high-performance liquid chromatography-tandem mass spectrometry. Journal of Chromatography A 2012;1270:41–50.

Brüggemann L, Morgenstern P, Wennrich R. Comparison of international standards concerning the capability of detection for analytical methods. Accred Qual Assur 2010;15(2):99–104.

European Chemicals Agency. Emission Scenario Document for Product Type 19 – Repellents and attractants. Helsinki: ECHA; 2015.

European Union. Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products; 2009.

Hall B, Tozer S, Safford B, Coroama M, Steiling W, Leneveu-Duchemin MC, et al. European consumer exposure to cosmetic products, a framework for conducting population exposure assessments. Food and Chemical Toxicology 2007;45(11):2097–108.

HERA. Human & Environmental Risk Assessment on Ingredients of Household Cleaning Products Guidance Document Methodology; 2005.

Kovalova L, Siegrist H, Singer H, Wittmer A, McArdell CS. Hospital wastewater treatment by membrane bioreactor: Performance and efficiency for organic micropollutant elimination. Environmental Science & Technology 2012;46(3):1536–45.

Ort C, Lawrence MG, Reungoat J, Mueller JF. Sampling for PPCPs in wastewater systems: comparison of different sampling modes and optimization strategies. Environmental Science & Technology 2010;44(16):6289–96.

Statistisches Bundesamt. Öffentliche Wasserversorgung in Deutschland von 2013 (Public water consumption in Germany 2013), 2013. https://www.destatis.de/DE/ZahlenFakten/GesamtwirtschaftUmwelt/Umwelt/UmweltstatistischeErhebungen/Wasserwirtschaft/Tabellen/Wasserabgabe_2013.html (accessed March 11, 2018).

van der Aa E, Kuppen I, Balk F. Environmental Emission Scenarios for biocides used as In-can Preservatives (Product type 6). Nijmegen; 2004 4L1 78 4.A0/R0 18/FBA/T L/Nijm.

van der Poel P. Emission Scenarios Document for Product Type 2: Private and public health area disinfectants and other biocidal products (sanitary and medical sector). Bilthoven: RIVM; 2001. RIVM Report 601450 008.

Verlicchi P, Al Aukidy M, Jelic A, Petrović M, Barceló D. Comparison of measured and predicted concentrations of selected pharmaceuticals in wastewater and surface water: a case study of a catchment area in the Po Valley (Italy). Science of The Total Environment 2014;470-471:844–54.

Wieck S, Olsson O, Kümmerer K. Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater. Environment International 2016;94:695–705.

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Fragrance allergens in household detergents

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Washing and cleaning agents

ABSTRACT

Consumers are confronted with a large number of fragrance allergens from various sources. Until now, the discussion of exposure sources has mainly addressed cosmetic products and neglected other scented products in households. For the first time, fragrance allergens were evaluated in a complete set of detergents in households. In 131 households, we investigated the prevalence of detergents and searched their lists of ingredients for 26 fragrance allergens liable to be indicated on products according to the European Detergents Regulations. On the ingredient lists of 1447 products, these 26 fragrance substances were named almost 2000 times, most often limonene, linalool and hexyl cinnamal. Benzyl salicylate was used frequently in all-purpose cleaners. Linalool and limonene, hexyl cinnamal and butylphenyl methylpropional and citronellol and linalool co-occurred most often together in products. Fragrance allergens co-occurring together most frequently within households were eugenol, coumarin and cinnamyl alcohol. The study shows that detergents could play a relevant role for the exposure of consumers towards fragrance allergens and that they should not be underestimated as an exposure source during the exposure assessment.

1. Introduction

1.1. Allergy to fragrance substances in washing and cleaning agents

For contact allergy, fragrance substances belong to the major culprits (Schnuch and Mahler, 2015). A recent study in various geographic European regions came to the conclusion that 5% of the general population reacted to any of the fragrance allergens (Diepgen et al., 2016). In the United States, prevalence of contact allergy to the fragrance mix I is even slightly higher than in Europe (De Groot and Maibach, 2010).

Detergents are already under discussion as an exposure source for some substance groups associated with contact allergy, such as isothiazolinones used as preservatives (Ezendam et al., 2018; Gallo et al., 2016; Garcia-Hidalgo et al., 2017). They should not contain more than 2.5% (w/w) of a fragrance, this international maximum level can be lowered based on the results obtained by quantitative risk assessment (IFRA, 2015). However, up to now, most exposure models used for risk assessments for consumers only consider cosmetic products as a possible exposure source and neglect the other sources, underestimating the real exposure to fragrance allergens (IDEA, 2016; Safford et al., 2017). Existing studies on fragrance allergens in detergents are describing the allergy risk from the exposure, e.g. through laundered fabric, as very low (Basketter et al., 2010; Corea et al., 2006; German Cosmetic, Toiletry, Perfumery and Detergent Association, 2016). Contact dermatitis through laundry detergents seems to be rare (Belsito et al., 2002). However, for certain users the exposure to fragrance allergens can indeed be mainly driven by the use of detergents (Nijkamp et al., 2015).

Even if household detergents might in general play a minor role for the induction of fragrance allergy, they can be relevant in the elicitation in already sensitized persons (Basketter et al., 2015) besides contributing to the aggregated exposure (Nijkamp et al., 2015). For this reason, the improvement of the assessment of aggregated exposure is an important approach to reduce the frequency of contact allergy further (Basketter and Safford, 2016; Peiser et al., 2012). Cross-reactions and co-exposures can aggravate the allergic reactions to fragrance allergens (Effendy and Maibach, 1995; Geier et al., 2012; Heydorn et al., 2003; Jacob and Amini, 2008; Schnuch et al., 2007). This enhanced sensitization due to the simultaneous exposure to mixtures of fragrances, which has been reported for cosmetics (Uter et al., 2013b), is relevant for detergents as well.

Consumers' daily exposure to fragrance allergens results from the multitude of scented products in their households (Dodson et al., 2012; Park et al., 2006; Rastogi et al., 2001) and from other applications (e.g. limonene is used as solvent in many products). In addition, exposure to fragrance allergens may be increased considerably by occupational exposure (Buckley et al., 2002; Uter et al., 2001). Further factors such

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as chemical transformation (e.g. by oxidation) into stronger allergens or new molecules of often unknown properties and individual use practices can increase the risk of allergy further (Bråred Christensson et al., 2016; Niu et al., 2017; Rossignol et al., 2013).

1.2. Legal situation

In Europe, manufacturers are responsible for the safety of their products according to the Regulation (EC) 648/2004 on detergents (European Union, 2004). Twenty-six individual fragrance allergens must be listed with their INCI names (International Nomenclature of Cosmetic Ingredients) on the detergents containers if their concentrations exceed 0.01% in the products (European Union, 2004). This labelling requirement is based on the Regulation (EC) 648/2004 on detergents, referring to the Regulation (EC) No 1223/2009 on cosmetic products (European Union, 2009). It is only applicable if the 26 fragrance allergens are added as single substances and does not apply if they are part of natural extracts or the like. All other fragrances are summarized under the term ‘perfume’ or similar wording, including concentrations below 0.01% of those fragrances that must be declared by INCI name above this concentration limit. Many other important fragrance allergens are known, and since several years it has been under debate whether the list of the 26 fragrance allergens to be declared should be extended (SCCS, 2012; Uter et al., 2013a). The regulation defines maximum concentrations only for certain fragrance allergens, there are no general concentration limits.

In other countries, such as Australia, there is no legal obligation to disclose fragrances on detergents, only voluntary initiatives from industry exist (Lunny et al., 2017). In the United States, labelling requirements for detergents are only starting to be implemented on State level. The Californian Cleaning Product Right to Know Act of 2017 directly refers to the labelling requirements for fragrance allergens laid down in the European regulations on cosmetics and detergents (State of California, 2017).

1.3. Objectives

The study evaluates fragrance allergens in a set of detergents present in 131 households, covering a large number of single products. The aim is to analyze detergents as a further exposure source of fragrance allergens. This could help in identifying sources of fragrance allergens and minimizing consumers' exposure to them. Special emphasis is laid on the exposure to combinations of different fragrance allergens due the occurrence of two or more fragrance allergens in products and households (co-occurrence).

2. Methods

In this study, product inventories, which were collected as described in Wieck et al. (2016), were used to evaluate the presence of fragrance allergens in a large range of detergents. The product inventories included all types of detergents present in the households, for example including all-purpose cleaners, cleaning preparations for special purposes (e.g. bathroom, kitchen, dish-washing) and laundry detergents.

2.1. Study site

Members of 131 private households in Northern Germany were interviewed and product inventories were collected. The households were situated in three different neighborhoods, representing the three different urban–rural typologies in Europe: predominantly urban, intermediate and predominantly rural regions (BBSR, 2009). In the rural neighborhood, 145 households were approached by letter supported by the mayor of the village. This letter contained information regarding the project and the planned study. The interviews were conducted from March until May 2015. Households were contacted several times during this period and only one member of each households was asked to answer the questions. In this neighborhood, members of 94 households (65%) took part in this survey. In the intermediate neighborhood, 80 households were approached by a letter of the Leuphana University of Lüneburg, containing information regarding the project and the planned study. The interviews were conducted from July until August 2015. Nineteen households took part in this study. In the urban neighborhood, a notice of the Leuphana University of Lüneburg containing information regarding the project and the planned study was displayed in multi-family homes. Twenty households took part in this neighborhood. In these latter two neighborhoods, a convenience sampling strategy was used. This type of sampling strategy is based on the willingness of potential participants to take part in the study (Robinson, 2014). An overview over the demographic characteristics is presented in Table 1. More details on the neighborhoods and the demographic characteristics of the households can be found in Wieck et al. (2016).

Table 1
Demographic characteristics of those 131 households in Northern Germany, where the product inventories were taken in 2015 (Wieck et al., 2016, modified).

	n	%
Household members [a]		
1 adult	27	20,3
2 adults	51	38,3
3 adults	13	9,8
2 adults, 1 child	19	14,3
2 adults, 2 children	4	3,0
2 adults, 3 children	3	2,3
Other	14	10,5
Time in school until graduation [b]		
Without graduation	3	2.3
Graduation after 9 years of education	35	26.7
Graduation after 10 years of education	34	26.0
Graduation after ≥12 years of education	52	39.7
Other	5	3.8
Not specified	2	1.5
Professional education [b,c]		
No job training (yet)	11	8.4
Apprenticeship	91	69.5
Foreman or similar	12	9.2
University degree	43	32.8
Other	1	0.8
Not specified	3	2.3
Total net household income per month		
< 850 €	9	6.9
851–1500 €	17	13.0
1501–2000 €	15	11.5
2001–3000 €	26	19.8
3001–4000 €	30	22.9
4001–5000 €	10	7.6
5001–6000 €	7	5.3
> 6000 €	7	5.3
Not specified	10	7.6

[a] Children: household members < 18 years.
[b] Of the household member with the highest income.
[c] Multiple selections possible.

2.2. Data collection and analysis

The detergents present in the households were registered with barcode scanners as described in Wieck et al. (2016). All detergents present in the households were registered, including e.g. dish-washing liquids, all-purpose cleaners, textile detergents, toilet cleaners, glass cleaners, detergents for dish-washing machines, scouring agents and other detergents for special purposes. The barcodes were used to identify the products and their ingredients by using the public database www.codecheck.info. A similar approach has already been used for cosmetics in the Danish market (Bennike et al., 2018). The Swiss database “Codecheck” contains information on the ingredients of more

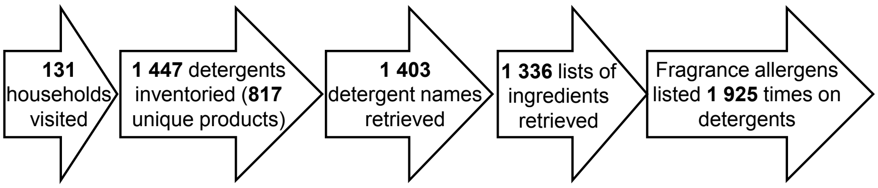

Fig. 1. Flowchart presenting the data collection to identify the fragrance allergens in detergents in households in Northern Germany in 2015.

than 40 000 products using data that is provided and kept up-to-date by users (Codecheck, 2018). The search system for products is based on barcodes. The 26 fragrance allergens legally required to be disclosed on the ingredient lists of detergents were compiled based on the results from this database (Fig. 1). Several spellings and alternative names of the fragrance allergens were used to search the data because the entries are maintained by consumers and writing errors are likely to occur. For example, the exact declaration of limonene in the database was variable. As most listings did not specify the specific isomers of limonene. We summarized all entries under 'limonene'. In this publication, official INCI names of fragrance substances are used as recommended by the 'Scientific Committee on Cosmetic Products and Non-food products intended for Consumers' (SCCNFP, 2000). In addition, it was evaluated whether the product contained 'perfume', 'fragrances', 'aroma' or similar wording.

Data was analyzed using IBM SPSS Statistics 24.0.0.0 (IBM, Armonk, USA). To analyze the co-occurrence of fragrance allergens in products and households, we used hierarchical clustering. For the analysis of co-occurrence in products, we used complete linkage and Dice measure, for the analysis of the co-occurrence of fragrance allergens in households we used average linkage and Squared Euclidean Distance measure. This was only possible for the frequently occurring fragrances. Fragrances occurring in less than 20 products were not included in the cluster analysis.

3. Results

In the households, 1447 detergents were scanned in total. Among them were 817 unique barcodes as the same products have been inventoried in several households. Duplicates were removed for the discussion of the presence of fragrance allergens in detergents (n = 817). The complete dataset was used for the discussion of fragrance allergens in households (n = 1447).

3.1. Fragrance allergens in detergents

Limonene (23.1%), linalool (20.1%), hexyl cinnamal (14.8%) and butylphenyl methylpropional (14.7%) were listed most often on the unique scanned detergents (Fig. 2, n = 817). Looking at the different types of detergents, limonene and linalool are the most frequently listed fragrance allergens for all types, except for all-purpose cleaners. Benzyl salicylate was listed most often on these detergents. For dish-washing liquids (hand and machine) and toilet and glass cleaners, hexyl cinnamal was the fragrance allergen listed third. Butylphenyl methylpropional was listed third most often on textile detergents and citronellol on glass cleaners and scouring agents.

The average number of the 26 fragrance allergens per product was 1.4, the maximum number of fragrance allergens listed on a single product label being 8 substances (Table 2). The detergent group containing the highest share of products listing fragrance allergens were textile detergents and toilet cleaners. The average number of fragrance allergens per product is highest for textile detergents and all-purpose cleaners. Detergents listing the least fragrance allergens on average were detergents used in dishwashing machines.

Looking at the co-occurrence of fragrance allergens, hexyl cinnamal and butylphenyl methylpropional next to citronellol and linalool showed the most similar use patterns of all detergents (n = 817, Fig. 3). Hexyl cinnamal and butylphenyl methylpropional also often appear together with benzyl salicylate and benzyl alcohol. Citronellol and linalool often appear in combination with limonene and citral (see also supplementary material for a cross table).

3.2. Fragrance allergens in households

In 131 households, 1447 detergents were inventoried. The 26 selected fragrances were named 1925 times on their lists of ingredients (n = 1447 products). 46% of the 1447 products listed at least one of the 26 fragrance allergens on their ingredient lists, 60% listed 'perfume' or the like.

The co-occurrence of fragrance allergens in the households was analyzed. For this analysis, all fragrance allergens that were listed on the detergents scanned were summed up per household (see also supplementary material for a cross table). Fig. 4 shows that products listing eugenol, coumarin and cinnamyl alcohol often are present together in one household. Also, the co-occurrence within a household of the fragrances geraniol and citronellol or alpha-isomethyl ionone and benzyl salicylate was often seen.

4. Discussion

4.1. Listed fragrance allergens on detergents

The study shows the widespread use of fragrances and fragrance allergens in household detergents. Limonene and linalool were listed most often on the labels of detergents (Fig. 2). They belong to the established fragrance contact allergens of special concern in their oxidized form (Uter et al., 2013a). Hexyl cinnamal and butylphenyl methylpropional were also listed frequently. Both belong to the group of established fragrance contact allergens in humans, although they are associated with a low frequency of incidence of contact allergy. A high occurrence combined with lower sensitization rates may indicate a lower potential of sensitization associated with these substances (Schnuch et al., 2015). During the evaluation of the different product categories in more detail, it became clear that the occurrence to the 26 fragrance allergens varies over the different product categories (Fig. 2). Benzyl salicylate was listed on 28.2% of the all-purpose cleaners, while it was only listed on 7.0% of the dish-washing liquids within our study. Differences between the fragrance allergens listed on these two product categories have been reported previously (Magnano et al., 2009; Yazar et al., 2011), although for other substances.

Our ranking of frequency of the fragrance allergens in detergents is generally in good agreement with previous studies that had analyzed much smaller number of products (Buckley, 2007; Gerster et al., 2014; Magnano et al., 2009; Yazar et al., 2011). However, the average number of listed fragrances is lower in our study than in the study performed in the U.K. in 2006, where, on average, three fragrance allergens have been listed (Buckley, 2007). We also found considerably less dish-washing liquids and all-purpose cleaners listing one of the 26 fragrance allergens than Magnano et al. (2009). It has already been discussed by Tanaka et al. (2004) that if substances do not need to be declared, they might be used more frequently. It is possible that today producers apply less fragrance allergens that need to be declared and on occasion substitute them with other fragrance compounds with unknown allergy potential, which are summarized on the label in the term

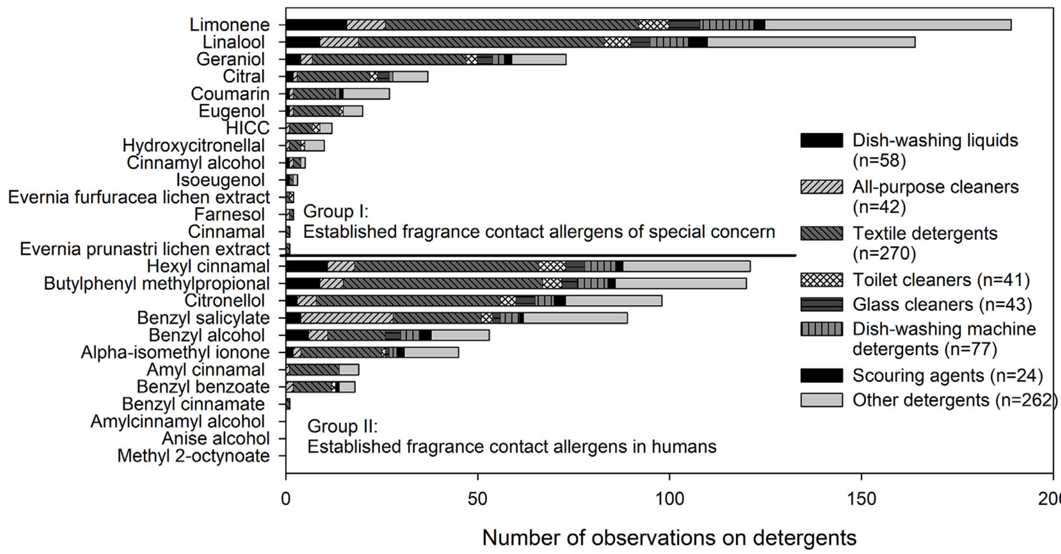

Fig. 2. The 26 fragrance allergens to be named on detergents in the EU and their appearance on lists of ingredients on detergents (n = 817). The substances are grouped by the categorization of established contact allergens in humans. Group I includes the established fragrance contact allergens of special concern due to the high number of reported cases, group II includes other established contact allergens in humans (Uter et al., 2013a). HICC: Hydroxyisohexyl 3-cyclohexene carboxaldehyde. Detailed data can be found in the supplementary material.

Table 2
The total number of unique products, the products containing fragrance allergens and the average number of fragrance allergens per product for the different detergent types (n = 817).

	Total number of unique products	Products containing fragrance allergens		Average number of fragrance allergens per product
	[n]	[n]	[%]	[n]
Dish-washing liquids	58	28	47.5	1.2
All-purpose cleaners	42	20	47.6	1.6
Textile detergents	270	135	50.0	1.7
Toilet cleaners	41	20	48.8	1.2
Glass cleaners	43	14	32.6	1.0
Dishwashing machine detergents	77	26	33.8	0.9
Scouring agents	24	8	33.3	1.0
Other detergents	262	114	43.7	1.2

'perfume'. This term was listed on 60% of the detergents. This corresponds to previously published results, where for example 73.5% of the liquid household cleaning products analyzed in Italy listed 'parfum' (Magnano et al., 2009).

4.2. Aggregate exposure to fragrance allergens

Our results demonstrate that detergents could contribute to the aggregated exposure to fragrance allergens. To enhance the risk assessment for the fragrance allergens, detergents (as a possible exposure source) need to be included in the existing exposure models as it has already been done recently by Nijkamp et al. (2015) and Ezendam et al. (2018).

4.3. Co-exposure to fragrance allergens

The exposure of consumers to combinations of two or more fragrance allergens (co-exposure) may enhance sensitization and has already been described for some fragrance allergens in cosmetics (Uter et al., 2013b). The results of our study highlight that detergents can also lead to co-exposure of consumers (Fig. 3). Several fragrance substances were listed simultaneously on one detergent within our study, as has already been reported for German detergents in 2001 (Luger, 2001). A Danish survey also found up to nine different fragrance allergens in detergents (Rastogi, 2002).

The two pairs of fragrance allergens showing the highest similarity of use in products in hierarchical cluster analysis were hexyl cinnamal and butylphenyl methylpropional next to citronellol and linalool (Fig. 3). This means that they more often occurred together in products than with other fragrance allergens. The combination of these fragrances is also frequent in cosmetic products (Uter et al., 2013b). Preferably, these pairs of fragrance allergens should be further investigated regarding potential enhancing effects on sensitization.

The co-occurrence of citral and geraniol, both leading to the exposure of consumers to geranial, has been discussed previously for cosmetics (Uter et al., 2013b). These two fragrance allergens also co-occurred in twelve detergents (n = 817).

However, the co-exposure of consumers to different fragrance allergens can not only happen due to their co-occurrence within one product but can also be due to the occurrence in different products that are used in the same household in parallel, e.g. during cleaning activities. The evaluation of the household data by hierarchical clustering shows that the composition of the fragrance allergen mixture across the entire range of products within a household is very different from the co-occurring fragrance allergens in one product. Over the entire range of detergents within one household, the highest similarity was calculated for the combination of eugenol, coumarin and cinnamyl alcohol (Fig. 4). Also, alpha-isomethylionone and benzyl alcohol were often used together in the same household, as well as geraniol and citronellol. These combinations of fragrance allergens should also be further investigated regarding potential enhancing effects on sensitization.

4.4. Limitations

Despite our extensive effort to get a realistic picture of fragrance allergens in household detergents, there are still limitations leading to a possible underestimation of the exposure to fragrance allergens. There are already known allergenic fragrances which so far are not required to be declared by law (Uter et al., 2013a). Further on, many natural extracts or oils have been identified to be established contact allergens,

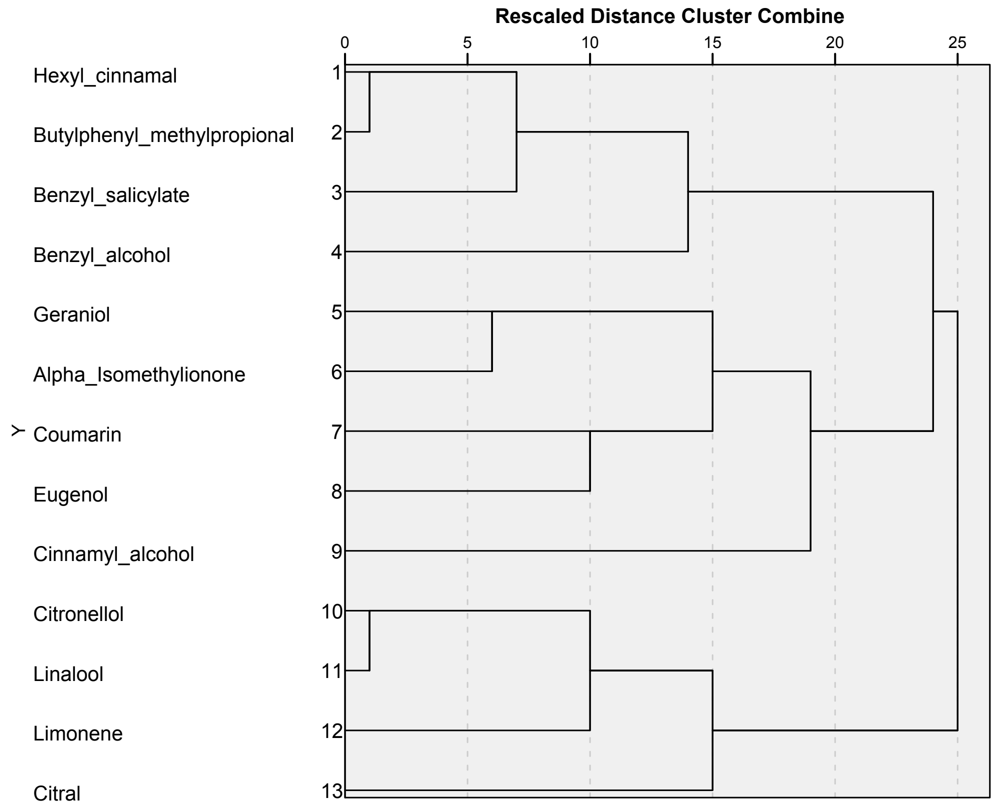

Fig. 3. Dendrogram (complete linkage, Dice measure) showing the co-occurrence of those fragrance allergens that were listed on more than 20 products (n = 817).

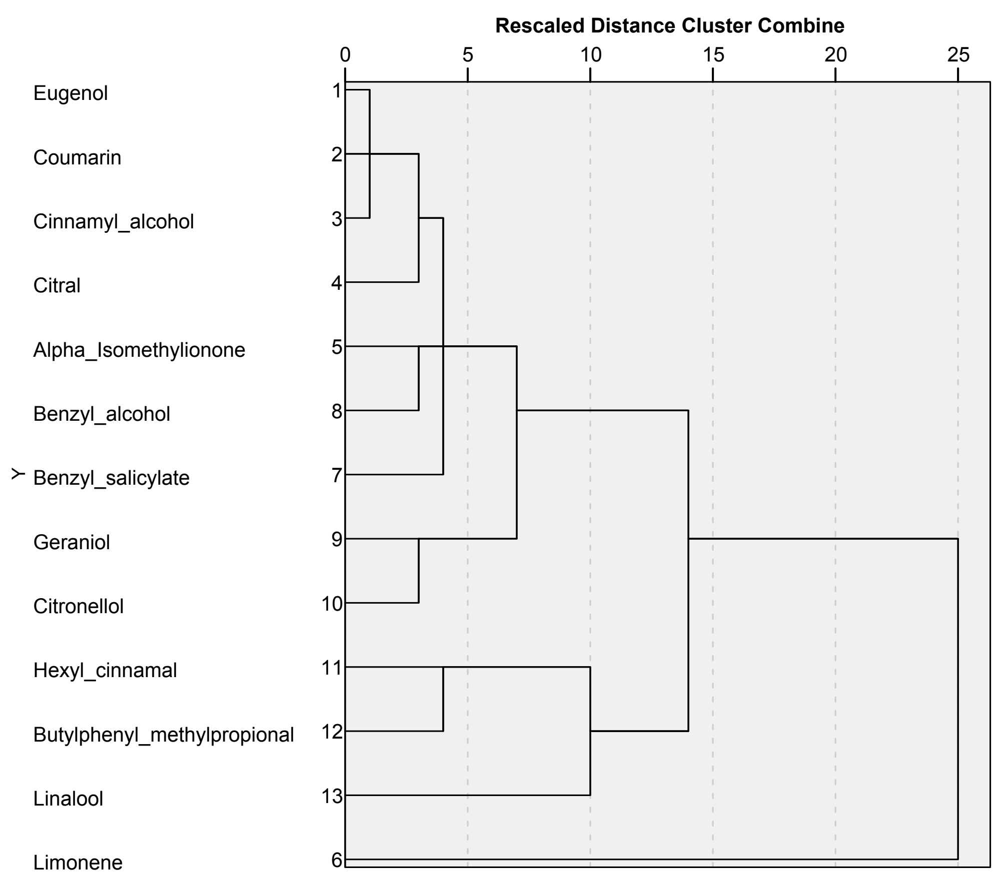

Fig. 4. Dendrogram (average linkage, Squared Euclidean Distance measure) showing the co-occurrence within households of those fragrance allergens that were listed on more than 20 products (n = 1447).

such as various *Citrus* preparations or *Lavandula hybrida* (SCCS, 2012). The allergenic components of these natural substances contribute to the aggregated as well as the combined exposure in addition to the 26 individual fragrance allergens listed on the containers (Klaschka, 2016). Those natural oils and extracts have also been listed on the inventoried detergents (data not presented here), demonstrating that our study probably underestimates the occurrence.

In addition, there are also methodological reasons, why our exposure estimation by exclusively using the ingredient lists has to be considered as an underestimate of occurrence. The 26 fragrance allergens are only listed if they are present above the thresholds for declaration (0.01%) and if they are used as fragrance ingredients, otherwise they do not need to be disclosed. Furthermore, it has been shown in the previous analyses of the data that it had a significant effect, whether the interviewees were bringing the products to the interviewers or whether the interviewer was allowed to walk around in the houses for scanning (Wieck et al., 2016). With the latter scenario, higher numbers of products were detected in a household. This leads to an additional possible underestimation of the number of detergents as not all household members allowed us to walk around.

The use of the public database was successful for identifying the products scanned in the households and their ingredients. For 95.7% of the barcodes, the names of the products could be retrieved, and for 89.6%, the ingredients were available (n = 817). These retrieval rates were slightly lower than in a previous study based on the same database, where not only detergents were analyzed but also some cosmetics and biocidal products (Wieck et al., 2016). As the database is maintained by public users, it is possible, that it contains wrong declarations. Regarding product names, a study on the database used showed that the correctness of product names was 98% (n = 13 702, Karpischek et al., 2014). Problems were encountered with spelling errors, as already described in the Methods section. These were solved by manual review and correction of the retrieved lists of ingredients.

The derivation of quantitative usage and exposure estimates was not possible, as amounts used per household member over time were not collected and the listing of the fragrance allergens on the labels only gives qualitative information on occurrence. The survey could not discriminate between products never or rarely used and products regularly used. We also did not collect any information whether consumers applied measures to reduce their personal exposure such as using gloves and whether the measures were effective. The households participating in the study are not necessarily representative for the general population. The voluntary participation of household members might lead to a bias towards participants who are more aware of fragrance allergens and suggests that the occurrence of fragrance allergens might be even higher for the general population than derived from the presented data. Regional differences in user behavior might reduce the transferability of our results to users in other regions.

5. Conclusions

The present study focuses on the analysis of the occurrence of fragrance allergens in a very large number of detergents found in households. This is the first study of this size and contributes to the discussion of consumers' exposure to the 26 fragrance allergens to be declared on the labels of detergents in the EU. The results indicate that detergents, next to cosmetics, should be included in exposure scenarios calculating the aggregate exposure. Furthermore, detergents can also contribute to the co-exposure of consumers, possibly leading to enhanced sensitization. The combinations of fragrance allergens that are relevant for co-exposure are not necessarily only the ones that co-occur in detergents or cosmetics but also those that are present in other types of products, such as do-it-yourself products, scented candles or air fresheners for houses and cars.

The results emphasize the ubiquitous exposure of consumers to fragrance allergens. It would be desirable to enable consumers to decide consciously whether they want to be exposed to these substances. The necessity to declare the names of potential allergens on the product, as requested by the Regulation (EC) 648/2004 on detergents for the European Union, is a tool for consumers wanting to avoid specific substances. However, other countries, for example the United States or Australia, do not have such legislation. Implementation of regulations similar to the European regulation on detergents could enable equally informed buying decisions of consumers in these countries. On the other hand, lists of ingredients on products can only inform consumers with detailed knowledge on potential sensitizers. Further strategies that also protect consumers without this detailed knowledge should be implemented to avoid new sensitizations and elicitations of skin effects.

Conflicts of interest

Stefanie Wieck is also working at the German Environment Agency. This paper does not necessarily reflect the opinion or the policies of the German Environment Agency.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.yrtph.2018.06.015.

Transparency document

Transparency document related to this article can be found online at http://dx.doi.org/10.1016/j.yrtph.2018.06.015.

References

Basketter, D., Safford, B., 2016. Skin sensitization quantitative risk assessment: a review of underlying assumptions. Regul. Toxicol. Pharmacol. 74, 105–116. http://dx.doi.org/10.1016/j.yrtph.2015.11.013.

Basketter, D.A., Lemoine, S., McFadden, J.P., 2015. Skin sensitisation to fragrance ingredients: is there a role for household cleaning/maintenance products? Eur. J. Dermatol. 25 (1), 7–13. http://dx.doi.org/10.1684/ejd.2014.2472.

Basketter, D.A., Pons-Guiraud, A., van Asten, A., Laverdet, C., Marty, J.-P., Martin, L., Berthod, D., Siest, S., Giordano-Labadie, F., Tennstedt, D., Baeck, M., Vigan, M., Laine, G., Le Coz, C.J., Jacobs, M.-C., Bayrou, O., Germaux, M.-A., 2010. Fragrance allergy: assessing the safety of washed fabrics. Contact Dermatitis 62 (6), 349–354. http://dx.doi.org/10.1111/j.1600-0536.2010.01728.x.

BBSR, 2009. Raumtypen 2010. http://www.bbsr.bund.de/BBSR/DE/Raumbeobachtung/Raumabgrenzungen/Raumtypen2010_vbg/Download_RefTypenLageSied.xls?__blob=publicationFile&v=2, Accessed date: 28 February 2017.

Belsito, D.V., Fransway, A.F., Fowler, J.F., Sherertz, E.F., Maibach, H.I., Mark, J.G., Mathias, C.G.T., Rietschel, R.L., Storrs, F.J., Nethercott, J.R., 2002. Allergic contact dermatitis to detergents: a multicenter study to assess prevalence. J. Am. Acad. Dermatol. 46 (2), 200–206.

Bennike, N.H., Oturai, N.B., Müller, S., Kirkeby, C.S., Jørgensen, C., Christensen, A.B., Zachariae, C., Johansen, J.D., 2018. Fragrance contact allergens in 5588 cosmetic products identified through a novel smartphone application. J. Eur. Acad. Dermatol. Venereol.: JEADV 32 (1), 79–85. http://dx.doi.org/10.1111/jdv.14513.

Bråred Christensson, J., Karlberg, A.-T., Andersen, K.E., Bruze, M., Johansen, J.D., Garcia-Bravo, B., Gimenez Arnau, A., Goh, C.-L., Nixon, R., White, I.R., 2016. Oxidized limonene and oxidized linalool - concomitant contact allergy to common fragrance terpenes. Contact Dermatitis 74 (5), 273–280. http://dx.doi.org/10.1111/cod.12545.

Buckley, D.A., 2007. Fragrance ingredient labelling in products on sale in the U.K. Br. J. Dermatol. 157 (2), 295–300. http://dx.doi.org/10.1111/j.1365-2133.2007.08018.x.

Buckley, D.A., Rycroft, R.J.G., White, I.R., McFadden, J.P., 2002. Fragrance as an occupational allergen. Occup. Med. 52 (1), 13–16.

Codecheck, 2018. Jahresrückblick 2017. https://corporate.codecheck.info/2017/12/21/jahresrueckblick-2017/, Accessed date: 26 April 2018.

Corea, N.V., Basketter, D.A., Clapp, C., van Asten, A., Marty, J.-P., Pons-Guiraud, A., Laverdet, C., 2006. Fragrance allergy: assessing the risk from washed fabrics. Contact Dermatitis 55 (1), 48–53. http://dx.doi.org/10.1111/j.0105-1873.2006.00872.x.

Groot, Anton C. De, Maibach, Howard I., 2010. Frequency of sensitization to common allergens: comparison between Europe and the USA. Contact Dermatitis 62 (6), 325–329. http://dx.doi.org/10.1111/j.1600-0536.2009.01666.x.

Diepgen, T.L., Ofenloch, R.F., Bruze, M., Bertuccio, P., Cazzaniga, S., Coenraads, P.-J., Elsner, P., Goncalo, M., Svensson, A., Naldi, L., 2016. Prevalence of contact allergy in the general population in different European regions. Br. J. Dermatol. 174 (2), 319–329. http://dx.doi.org/10.1111/bjd.14167.

Dodson, R.E., Nishioka, M., Standley, L.J., Perovich, L.J., Brody, J.G., Rudel, R.A., 2012. Endocrine disruptors and asthma-associated chemicals in consumer products. Environ. Health Perspect. 120 (7), 935–943. http://dx.doi.org/10.1289/ehp.1104052.

Effendy, I., Maibach, H.I., 1995. Surfactants and experimental irritant contact dermatitis. Contact Dermatitis 33 (4), 217–225.

European Union, 2004. Regulation (EC) No 648/2004 of the European Parliament and of the Council of 31 March 2004 on Detergents.

European Union, 2009. Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on Cosmetic Products.

Ezendam, J., Bokkers, B.G.H., Bil, W., Delmaar, J.E., 2018. Skin sensitisation quantitative risk assessment (QRA) based on aggregate dermal exposure to methylisothiazolinone in personal care and household cleaning products. Food Chem. Toxicol. 112, 242–250. http://dx.doi.org/10.1016/j.fct.2017.12.054.

Gallo, R., Signori, A., Gervasio, S., Riva, S., Parodi, A., 2016. Methylisothiazolinone contact allergy - are rinse-off cosmetics and household products relevant sources of exposure? Contact Dermatitis 75 (5), 319–321. http://dx.doi.org/10.1111/cod.12595.

Garcia-Hidalgo, E., Sottas, V., Goetz, N., von, Hauri, U., Bogdal, C., Hungerbühler, K., 2017. Occurrence and concentrations of isothiazolinones in detergents and cosmetics in Switzerland. Contact Dermatitis 76 (2), 96–106. http://dx.doi.org/10.1111/cod.12700.

Geier, J., Lessmann, H., Schnuch, A., Uter, W., 2012. Recent increase in allergic reactions to methylchloroisothiazolinone/methylisothiazolinone: is methylisothiazolinone the culprit? Contact Dermatitis 67 (6), 334–341. http://dx.doi.org/10.1111/j.1600-0536.2012.02157.x.

German Cosmetic, Toiletry, Perfumery and Detergent Association, 2016. Jahresbericht 2015/2016. http://www.ikw.org/fileadmin/content/downloads/IKW-Allgemein/IKW_Jahresbericht_2015_2016.pdf, Accessed date: 9 February 2017.

Gerster, F.M., Vernez, D., Wild, P.P., Hopf, N.B., 2014. Hazardous substances in frequently used professional cleaning products. Int. J. Occup. Environ. Health 20 (1), 46–60. http://dx.doi.org/10.1179/2049396713Y.0000000052.

Heydorn, S., Andersen, K.E., Johansen, J.D., Menne, T., 2003. A stronger patch test elicitation reaction to the allergen hydroxycitronellal plus the irritant sodium lauryl sulfate. Contact Dermatitis 49 (3), 133–139.

IDEA, 2016. Skin Sensitisation Quantitative Risk Assessment for Fragrance Ingredients. http://www.ideaproject.info/uploads/Modules/Documents/qra2-dossier-final–september-2016.pdf, Accessed date: 9 February 2017.

IFRA, 2015. Overview of the IFRA Standards. http://www.ifraorg.org/Upload/DownloadButtonDocuments/5b52e4ad-268a-4394-91f5-51c648941369/Overview%20of%20the%20IFRA%20Standards%20-%2048th%20Amendment.xls, Accessed date: 7 September 2017.

Jacob, S.E., Amini, S., 2008. Cocamidopropyl betaine. Dermatitis 19 (3), 157–160.

Karpischek, S., Michahelles, F., Fleisch, E., 2014. Detecting incorrect product names in online sources for product master data. Electron. Market. 24 (2), 151–160. http://dx.doi.org/10.1007/s12525-013-0136-4.

Klaschka, U., 2016. Natural personal care products—analysis of ingredient lists and legal situation. Environ. Sci. Eur. 28 (1). http://dx.doi.org/10.1186/s12302-016-0076-7. 477.

Luger, A., 2001. Duftstoffe in Wasch- und Reinigungsmitteln, Bericht über die Messung des Einsatzes von Duftstoffen in diversen Wasch- und Reinigungsmittel, Hannover. http://www.laves.niedersachsen.de/download/40953/Bericht_ueber_Messungen_des_Einsatzes_von_Duftstoffen_in_Wasch-_und_Reinigungsmitteln.pdf, Accessed date: 20 March 2017.

Lunny, S., Nelson, R., Steinemann, A., 2017. Something in the air but not on the label: a call for increased regulatory ingredient disclosure for fragranced consumer products. UNSW Law Journal 40 (4), 1366–1391.

Magnano, M., Silvani, S., Vincenzi, C., Nino, M., Tosti, A., 2009. Contact allergens and irritants in household washing and cleaning products. Contact Dermatitis 61 (6), 337–341. http://dx.doi.org/10.1111/j.1600-0536.2009.01647.x.

Nijkamp, M.M., Bokkers, B.G.H., Bakker, M.I., Ezendam, J., Delmaar, J.E., 2015. Quantitative risk assessment of the aggregate dermal exposure to the sensitizing fragrance geraniol in personal care products and household cleaning agents. Regul. Toxicol. Pharmacol. 73 (1), 9–18. http://dx.doi.org/10.1016/j.yrtph.2015.06.004.

Niu, X., Ho, S.S.H., Ho, K.F., Huang, Y., Cao, J., Shen, Z., Sun, J., Wang, X., Wang, Y., Lee, S., Huang, R., 2017. Indoor secondary organic aerosols formation from ozonolysis of monoterpene: an example of d-limonene with ammonia and potential impacts on pulmonary inflammations. Sci. Total Environ. 579, 212–220. http://dx.doi.org/10.1016/j.scitotenv.2016.11.018.

Park, M., Janssen, P., van Raaij, M., 2006. Risk Assessment for Scented Products: a Prestudy RIVM Report 320105002. . http://www.rivm.nl/bibliotheek/rapporten/320105002.html, Accessed date: 9 February 2017.

Peiser, M., Tralau, T., Heidler, J., Api, A.M., Arts, J.H.E., Basketter, D.A., English, J., Diepgen, T.L., Fuhlbrigge, R.C., Gaspari, A.A., Johansen, J.D., Karlberg, A.T., Kimber, I., Lepoittevin, J.P., Liebsch, M., Maibach, H.I., Martin, S.F., Merk, H.F., Platzek, T., Rustemeyer, T., Schnuch, A., Vandebriel, R.J., White, I.R., Luch, A., 2012. Allergic contact dermatitis: epidemiology, molecular mechanisms, in vitro methods and regulatory aspects. Current knowledge assembled at an international workshop at BfR, Germany. Cell. Mol. Life Sci.: CM 69 (5), 763–781. http://dx.doi.org/10.1007/s00018-011-0846-8.

Rastogi, S.C., 2002. Contents of Selected Fragrance Materials in Cleaning Products and Other Consumer Products. National Environmental Research Institute. http://eng.mst.dk/media/mst/69131/8.pdf, Accessed date: 16 December 2017.

Rastogi, S.C., Heydorn, S., Johansen, J.D., Basketter, D.A., 2001. Fragrance chemicals in domestic and occupational products. Contact Dermatitis 45 (4), 221–225.

Robinson, O.C., 2014. Sampling in interview-based qualitative research: a theoretical and practical guide. Qual. Res. Psychol. 11 (1), 25–41. http://dx.doi.org/10.1080/14780887.2013.801543.

Rossignol, S., Rio, C., Ustache, A., Fable, S., Nicolle, J., Même, A., D'Anna, B., Nicolas, M., Leoz, E., Chiappini, L., 2013. The use of a housecleaning product in an indoor environment leading to oxygenated polar compounds and SOA formation: gas and particulate phase chemical characterization. Atmos. Environ. 75, 196–205. http://dx.doi.org/10.1016/j.atmosenv.2013.03.045.

Safford, B., Api, A.M., Barratt, C., Comiskey, D., Ellis, G., McNamara, C., O'Mahony, C., Robison, S., Rose, J., Smith, B., Tozer, S., 2017. Application of the expanded Creme RIFM consumer exposure model to fragrance ingredients in cosmetic, personal care and air care products. Regul. Toxicol. Pharmacol. 86, 148–156. http://dx.doi.org/10.1016/j.yrtph.2017.02.021.

SCCNFP, 2000. Opinion Concerning the First Update of the Inventory of Ingredients Employed in Cosmetic Products - Section II: Perfume and Aromatic Raw Materials. http://ec.europa.eu/health/archive/ph_risk/committees/sccp/documents/out131_en.pdf, Accessed date: 20 March 2017.

SCCS, 2012. Opinion on Fragrance Allergens in Cosmetic Products. Scientific Committee on Consumer Safety. http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_073.pdf, Accessed date: 20 March 2017.

Schnuch, A., Mahler, V., 2015. Volkskrankheit kontaktallergie. Der Hautarzt; Zeitschrift fur Dermatologie, Venerologie, und verwandte Gebiete 66 (9), 644–645. http://dx.doi.org/10.1007/s00105-015-3669-y.

Schnuch, A., Uter, W., Geier, J., Lessmann, H., Frosch, P.J., 2007. Sensitization to 26 fragrances to be labelled according to current European regulation. Results of the IVDK and review of the literature. Contact Dermatitis 57 (1), 1–10. http://dx.doi.org/10.1111/j.1600-0536.2007.01088.x.

Schnuch, A., Uter, W., Lessmann, H., Geier, J., 2015. Risk of sensitization to fragrances estimated on the basis of patch test data and exposure, according to volume used and a sample of 5451 cosmetic products. Flavour Fragrance J. 30 (3), 208–217. http://dx.doi.org/10.1002/ffj.3241.

State of California, 2017. Cleaning Product Right to Know Act of 2017 (SB-258).

Tanaka, S., Royds, C., Buckley, D., Basketter, D.A., Goossens, A., Bruze, M., Svedman, C., Menne, T., Johansen, J.D., White, I.R., McFadden, J.P., 2004. Contact allergy to isoeugenol and its derivatives: problems with allergen substitution. Contact Dermatitis 51 (5–6), 288–291. http://dx.doi.org/10.1111/j.0105-1873.2004.00446.x.

Uter, W., Johansen, J.D., Börje, A., Karlberg, A.-T., Lidén, C., Rastogi, S., Roberts, D., White, I.R., 2013a. Categorization of fragrance contact allergens for prioritization of preventive measures: clinical and experimental data and consideration of structure-activity relationships. Contact Dermatitis 69 (4), 196–230. http://dx.doi.org/10.1111/cod.12117.

Uter, W., Schnuch, A., Geier, J., Pfahlberg, A., Gefeller, O., 2001. Association between occupation and contact allergy to the fragrance mix: a multifactorial analysis of national surveillance data. Occup. Environ. Med. 58 (6), 392–398.

Uter, W., Yazar, K., Kratz, E.-M., Mildau, G., Liden, C., 2013b. Coupled exposure to ingredients of cosmetic products: I. Fragrances. Contact Dermatitis 69 (6), 335–341. http://dx.doi.org/10.1111/cod.12125.

Wieck, S., Olsson, O., Kümmerer, K., 2016. Possible underestimations of risks for the environment due to unregulated emissions of biocides from households to wastewater. Environ. Int. 94, 695–705. http://dx.doi.org/10.1016/j.envint.2016.07.007.

Yazar, K., Johnsson, S., Lind, M.-L., Boman, A., Liden, C., 2011. Preservatives and fragrances in selected consumer-available cosmetics and detergents. Contact Dermatitis 64 (5), 265–272. http://dx.doi.org/10.1111/j.1600-0536.2010.01828.x.

Supplementary information to:

Fragrance allergens in household detergents

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1. Overview over fragrance allergens in detergent types

This table shows the listings of fragrance allergens in the scanned detergents and is based on unique products (n=817). If one product was scanned in several households, it was only included once in the table.

		Dish-washing liquids	All-purpose cleaners	Textile detergents	Toilet cleaners	Glass cleaners	Dishwashing machine products	Scouring agents	Other detergents
Alpha-isomethyl ionone	127-51-5	2	2	21	1	1	2	2	12
Amyl cinnamal	122-40-7	0	1	13	0	0	0	0	5
Benzyl alcohol	100-51-6	6	5	15	0	4	5	3	12
Benzyl benzoate	120-51-4	0	2	10	1	0	0	1	3
Benzyl cinnamate	103-41-3	0	0	1	0	0	0	0	0
Benzyl salicylate	118-58-1	4	24	23	3	2	5	1	24
Butylphenyl methylpropional	80-54-6	9	6	52	5	4	8	2	29
Cinnamal	104-55-2	0	0	1	0	0	0	0	0
Cinnamyl alcohol	104-54-1	1	1	2	0	0	0	0	1
Citral	5392-40-5	2	1	19	2	3	1	0	8
Citronellol	106-22-9	3	5	48	4	5	5	3	20
Coumarin	91-64-5	1	1	11	0	0	1	1	10
Eugenol	97-53-0	1	1	12	1	0	0	0	5
***Evernia furfuracea lichen* extract**	90028-67-4	0	0	1	1	0	0	0	0
***Evernia prunastri lichen* extract**	90028-68-5	0	0	1	0	0	0	0	0
Farnesol	4602-84-0	0	1	1	0	0	0	0	0
Geraniol	106-24-1	4	3	40	3	4	3	2	11
Hexyl cinnamal	101-86-0	11	7	48	7	5	8	2	29
HICC	31906-04-4	0	1	6	2	0	0	0	3
Hydroxycitronellal	107-75-5	0	1	3	1	0	0	0	5
Isoeugenol	97-54-1	1	0	1	0	0	0	0	1
Limonene	138-86-3	16	10	66	8	8	14	3	57
Linalool	78-70-6	9	10	64	7	5	10	5	44

2. Cross table of fragrance allergens in detergents (n=817)

	Amyl cinnamal	Benzyl alcohol	Benzyl benzoate	Benzyl cinnamate	Benzyl salicylate	Butylphenyl methylpropional	Cinnamal	Cinnamyl alcohol	Citral	Citronellol	Coumarin	Eugenol	*Evernia furfuracea lichen* extract	*Evernia prunastri lichen* extract	Farnesol	Geraniol	Hexyl cinnamal	Hydroxycitronellal	HICC	Isoeugenol	Limonene	Linalool
Alpha-Isomethyl ionone	6	14	11	1	19	27	0	4	2	31	12	10	2	1	0	29	23	5	4	1	23	38
Amyl cinnamal		5	4	1	2	13	0	1	0	9	3	3	0	1	1	8	6	3	1	1	9	8
Benzyl alcohol			4	0	16	25	1	3	2	21	9	6	0	0	1	14	24	3	1	0	26	33
Benzyl benzoate				1	4	6	0	3	3	13	8	6	2	1	1	13	6	5	4	1	12	16
Benzyl cinnamate					0	1	0	0	0	1	0	1	0	0	0	1	0	0	0	1	1	1
Benzyl salicylate						42	1	3	4	29	11	9	0	0	0	14	42	4	6	1	30	50
Butylphenyl methylpropional							1	4	4	50	14	8	2	0	1	42	75	2	8	2	49	68
Cinnamal								0	0	1	0	0	0	0	0	0	0	0	0	0	1	1
Cinnamyl alcohol									0	6	4	2	0	0	1	6	3	3	0	0	3	6
Citral										18	5	3	0	0	1	12	9	1	0	1	38	26
Citronellol											16	14	2	1	2	52	43	8	6	3	56	79
Coumarin												9	0	1	1	14	9	4	2	0	18	23
Eugenol													0	0	1	12	8	3	2	2	16	17
***Evernia furfuracea lichen* extract**														0	0	2	2	0	2	0	0	2
***Evernia prunastri lichen* extract**															0	1	0	1	0	0	1	1
Farnesol																2	0	1	0	0	1	2
Geraniol																	29	6	3	2	43	55
Hexyl cinnamal																		3	7	1	45	64
Hydroxycitronellal																			2	1	8	9
HICC																				0	6	10
Isoeugenol																					2	3
Limonene																						101

3. Cross table of fragrance allergens listed on detergents scanned in households (n=131)

	Amyl cinnamal	Benzyl alcohol	Benzyl benzoate	Benzyl cinnamate	Benzyl salicylate	Butylphenyl methylpropional	Cinnamal	Cinnamyl alcohol	Citral	Citronellol	Coumarin	Eugenol	*Evernia furfuracea lichen* extract	*Evernia prunastri lichen* extract	Farnesol	Geraniol	Hexyl cinnamal	Hydroxycitronellal	HICC	Isoeugenol	Limonene	Linalool
Alpha-Isomethyl ionone	9	22	9	1	27	30	0	4	14	27	13	10	2	1	0	25	30	7	5	2	28	32
Amyl cinnamal		9	4	1	11	13	0	1	7	10	7	6	0	1	2	8	14	4	1	1	14	14
Benzyl alcohol			8	1	27	32	1	4	14	34	13	9	1	1	1	24	33	7	5	2	33	36
Benzyl benzoate				1	9	11	0	3	7	12	9	8	2	1	1	12	14	5	5	1	12	14
Benzyl cinnamate					1	1	0	0	1	1	1	1	0	1	0	1	1	1	0	1	1	1
Benzyl salicylate						44	1	5	16	34	19	12	0	1	1	29	46	9	8	2	45	46
Butylphenyl methylpropional							1	5	26	47	19	14	2	1	2	45	61	8	8	2	60	57
Cinnamal								0	0	1	1	0	0	0	0	0	1	0	1	0	1	1
Cinnamyl alcohol									3	6	5	3	0	0	1	6	6	3	1	0	5	6
Citral										31	13	10	0	1	2	28	29	4	3	3	39	33
Citronellol											20	13	2	1	2	43	52	9	8	3	55	58
Coumarin												11	0	1	1	15	22	5	5	2	22	22
Eugenol													0	1	1	12	14	6	3	2	17	15
***Evernia furfuracea lichen* extract**														0	0	2	2	0	2	0	1	2
***Evernia prunastri lichen* extract**															0	1	1	1	0	1	1	1
Farnesol																2	2	1	0	0	2	2
Geraniol																	42	8	6	3	46	49
Hexyl cinnamal																		9	10	2	63	63
Hydroxycitronellal																			3	2	10	10
HICC																				0	9	11
Isoeugenol																					3	3
Limonene																						70