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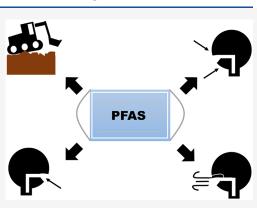
Letter

Per- and Polyfluoroalkyl Substances (PFAS) in Facemasks: Potential Source of Human Exposure to PFAS with Implications for Disposal to Landfills

Derek J. Muensterman, $^{\nabla}$ Liliana Cahuas, $^{\nabla}$ Ivan A. Titaley,^{*, ∇} Christopher Schmokel, Florentino B. De la Cruz, Morton A. Barlaz, Courtney C. Carignan, Graham F. Peaslee, and Jennifer A. Field



including Covid-19 and its variants, and some may be treated with per- and polyfluoroalkyl substances (PFAS). Nine facemasks over a range of prices were analyzed for total fluorine and PFAS. The PFAS compositions of the masks were then used to estimate exposure and the mass of PFAS discharged to landfill leachate. Fluorine from PFAS accounted only for a small fraction of total fluorine. Homologous series of linear perfluoroalkyl carboxylates and the 6:2 fluorotelomer alcohol indicated a fluorotelomer origin. Inhalation was estimated to be the dominant exposure route (40%-50%), followed by incidental ingestion (15%-40%) and dermal (11%-20%). Exposure and risk estimates were higher for children than adults, and high physical activity substantially increased inhalation exposure. These preliminary findings indicate that wearing masks treated with high levels of PFAS for extended periods of time can be a notable source of exposure and have the potential to pose a health risk. Despite modeled annual



disposal of ~29–91 billion masks, and an assuming 100% leaching of individual PFAS into landfill leachate, mask disposal would contribute only an additional 6% of annual PFAS mass loads and less than 11 kg of PFAS discharged to U.S. wastewater.

KEYWORDS: PFAS, facemasks, Covid-19, total fluorine, LC-qTOF, GC-MS, exposure, landfill

INTRODUCTION

Facemasks are important tools to combat the spread of Sars-CoV-2 and its variants and as protection during wildfires.^{1,2} Types of facemasks range from homemade to medical grade masks.^{3,4} Characterizations of facemasks reveal the presence of chemicals including hydrocarbons,^{5,6} phthalates,^{7,8} organo-phosphate ester compounds,^{9,10} amides, paraffins, olefins, polyethylene terephthalate oligomers,⁶ and microplastics.¹¹

Facemasks are designed to not only prevent inhalation of particles or pathogens but also to repel fluids (e.g., bodily).⁴ The repellency factor indicates the potential presence of perand polyfluoroalkyl substances (PFAS), which are known components of specialty, water-repellant fabrics, such as firefighter turnout gear, jackets,^{12–14} and surgical gowns.¹⁵ While there are numerous reports of PFAS in consumer products,^{16–19} except for a news story on unnamed PFAS and a cross-linker used in textile treated with PFAS in facemasks,²⁰ there is no published information on the presence of PFAS in facemasks. Facemasks treated with PFAS have the potential to act as sources of human exposure to PFAS from dermal absorption, inhalation of gas-phase PFAS, and ingestion of particulate-phase PFAS. While estimates showed low daily intakes and inhalation risk of organophosphate ester and phthalates due to wearing facemasks,^{7,9,10} there is no exposure assessment for PFAS in facemasks yet to our knowledge.

Facemasks, particularly single-use surgical masks, are ultimately disposed to landfills or combusted in incineration facilities. Estimates of mask disposal presented below are based on consumer use, although an unknown fraction of these masks is used in hospitals and are burned in dedicated medicalwaste incinerators. The U.S. EPA estimates that about 50% of all municipal solid waste (MSW) is landfilled and about 12% is combusted, with the balance treated biologically or recycled.²¹ While the overall MSW recycling rate is 24%, we are not aware of any recycling of single-use facemasks.²¹ The presence of PFAS in landfill leachate is well documented and results from PFAS release as water infiltrates through PFAS-treated

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Type of facemask ^{b}	Price per unit ^c	Total fluorine $(nmol F/cm^2)^d$	Nonvolatile PFAS (nmol F/cm ²)	Volatile PFAS (nmol F/cm ²) ^e
SUD	\$	<lod< td=""><td>0.0016 ± 0.00043</td><td><lod< td=""></lod<></td></lod<>	0.0016 ± 0.00043	<lod< td=""></lod<>
N95	\$	<lod< td=""><td>0.00054</td><td><lod< td=""></lod<></td></lod<>	0.00054	<lod< td=""></lod<>
RC-1	\$	<lod< td=""><td>0.0048^f</td><td><lod< td=""></lod<></td></lod<>	0.0048 ^f	<lod< td=""></lod<>
RC-2	\$\$\$	7100 ^h	0.0050 ^f	0.079 ^h
RC-3	\$	<lod< td=""><td>0.0055</td><td><lod< td=""></lod<></td></lod<>	0.0055	<lod< td=""></lod<>
RC-4	\$	7600 ^h	0.010 ^f	0.85 ^g
RC-5	\$\$	17,000 ^f	0.0063 ^f	1.2^{f}
RC-6	\$\$	$40,000 \pm 18,000$	0.024 ± 0.0041	0.90 ± 0.057

Table 1. Facemasks by Type, Price per Unit, Total Fluorine, and Summed Concentrations of Nonvolatile and Volatile PFAS^a

^aSamples SUD and RC-6 were analyzed in triplicates, and the data are provided as average \pm standard error. ^bSUD = surgical single-use disposable; N95 = N95; RC = reusable cloth facemasks; FF = facemask advertised to firefighters. ^cPrice per unit (US dollars): \$ = <1-14; \$\$ = 14-28; \$\$\$ = 28-42; \$\$\$\$ = 42-56, as of Dec 2021. ^dLOD = limit of detection (6.8 nmol F/cm²); LOQ = limit of quantification (20 nmol F/cm²). ^eLOD = 0.00027-0.047 nmol F/cm². ^fTotal fluorine or PFAS was measured in all three layers. ^gTotal fluorine or PFAS was measured in two of three layers.

640⁴

consumer products disposed in landfills.^{16–19,22} On the basis of a recent survey, \sim 1.1 billion facemask wastes were generated per week in the U.S.²³ However, the mass of PFAS released to landfill leachate as a result of facemask disposal has yet to be characterized.

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The objective of this study was to characterize PFAS associated with different types of facemasks. Nine masks were collected and characterized for their total fluorine using particle-induced gamma emission (PIGE)^{16,24} and for non-volatile and volatile PFAS by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF) and gas chromatography MS (GC-MS), respectively. On the basis of the PFAS analysis, exposure and environmental implications are discussed. It is important to emphasize that this study does not discourage the public from wearing facemasks, particularly during an active pandemic. Rather, the study results are intended to aid the public in making informed decisions regarding the types of facemasks to wear and to encourage manufacturers to consider the chemicals that are incorporated into facemasks.

MATERIALS AND METHODS

Materials. Water and solvents for analyses are listed in the Supporting Information (SI). Target chemicals and surrogate standards are provided in Tables S1–S3.

Samples. Nine facemasks were collected and manually separated into their respective layers, if composed of multiple layers. The material composition was based on information provided on the website of the facemasks (see SI). Packaging for two samples, RC-4 and RC-5, indicated *stain resistant chemical*. There were four types of facemasks: a surgical, single-use disposable mask (SUD); an N95 mask (N95); six reusable cloth masks (RC-1 to RC-6); and a specialty mask advertised to firefighters (FF) (Table 1). No homemade cloth facemasks were collected.

Total Fluorine Analysis. Samples were analyzed for total fluorine using PIGE,¹² with fluorine signal normalized to Ar.²⁵ See SI for details on PIGE analysis, including the conversion to nmol F/cm^2 and method limit of detection (LOD) and limit of quantitation (LOQ).

PFAS Analysis. Extraction and analysis of PFAS were performed using the method described in Muensterman et al.¹⁴ with further details given in the SI. Briefly, facemasks were cut into pieces using methanol-rinsed scissors. Nonvolatile PFAS were determined by spiking the textiles with 31 mass-labeled

surrogate standards and extracting with methanol. Nonvolatile PFAS extracts were spiked with two mass-labeled internal standards and analyzed for 50 target and 4886 suspect nonvolatile PFAS by LC-qTOF. For volatile PFAS, methanol was added to samples and spiked with 10 surrogate standards, followed by sonication at ambient temperature. Extracts were cleaned using solid phase extraction, spiked with a mass-labeled internal standard, and analyzed for 15 target and 24 suspect volatile PFAS by GC-MS. Whole method LOD and LOQ were determined using a previous method,²⁶ while accounting for potential false positives arising from addition of volatile PFAS surrogate standards.²⁷ See SI and Tables S4–S7 for additional details on extraction methods, analyses, method performance, LODs, and LOQs.

PFAS Exposure Estimation. Exposure estimates for children (2 years old) and adults (women and men, 18 years old) were based on the total PFAS concentration for each mask type, assuming 10 h of wear time per day, via inhalation, dermal contact, and incidental ingestion routes. The 10-h exposure duration was selected based on time spent at daycare (children), work (adults), and in public where facemask wearing may be mandated or chosen. Exposure modeling for the inhalation and incidental ingestion exposure routes was preformed using ConsExpo,²⁸ an online tool developed by the Danish National Institute for Public Health and the Environment. Model inputs are provided in Table S8. Modeling was performed on SUD, RC-6, and FF as representative facemasks. Because the FF mask had three layers and PFAS can potentially migrate through fabric, the maximum value for each PFAS across the layers was applied, and the PFAS concentrations were summed. The reference dose was selected a priori for 6:2 fluorotelomer alcohol (FTOH) from the Danish Ministry of the Environment, which identified a no observed adverse effect level of 5000 μ g/kg-bw/day for male rats.²⁹ A reference dose of 5 μ g/kg-day was derived by applying a safety factor of 1000 to account for the conversion from animals to humans, human variation in sensitivity, and conversion from subchronic to chronic exposure.³⁰ The reference dose was chosen for a single PFAS (6:2 FTOH) to reduce complexity for this preliminary assessment because it was detected at the highest concentration in the facemasks.

Estimate of PFAS Mass Release to Leachates. The methanol-extractable PFAS content of the various masks was used to estimate a range of potential PFAS release to landfill leachate. Two cases were evaluated, a "likely case" and an

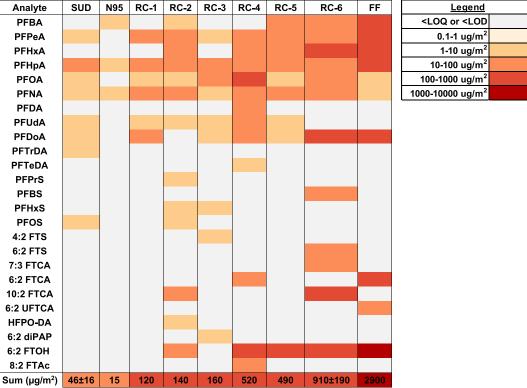


Figure 1. Heat map of nonvolatile and volatile PFAS ($\mu g/m^2$) in facemasks. (Only PFAS with at least one greater than LOQ concentration was included.) Layer concentration summed for samples with multiple layers (RC-1, RC-2, RC-4, RC-5, and FF). Average concentrations ± standard error for n = 3 replicates of SUD and RC-6. A similar heat map in units of ng/g is provided in the Figure S1.

"extreme case" (Table S9). In the "likely case", 60% of the U.S. population was assumed to wear facemasks. Also, the mask disposal rate is 3.6 facemasks per week,²³ and 1% of the methanol-extractable PFAS is released to leachate. The corresponding values for the "extreme case" are 100% facemask use, seven facemasks disposed per week, and 100% of the methanol-extractable PFAS released to leachate. In both cases, children under five, comprising 6% of the U.S. population,³ are assumed to not wear facemasks. Given the absence of recycling, 81% of facemasks are estimated to be disposed in landfills. The annual leachate volume was estimated to be 61.5 million m³.¹⁸

RESULTS AND DISCUSSION

Total Fluorine. Total fluorine was quantifiable in five of nine facemasks and ranged from less than LOD to 40,000 nmol F/cm^2 (Table 1). In facemasks with multiple layers (RC-2, RC-4, RC-5, and FF), total fluorine was the highest in the outer layer (Table S10). The least expensive facemasks (SUD and N95) were less than LOD (Table 1 and Table S10). The most expensive facemask (FF) gave the lowest total fluorine among facemasks with quantifiable levels of total fluorine. Total fluorine in this study was among the highest measured in consumer products including textiles, papers, cosmetics, and food packaging.^{16,32-37} No correlation was observed between the price of facemasks and total fluorine, total fluorine and PFAS, or the price of facemasks and PFAS. The contribution of PFAS to total fluorine was insignificant (Table 1) and consistent with other measurements for textiles.^{14,32} The gap in fluorine between total fluorine and PFAS from facemask to facemask is likely due to the presence of fluoropolymers, such as side-chain fluoropolymers,³⁸ in some of these facemasks.

PFAS in Facemasks. Nonvolatile PFAS were found in all facemasks, and volatile PFAS were found in five facemasks. Summed PFAS concentrations ranged from 15 to 2900 μ g/m² (Figure 1). The SUD and N95 masks gave the lowest measured total PFAS, with FF the highest total PFAS (Figure 1), yet the total fluorine of FF was the lowest among the facemasks (Table 1). The frequency of detection among the RC masks were similar (Figure 1). Detailed PFAS data per layer are provided in the Tables S11 and S12.

Of the nonvolatile PFAS, perfluoroalkyl carboxylates (PFCAs) gave the highest detection frequency, followed by fluorotelomer-based PFAS, and perfluoroalkyl sulfonates (PFSAs) (Figure 1, Figure S2, Table S11). The highest summed PFCAs on facemasks were generally similar or greater than those reported for other various textiles and car seats^{14,32,39–45} but lower than that of outdoor clothes and treated textiles,^{45,46} while PFSAs were less than those that included older (1988) textiles^{32,44} or were in the same range as $\frac{3240}{10}$ and $\frac{3240}{10}$ an that of outdoor clothing, furniture textiles, and jackets.^{39,40} The C5 and C6 PFCAs (e.g., PFHxA, PFHpA, respectively) were detected at the highest concentration, with the exception of C11 in RC-6 (PFDoA = 140 μ g/m², Table S11). Members of the PFCAs appeared as homologous series, and only the linear isomers were detected (Table S11), indicating a fluorotelomer origin. In RC-6, the concentration of 10:2 FTCA (110 μ g/m²) was at comparable levels with PFHxA and PFDoA. Members of the PFSAs were infrequently detected and not as a homologous series (Table S11, Figure S2). Nonvolatile PFAS suspect screening revealed tentative identification of only three PFAS (Table S13).

Of the volatile PFAS, 6:2 FTOH was found on nine layers associated with five facemasks, while 8:2 FTAc was found in

Table 2. Estimated Exposure (μ g/kg-day) Wearing a Facemask for 10 h/day^a

		Inhalation				
Population	Mask sample	Moderate activity	High activity	Incidental ingestion	Dermal	Total exposure ^b
			Median Exposure E	stimates		
Child ^c	SUD	0.10 (0.02)	0.24 (0.05)	0.10 (0.02)	0.04 (0.01)	0.23 (0.05)
	RC-6	1.10 (0.22)	2.70 (0.54)	1.20 (0.24)	0.51 (0.10)	2.81 (0.56)
	FF	2.90 (0.58)	7.20 (1.44)	3.00 (0.60)	1.14 (0.23)	7.04 (1.41)
Woman ^d	SUD	0.04 (0.01)	0.13 (0.03)	0.03 (0.01)	0.01 (0.002)	0.08 (0.02)
	RC-6	0.48 (0.10)	1.50 (0.30)	0.11 (0.02)	0.15 (0.03)	0.74 (0.15)
	FF	1.20 (0.24)	3.40 (0.68)	0.29 (0.06)	0.33 (0.07)	1.82 (0.36)
Man ^d SUD RC-6 FF	SUD	0.05 (0.01)	0.14 (0.03)	0.03 (0.01)	0.01 (0.002)	0.09 (0.02)
	RC-6	0.54 (0.11)	1.50 (0.30)	0.30 (0.06)	0.13 (0.03)	0.97 (0.19)
	FF	1.40 (0.28)	4.00 (0.80)	0.79 (0.16)	0.30 (0.06)	2.49 (0.50)
		99	9th Percentile Exposu	e Estimates		
Child ^c	SUD	0.13 (0.03)	0.34 (0.07)	0.14 (0.03)	0.05 (0.01)	0.32 (0.06)
	RC-6	1.50 (0.30)	3.80 (0.76)	1.60 (0.32)	0.65 (0.13)	3.75 (0.75)
	FF	3.90 (0.78)	10.0 (2.00)	4.10 (0.82)	1.45 (0.29)	9.45 (1.89)
	SUD	0.10 (0.02)	0.27 (0.05)	0.16 (0.03)	0.01 (0.003)	0.27 (0.05)
	RC-6	1.10 (0.22)	3.30 (0.66)	0.25 (0.05)	0.21 (0.04)	1.56 (0.31)
	FF	2.80 (0.56)	7.50 (1.50)	0.65 (0.13)	0.46 (0.09)	3.91 (0.78)
Man ^d	SUD	0.10 (0.02)	0.28 (0.06)	0.06 (0.01)	0.01 (0.003)	0.17 (0.03)
	RC-6	1.10 (0.22)	3.10 (0.62)	0.60 (0.12)	0.18 (0.04)	1.88 (0.38)
	FF	2.90 (0.58)	8.10 (1.62)	1.60 (0.32)	0.41 (0.08)	4.91 (0.98)

^{*a*}The hazard index (unitless) is provided in parentheses, and bold values indicate exceedance of the reference dose (5 μ g/kg-day). Median and 99th percentiles reflect population body weight variability. ^{*b*}With moderate activity level. ^{*c*}2 to <3 years old. ^{*d*}18 to <19 years.

one layer (Figure 1, Table S12). The highest 6:2 FTOH concentration was for FF-O (1200 μ g/m², Table S12), and the 6:2 FTOH concentration exceeded those of individual nonvolatile PFAS (Table S11). The concentrations of FTOHs in the samples were generally similar to levels found in outdoor jackets and treated textiles, ^{19,32,39,41,44–46} lower than that of older (1988) jackets and firefighter turnout gear, ^{14,19,32} and higher than that of car seats and household linens. ^{40,42} The PFAS found in the facemasks could originate from sources such as PFAS-impacted water used in manufacturing, PFAS in components to maintain or operate machinery,⁴⁷ or as a result of intentional addition of side-chain fluoropolymers. ^{13,42,48} If repellency characteristics are needed in facemasks, PFAS alternatives such as silicone- and hyperbranched polymers-based repellant and hydrocarbon-based wax may be considered. ^{49,50}

Preliminary Estimates of Human Exposure and Risk. Inhalation, based on the octanol—air partition coefficient of 6:2 FTOH, was estimated to be the dominant exposure route, accounting for over 40% (children) and 50% (adults) of total median exposure to PFAS in facemasks (Table 2). Of the total exposure related to facemasks, incidental ingestion accounted for over 40% (children), 15% (women), and 30% (men). The lowest exposures were for the dermal route, which accounted for 11%–20% of total exposure to PFAS from facemasks. High physical activity increased inhalation exposure estimates to over 70% (children), 700% (women), and 400% (men) more than the summed ingestion and dermal exposure routes. Total estimated exposures exceeded the reference dose for 6:2 FTOH of 5 μ g/kg-day for a child wearing the FF mask at moderate physical activity level and via the inhalation exposure route for both children and adults wearing it at a high physical activity level for an extended period of time. These preliminary findings indicate that wearing masks treated with high levels of PFAS for extended periods of time can be a notable source of exposure and have the potential to pose a health risk.

The exposure models are based on assumptions that are sources of uncertainty. Concentrations of PFAS were based on results of the methanol extraction, which may underestimate PFAS, such as FTOHs, released from side-chain fluoropolymers^{51,52} and thus may underestimate exposure, but methanol-extractable concentrations may be a better estimate for the bioavailable fraction. Another assumption that contributed to a possible exposure underestimation is the room volume, which was required to be a minimum of 0.001 m³, when the estimated volume of air between the mask and face was an order of magnitude lower ($\sim 0.0002 \text{ m}^3$). The ventilation rate is the number of total air exchanges per hour, which was assumed to occur every 10 breaths based on 30 breaths/min for children and 20 breaths/min for adults. A textile-air partition coefficient was not available for 6:2 FTOH; therefore, the octanol-air partition coefficient from EpiSuite as reported by ChemSpider⁵³ was utilized. Exposure scenarios were chosen to represent realistic exposure for children and adults wearing facemasks at school and work, so the scenario overestimates exposure for those who wear one for fewer hours per day. Finally, 100% absorption for each exposure route was assumed, which may overestimate exposure for some of the PFAS.

Landfill and Wastewater Environment Implications. In the "likely case", it is estimated that ~28 billion masks will be disposed in U.S. landfills annually while the pandemic persists and will result in ~0.11 kg PFAS/year released to leachate. About 90% of the PFAS release to landfill leachate due pandemic-related mask use can be attributed to SUD, with 10% to N95 masks. This PFAS mass release is insignificant relative to the 600 kg PFAS/year that was estimated to be released in U.S. landfill leachate as collected for wastewater treatment in 2017.¹⁸ In the "extreme case", ~91 billion masks will be disposed with an estimated 37 kg PFAS/year released to leachate. The "extreme case" is an upper bound of PFAS released from landfills to leachate as it assumes 100% of methanol-extractable PFAS is released to leachate. This value is uncertain as there is not a good understanding of the relationship between methanol-extractable PFAS and the release of PFAS in solid waste to leachate under landfillrelevant conditions. While the same PFAS measured in facemasks were measured in landfill leachates prior to the Covid-19 pandemic,¹⁸ even in the "extreme case" the mass of PFAS release is only 6% of the current estimated total mass of PFAS mass released as landfill leachate. Thus, the concentration of PFAS in leachate is not predicted to be significantly impacted by facemask disposal. The model assumed no degradation of precursors, such as side-chain fluoropolymers,^{42,49} which are known to degrade to nonvolatile PFAS.^{54–56} The FF facemask was not included in the calculations because their use is limited. The RC facemasks were not included in the landfill mass release calculations since these facemasks are designed for reuse. Assuming an RC facemask lifetime of one year, it is estimated that 0.7-2.2 billion RC facemasks will be used annually in the "likely case" and "extreme case" scenarios. However, laundering of RC facemasks will likely transfer the PFAS to municipal wastewater, 57,58 resulting in an estimated 0.04 ("likely case") to 11 kg ("extreme case") PFAS input to wastewater treatment plants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.2c00019.

Detailed experimental methods; list of target and suspect PFAS analytes; method precision, accuracy, LOD, and LOQ of target PFAS analytes; surrogate standard recoveries; target analyte concentrations; model parameters for landfill leachate and exposure estimations; results from exposure estimations; and results from suspect screening of nonvolatile PFAS (PDF)

AUTHOR INFORMATION

Corresponding Author

Ivan A. Titaley – Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States; orcid.org/0000-0003-4683-1160; Phone: +1 541 737 9208; Email: ivan.titaley@ oregonstate.edu; Fax: +1 541 737 0497

Authors

- **Derek J. Muensterman** Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, United States; orcid.org/0000-0002-7911-3563
- Liliana Cahuas Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, United States; orcid.org/0000-0002-5973-2674

- Christopher Schmokel Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, United States
- Florentino B. De la Cruz Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695-7908, United States; • orcid.org/0000-0002-0936-3778
- Morton A. Barlaz Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695-7908, United States; orcid.org/0000-0001-8028-3917
- **Courtney C. Carignan** Department of Food Science and Human Nutrition and Department of Pharmacology and Toxicology, Michigan State University, East Lansing, Michigan 48824, United States
- Graham F. Peaslee Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States; orcid.org/0000-0001-6311-648X
- Jennifer A. Field Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States; Orcid.org/0000-0002-9346-4693

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.estlett.2c00019

Author Contributions

^VDerek J. Muensterman, Liliana Cahuas, and Ivan A. Titaley are cofirst authors. Each cofirst author is given the liberty to list their name as the first author in their respective CVs.

Notes

The authors declare no competing financial interest.

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