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Parabens and antimicrobial compounds in conventional and "green" personal care products

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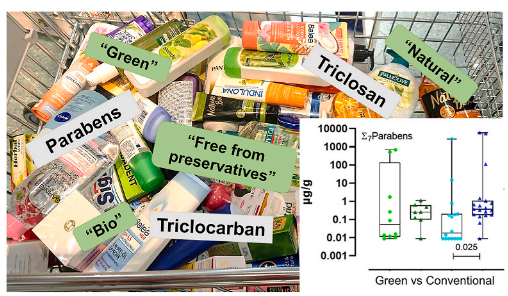
HIGHLIGHTS

- Parabens and antimicrobials were detected in 83% of personal care products.
- No difference in paraben levels between green and conventional products.
- Methylparaben was typically present at the highest concentrations.
- Estimated exclusive use of green cosmetics lowered cumulative paraben exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

The personal care product (PCP) industry is a worldwide multi-billion-dollar industry. Several synthetic compounds like parabens and antimicrobial agents triclosan (TCS) and triclocarban (TCC) are ingredients in many PCPs. Due to growing public awareness of potential risks associated with parabens and other synthetic compounds, more PCPs are being marketed as "green," "alternative," or "natural." We analyzed 19 green and 34 conventional PCP products obtained from a European store for seven parabens, TCC, and TCS. We found no statistically significant difference in the concentrations between green and conventional products. Only four products mentioned parabens in the list of ingredients; however, parabens were detected in 43 products, and at µg/g levels in seven PCPs. Methylparaben was typically present at the highest concentration, and one mascara exceeded the European legal concentration limit of methylparaben. Low concentrations of isopropyl-, isobutyl-, and benzylparabens, which are banned in the EU, were detected in 70% of PCPs. The cumulative estimated daily intake of parabens is an order of magnitude higher for people using only conventional products than those using green products exclusively. We propose that legislation be developed with more explicit rules on when a product can be advertised as "green" to aid consumers' choices.

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1. Introduction

Personal care products (PCPs) have been used since ancient times for cosmetic and hygienic purposes. The global value of PCPs is estimated to reach $716.6 billion by 2025 (Grand View Research, 2018). Consumer awareness of potentially hazardous compounds in PCPs has increased (Zollo et al., 2021). As a result, global market demand for products that promote wellness, healthy aging, and environmental safety has also increased (Ghazali et al., 2017). Certain PCPs are advertised as "green" products, supposedly containing fewer and less harmful synthetic compounds than conventional products. By using these products, consumers are allegedly exposed to fewer harmful compounds (Harley et al., 2016). The most effective way for manufacturers to communicate the green status to potential consumers is by indicating it on the label. Words like "natural," "organic," or "without artificial preservatives" are used on product labels to persuade buyers to purchase the product. However, these terms are largely unregulated, with few parameters and no standardization (Dodson et al., 2012; Rubin and Brod, 2019). While some producers are truthful, others have employed green labels as a marketing strategy without significantly reducing the concentrations of harmful compounds in their products (Jog and Singhal, 2019). This strategy is known as "greenwashing" (Urbański & ul Haque, 2020). One group of compounds that are often prioritized for elimination or reduction in green products are parabens.

Parabens, esters of *p*-hydroxybenzoic acid, are low-cost, broad-spectrum antimicrobial, and antiseptic preservatives (Guo and Kannan, 2013; Li et al., 2021). They have been used widely in PCPs since the 1920s (Ana and Paula, 2016). Although parabens typically have short half-lives and rapid excretion rates in mammalian systems (Janjua et al., 2007), they have been quantified in human bodily fluids such urine, breast milk, and plasma in ng/ml concentration levels (Honda et al., 2018; Dualde et al., 2020; Sosvorova et al., 2017). The continuous presence of parabens in various bodily fluids suggests that these compounds are pseudo-persistent in the human body. Studies have found that the most prevalent route of human exposure to parabens is dermal exposure (Guo and Kannan, 2013; Liao et al., 2013). Parabens are known endocrine disrupting compounds with androgenic and estrogenic effects on humans (Darbre and Harvey, 2008). Long-chained parabens, such as butylparaben (BuP) and propylparaben (PrP), have higher endocrine disruptive potency than short-chained compounds such as methylparaben (MeP) and ethylparaben (EtP) (Oishi, 2001). Parabens with a branched structure, such as isobutyl- and isopropylparabens (iso-BuP and iso-PrP), are the most estrogenic paraben congeners (Darbre et al., 2002, 2003). Studies have linked topical application of PCPs containing parabens with the onset of breast cancer, obesity, gestational diabetes mellitus, and reduced sperm quality (Anderson, 1995; Darbre et al., 2004; Kolatorova et al., 2018; Li et al., 2019). Therefore, the European Union (EU) limited short-chained parabens to 0.4% w/w of a total product and long-chained parabens to 0.19% w/w in PCPs (Commission regulation (EU) no. 1004/2014). Isopropyl-, isobutyl-, phenyl-, benzyl-, and pentylparabens have been banned from use in PCPs in Europe since 2014 (Commission regulation (EU) no. 1004/2014)).

Triclosan (TCS) and triclocarban (TCC) are also popular additives to PCP formulations, particularly to products that hold antimicrobial and antibacterial properties (Nowak et al., 2021). TCC and TCS are known to suppress thyroid hormone production in rats and are bioaccumulative and persistent in the environment (Halden et al., 2017). More than 200 scientists and medical experts have signed the Florence Statement on Triclosan and Triclocarban in 2016, stating that potential health and environmental hazards caused by these compounds outweigh their benefits thereof (Halden et al., 2017).

The endocrine disrupting properties of PCP compounds such as parabens and TCS have been receiving increased attention. They are among the compounds included in the target list of several projects of the Horizon 2020 European Cluster to Improve Identification of Endocrine Disruptors (EURION cluster: https://eurion-cluster.eu/). Their possible associations with metabolic diseases (Kolatorova et al., 2018; Han et al., 2021; Reimann et al., 2021), for instance, have received attention in the OBERON project; a collaborative inter-European research project examining the exposures and effects of endocrine disrupting chemicals associated with metabolic disorders (https://oberon-4eu.com/). To support the understanding of adverse health effects of these compounds, current knowledge on human exposures is needed, incorporating current levels of chemical use in products as well as the consumer trends driving exposures.

The definition of a "cosmetic product" is made on a case-by-case assessment, but all products used in this study are accepted as cosmetics by Regulation (EC) no. 1223/2009 of the European Parliament and of the Council (Regulation (EC) no. 1223/2009). However, following the accepted scientific terminology, we will refer to the products as "personal care products" throughout the manuscript.

This study compares the concentrations of parabens and antimicrobial agents in PCP products marketed as a) green products and b) conventional PCPs purchased from a popular European retail store. We hypothesize that green products contain lower concentrations of parabens and other antimicrobial compounds than conventional products. We also present a determination of cumulative estimated daily intake (EDI) of parabens that consumers may be exposed to by using multiple green and conventional products.

2. Materials and methods

2.1. Sample collection

Fifty-three individual PCPs were purchased from a popular drug store (part of a multinational chain) in Brno, Czech Republic, in August 2019 (Table 1). All items are commonly used types of PCPs according to product use surveys (Wu et al., 2010). For the sake of anonymity, the store and products are not mentioned by name or brand. Green-labeled brands were identified by one of the specific marketing terms (Table 2) printed on the product packaging. After purchasing, all products were stored at room temperature until sample preparation. Samples were opened directly before sample processing.

No permits or ethical requirements were necessary to collect or analyze the samples.

2.2. Extraction and cleanup

Depending on the sample matrix, two different extraction methods were used due to the inherent variability in the composition of different PCPs. Liquid and semi-liquid products that were expected to contain low-lipid content, namely nail polish, liquid deodorant, micellar water,

Table 1
Classification and number of PCPs used for analyses.

Product	Type	Green products	Conventional products
Shampoo	Rinse-off	3	3
Conditioner	Rinse-off	2	2
Sunscreen	Leave-on	1	3
Toothpaste	Rinse-off	1	3
Shower gel	Rinse-off	3	3
Hand soap	Rinse-off	0	2
Hand cream	Leave-on	1	2
Face cream	Leave-on	0	2
Body lotion	Leave-on	2	1
Lipstick	Leave-on	1	3
Deodorant	Leave-on	2	2
Face wash	Rinse-off	1	2
Micellar water	Rinse-off	0	1
Nail polish	Leave-on	0	4
Mascara	Leave-on	1	2
	TOTAL	18	35

Table 2
Marketing terms on PCP labels that qualified the product as "green" for selection purposes.

Inclusion criteria	
Paraben free/free from parabens	Natural cosmetic
Silicone free/without silicone	Without artificial preservatives
Without artificial colorants	Without artificial scents
Bio	Certified natural cosmetics
100/90% natural origin	Without phthalates

and mascara, were analyzed using an adaptation of a sample preparation method described by Young et al. (2018). The original extraction method used by Young et al. (2018) consisted of liquid-liquid extraction of phthalates and organophosphates with methanol and acetone:ethyl acetate (1:1 v/v); we optimized it for our purposes to liquid-liquid extraction only with methanol. Samples that were highly viscous, solid, or semi-solid matrix and a medium to high-lipid content were prepared for analyses using a modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) method. All samples and blanks were spiked with 100 μl of internal standard (IS; Supplementary Table S1) mix containing ^{13}C12- mass-labeled parabens (1 μg/ml) and with 100 μl of mass-labeled triclosan-^{13}C12 (1 μg/ml in isooctane) prior to extraction. A complete summary of both extraction methods is presented in the Supplementary Material.

Before instrumental analysis, samples were diluted with methanol to ensure the levels were within the calibration curve range. Low-lipid samples were diluted at 1:2; medium-lipid and turbid samples were diluted at 1:10, and high-lipid samples were diluted at 1:20. Although nail polish and mascara were considered low-lipid products, some samples exhibited turbidity until the end of the extraction and cleanup phase and were also diluted at 1:20.

2.3. Instrumental analyses

Samples were quantified for seven parabens (MeP, EtP, PrP, iso-PrP, BuP, iso-BuP, and BenzylP) and two antimicrobials (TCS and TCC). Analysis was conducted on a liquid chromatograph (Agilent 1290 Infinity II; Santa Clara, CA, USA) equipped with a vacuum degasser, binary pump, autosampler and column thermostat coupled to a mass spectrometer (ESI/QqQ Triple Quad 610; Santa Clara, CA, USA), and using Mass Hunter software. A Phenomenex Synergi Fusion C-18 end-capped (3 μm) 100 × 2.1 mm i.d. column was equipped with a Phenomenex SecureGuard C18 guard column (Phenomenex, Torrance, CA, USA). The mobile phase consisted of 5 mM ammonium acetate in water (A) and 5 mM ammonium acetate in methanol (B). The binary pump gradient increased from 30% to 40% B at 3 min, 50% B at 10 min, and finally to 100% B at 13 min, holding to 35 min, with 1 min column equilibration at initial conditions (30% B) with a flow rate of 0.12 mL/min 10 μL of the individual sample was injected for the analyses. Compounds were ionized with electrospray ionization. Ions were detected in the negative mode, and the ionization parameters were as follows: gas temperature 280 °C, gas flow 10 l/min, nebulizer 45 psi, capillary voltage 3.5 kV. Masses were quantified according to the relative response of corresponding internal standards.

2.4. Quality assurance and quality control

The analytical method was evaluated using replicates of six samples: a methanol solvent as a non-matrix blank sample, and matrix-spiked shampoo and face cream to evaluate the QuEChERS method, and a methanol solvent, and matrix-spiked mascara and face cream to evaluate the Young et al. (2018) extraction method. The spike-recovery samples were fortified at two levels (spike low and spike high) with native standards (Table S2) and analyzed as per the PCP samples. The relative recoveries for the native standards in the non-matrix spiked blanks were average 100% (range 92–115%) for parabens and 89% (64–112%) for TCS and TCC (Supplemental Figure S1). The low concentration matrix spiked sample recoveries were average 140% (range 83–406%) for parabens, and 126% (90–225%) for TCS and TCC, with the high recoveries from the spiked mascara sample (Figure S2). The high concentration matrix spiked sample recoveries were average 109% (range 95–138%) for parabens and 98% (73–139%) for TCS and TCC (Supplemental Figure S2).

Instrument calibration curves ranged from 0.1 ng/ml – 250 ng/ml with $R^2 > 0.99$ for all compounds. The researchers conducting laboratory analyses did not use any PCPs on the days that analyses or extractions were performed to limit external contamination and procedural blanks, consisting of methanol solvents spiked with IS were used to track contamination throughout the laboratory analyses. Two blanks were prepared for each extraction method and analyzed in parallel with each batch of samples. Ten blanks were processed with the QuEChERs method and two blanks with the Young et al. (2018) method. The concentrations of target analytes in blanks are presented in Table S3.

Procedural blanks were used to determine the method limit of detection (LOD). The LOD was set to equal the average of the blanks +3 times the standard deviation of the blanks. If a compound was not detected in any procedural blank, the LOD was set to equal the instrumental detection limit (Table 3). Sample values above LOD were adjusted to account for blank contamination by subtracting the average of the procedural blanks.

2.5. Statistical analyses and grouping

Graphpad Prism 8.0.2 (www.graphpad.com) was used for summary statistics. The products were grouped according to "green" or "conventional" classification, based on the marketing on the label. According to their mode of application, these groups were subdivided into "leave-on" and "rinse-off" products. We used Mann-Whitney U-tests to compare differences between the sample groups. Significance was set as $p < 0.05$. For the statistical analysis, values < LOD were substituted with LOD/2.

2.6. Estimated daily intake and hazard quotient

To contextualize the concentrations of parabens that humans are theoretically exposed to on a daily basis, the following formula of estimated daily intake (EDI) as used by Nakata et al. (2015) was adapted to determine estimated paraben exposure from PCPs in a European country.

$$\Sigma_i \frac{C_i \cdot E_i \cdot N_i \cdot A \cdot F_i}{BW}$$

C_i Concentration in product (μg/g);
E_i application quantities (g/time);
N_i application frequency (time per day applied);
A absorption factor through the skin;
F_i retention factor;
BW bodyweight.

Li et al. (2021) determined that the dermal absorption factor of parabens is 0.4. The retention factor for leave-on products is 1, and for rinse-off products, it is 0.01 (McGinty et al., 2011). The average adult body mass in the Czech Republic is 91.9 kg for men and 74.2 kg for women (WorldData, 2021). The application quantities of the selected PCPs are taken from Bremmer et al. (2006), and the application frequency of several PCPs is taken from questionnaire data from 300 Czech adults as a part of the CELSPAC: Young Adults study (Supplementary Figure S3; Fišerová et al. submitted). CELSPAC: Young Adults is an on-going follow-up study of the longitudinal ELSPAC study in the Brno region of the Czech Republic (Piler et al., 2017) and follows ELSPAC children born in 1991 and 1992, their siblings, and spouses. The CELSPAC: Young Adults study was approved by the ELSPAC Ethics Committee (Ref. No: ELSPAC/EK/2/2019, dated 13.03.2019). This cohort's

Table 3
Concentrations (μg/g) of parabens, triclosan, and triclocarban in green and conventional personal care products from a European store. LOD values are blank-based values, with the exception of BuP and iso-BuP, which are instrument detection limits. Where the quantified concentrations were lower than LOD values, the cell is marked as "<LOD", and the LOD/2 value used to calculate Σparabens is given in the bottom row.

Group	Product	MeP	EtP	PrP	iso-PrP	BuP	iso-BuP	BenzylP	Σparabens	TCC	TCS
Green rinse-off	Shampoo	<LOD	<LOD	0.0023	0.0031	<LOD	<LOD	<LOD	**0.012**	0.0029	<LOD
	Shampoo	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	**0.016**	<LOD	<LOD
	Shampoo	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Conditioner	526	0.077	0.023	0.018	0.07	0.071	0.032	**526**	0.055	0.17
	Conditioner	0.042	<LOD	<LOD	<LOD	<LOD	<LOD	0.22	**0.26**	<LOD	<LOD
	Toothpaste	505	0.20	92	82	0.021	0.037	0.025	**679**	0.036	0.059
	Shower gel	1.1	<LOD	0.30	0.3	<LOD	<LOD	<LOD	**1.7**	0.0054	<LOD
	Shower gel	<LOD	<LOD	0.0023	<LOD	<LOD	<LOD	<LOD	**0.01**	<LOD	<LOD
	Shower gel	<LOD	0.0065	<LOD	<LOD	<LOD	<LOD	<LOD	**0.014**	<LOD	<LOD
	Face wash gel	<LOD	0.022	0.014	0.0098	0.012	0.016	0.01	**0.088**	0.024	0.09
Green leave-on	Sunscreen	0.44	0.073	0.32	0.22	0.024	0.0084	0.028	**1.1**	0.065	0.23
	Body lotion	0.13	0.031	0.01	0.014	0.023	0.018	0.02	**0.25**	0.056	0.5
	Body lotion	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	0.022
	Hand cream	0.431	0.067	0.037	0.021	0.02	0.033	0.0072	**0.62**	0.033	0.083
	Lipstick	0.25	0.094	0.02	0.032	0.034	0.038	0.016	**0.48**	0.028	0.15
	Deodorant	0.088	0.0047	<LOD	<LOD	<LOD	<LOD	<LOD	**0.095**	<LOD	<LOD
	Deodorant	0.11	0.047	0.023	0.0089	0.021	0.025	0.016	**0.25**	0.086	0.06
	Mascara	0.028	0.043	0.0086	0.0044	0.0071	0.02	0.0093	**0.12**	0.019	0.15
Conventional rinseoff	Shampoo	6.1	8.5	<LOD	<LOD	<LOD	<LOD	<LOD	**14.6**	<LOD	<LOD
	Shampoo	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Shampoo	0.041	<LOD	<LOD	<LOD	<LOD	<LOD	0.14	**0.19**	<LOD	<LOD
	Conditioner	2670	0.12	0.034	0.025	0.019	0.013	<LOD	**2670**	0.019	0.6
	Conditioner	0.3	0.24	0.043	0.072	0.045	0.062	0.023	**0.78**	0.093	0.16
	Toothpaste	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Toothpaste	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Toothpaste	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Shower gel	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Shower gel	0.031	0.035	0.012	0.0098	0.027	0.019	0.0055	**0.14**	0.028	0.24
	Shower gel	0.0047	0.015	<LOD	<LOD	<LOD	<LOD	<LOD	**0.022**	<LOD	<LOD
	Face wash	0.067	0.032	0.019	0.038	0.024	0.01	0.011	**0.2**	0.057	0.1
	Face wash	0.0095	<LOD	<LOD	<LOD	<LOD	<LOD	0.00063	**0.014**	<LOD	0.05
	Micellar water	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Hand soap	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Hand soap	0.028	0.016	0.031	0.023	0.029	0.029	0.017	**0.17**	0.029	0.11
Conventional leave-on	Sunscreen	108	0.01	0.017	0.015	0.012	0.012	0.04	**108**	0.051	0.24
	Sunscreen	0.075	0.038	0.017	0.012	0.013	0.017	0.0086	**0.18**	0.019	0.13
	Sunscreen	0.30	0.19	0.016	0.021	0.047	0.054	0.029	**0.66**	0.065	0.26
	Body lotion	0.12	0.039	0.024	0.016	0.028	0.014	0.025	**0.27**	0.041	0.44
	Hand cream	0.067	0.07	0.018	0.027	0.048	0.055	0.021	**0.31**	0.05	0.25
	Hand cream	0.031	0.058	0.013	0.019	0.012	0.027	0.006	**0.17**	0.038	0.12
	Lipstick	0.023	0.038	<LOD	<LOD	<LOD	<LOD	<LOD	**0.064**	<LOD	0.28
	Lipstick	0.14	0.31	0.04	0.021	0.024	0.024	0.0081	**0.57**	0.022	0.33
	Lipstick	0.24	0.15	0.45	0.5	0.046	0.032	0.024	**1.4**	0.044	0.11
	Deodorant	0.15	0.077	0.05	0.0069	0.067	0.057	0.013	**0.42**	0.016	0.26
	Deodorant	0.076	0.046	0.012	0.0099	0.013	0.021	0.009	**0.19**	0.05	0.089
	Mascara	4522	0.15	464	393	223	386	0.026	**5987**	0.038	<LOD
	Mascara	0.16	0.076	0.038	0.022	0.019	0.011	0.0084	**0.33**	0.014	0.12
	Nail Polish	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0089**	<LOD	<LOD
	Nail Polish	0.22	0.021	0.05	0.023	0.016	0.032	0.0038	**0.37**	0.018	0.42
	Nail Polish	0.63	0.063	0.068	0.075	0.093	0.099	0.0055	**1.04**	0.011	0.22
	Nail Polish	0.44	0.045	0.089	0.03	0.054	0.09	0.023	**0.77**	0.0091	0.049
	Face cream	0.064	0.012	0.017	0.012	0.019	0.014	0.0073	**0.14**	0.037	0.19
	Face cream	3615	1810	0.04	0.042	0.031	0.029	0.014	**5425**	0.037	0.15
	LOD/2	**0.0047**	**0.0016**	**0.0011**	**0.0013**	**0.000008**	**0.000003**	**0.00024**		**0.00065**	**0.00045**

>10000 μg/g; 100-1000 μg/g; 10-100 μg/g; 1-10 μg/g; 0.1-1 μg/g; 0.01-0.1 μg/g; <0.001 μg/g

minimum and maximum application frequency were used to estimate two paraben exposure scenarios for both green and conventional products.

3. Results and discussion

3.1. Difference between green and conventional PCPs and product labels

We tested 35 conventional and 18 green products for nine compounds of interest. The concentrations of the target compounds in the selected PCPs ranged several orders of magnitude — from <0.0001 μg/g to >1000 μg/g (Table 3). Most of the quantifiable concentrations of parabens were in the 0.01–0.1 μg/g range. TCS was present at five times higher concentrations than TCC.

Parabens were detected in 89% of green products and 77% of conventional products, while antimicrobial compounds had less frequent detection (66% of green products and 69% of conventional products). One green and eight conventional products did not contain parabens or antimicrobial compounds above the LOD. Methylparaben was found at the highest concentrations in PCPs (Table 3), with a maximum measured concentration of 4522 μg/g MeP in mascara. Similar to what was found in other studies (Dodson et al., 2012; Matwiejczuk et al., 2020), MeP had the highest detection frequency (38 of 53 products; 72%), followed by EtP (36 of 53 products; 67%). Detectable concentrations of EtP were found in a green shower gel that was labeled as "free from parabens".

It was unexpected that conventional rinse-off products had the lowest detection frequency of parabens (Table 4); however this is primarily because no parabens were present above detectable concentrations in any of the four conventional toothpaste brands (Table 3).

In all product categories, for both parabens and TCS, concentrations varied several orders of magnitude, even within the same specific group of products, e.g., conditioners (Table 3). The measured concentrations did not support our hypothesis that green products should have lower levels of parabens, TCS and TCC; we found no significant difference between the concentrations in green PCPs and the corresponding conventional PCPs for any of the target compounds. The clearer differences were not between green/conventional products but rather between the leave-on and rinse-off products across green and conventional product categories. The conventional leave-on products had significantly higher median concentrations of $\Sigma_7$parabens than conventional rinse-off products (Mann-Whitney *U* test, $p = 0.025$, Fig. 1). Similarly, for TCS, the conventional leave-on products had statistically significantly higher TCS concentrations than the conventional rinse-off products ($p = 0.0072$, Fig. 1). However, due to the small sample size employed by this study, the results should be interpreted with caution.

3.2. Legislation regarding product composition and labelling

Current legislation states that the maximum concentration of parabens in PCP products is to be 0.8% of the ready for use preparation (Commission regulation (EU) no. 1004/2014). A distinction is made between short- and long-chained parabens because of the higher endocrine disruptive potential of long-chained parabens (Oishi, 2001). One conventional mascara sample exceeded these guidelines, where 0.452% (4521 μg/g) of the ready for use preparation consisted of MeP. However, waterproof mascara is a "borderline" or "extreme cosmetic" product. Borderline products are regulated on a case-by-case basis according to the *Manual on the Scope of Application of the Cosmetic Regulation*, which can suggest whether or not a product falls within the scope of the Regulation (EC) no. 1223/2009 (Lores et al., 2018). 80% of the extreme cosmetic products analyzed by Lores et al. (2018) exceeded concentrations of various compounds as prescribed by the Regulation (EC) no. 1223/2009.

Although the EU bans isopropyl-, isobutyl-, and benzylparabens (Commission regulation (EU) no. 1004/2014), quantifiable concentrations of these compounds were found in several products, including green and conventional mascaras, and conventional face wash gel. The highest concentration of a banned paraben was 81 μg/g isopropylparaben in the green toothpaste sample, labeled as "herbal gel for gums." The maximum concentration of TCS in a PCP is 0.3% of the total ready for use preparation and 1.5% for TCC (Regulation (EC) no. 1223/2009). No products had concentrations that were close to 0.3% or 1.5% of the product composition for either compound.

Even though parabens were quantified in 81% of the PCP samples in this study, only four products included parabens as an ingredient on the label: three conventional products (conditioner, face cream, and mascara) and one green toothpaste. Most of the products that included parabens in the ingredient list contained more than 400 μg/g of a compound. MeP was included as an ingredient in all four products, PrP in two, and EtP and BuP in one product each. One green conditioner contained 525 μg/g MeP without including MeP in the ingredient list. Neither TCC nor TCS was ever included in the ingredient lists, even in antimicrobial soap. According to the European Union cosmetics regulation (no. 1223/2009), compounds need not to be included in the ingredient list if they are present as impurities in raw materials or a subsidiary of technical materials used in the mixture but are not present in the final product (Regulation (EC) no. 1223/2009). Because most of the concentrations of parabens and other antimicrobial compounds were below 0.1 μg/g, they might have been considered impurities by the production companies or incidental ingredients from the processing and packaging procedure. Cosmetic packaging is not as strictly regulated as food packaging, which increases the chances of accidental inclusion of harmful substances from packaging materials in personal care products (Regulation (EC) no. 1272/2008).

3.3. Estimated daily intake and health risk of parabens through green and conventional PCPs

The daily use of PCPs is not restricted to a single product. Multiple PCPs are used daily to serve different cosmetic and hygienic purposes (Fisher et al., 2017). The application frequency of PCPs also differs between different groups of people. According to Czech questionnaire data (see section 2.6; Figure S3), the response group with the highest application frequency of PCPs consisted exclusively of female respondents. The group with the lowest frequency was exclusively male; as a result, we separate our exposure assessments by gender (Figure S3). EDIs were calculated for male and female exposure to parabens using only the green and conventional products sampled during this study. The cumulative EDI was calculated to determine the cumulative effect of using multiple products (see section 2.6; Table 5). No information on toothpaste, conditioner, and shower gel was included in the questionnaire. These products (marked with an asterisk in Table 5) were included in the cumulative EDI calculation under the assumption that toothpaste and shower gel is used once a day (Bremmer et al., 2006) and that conditioner is used at the same application frequency as shampoo.

Even though only a snapshot of products were included in the study, a clear pattern could be seen with exposures differing by gender and selection of green vs. conventional products due to women's higher use of PCPs (Figure S3 and Table 5). The cumulative EDI of green products was an order of magnitude lower than conventional products for both men and women (Table 4). We also note that EDI is substantially higher for women than men due to their higher use of PCPs and lower body weight.

Table 4
The detection frequencies (df) of $\Sigma_7$parabens and TCS in different groups of PCPs. Different product groups are green rinse-off (GRO), green leave-on (GLO), conventional rinse-off (CRO), and conventional leave-on (CLO).

	GRO (n = 10)	GLO (n = 8)	CRO (n = 16)	CLO (n = 19)
Σ_7Parabens df	90%	88%	56%	95%
TCS df	30%	88%	38%	89%

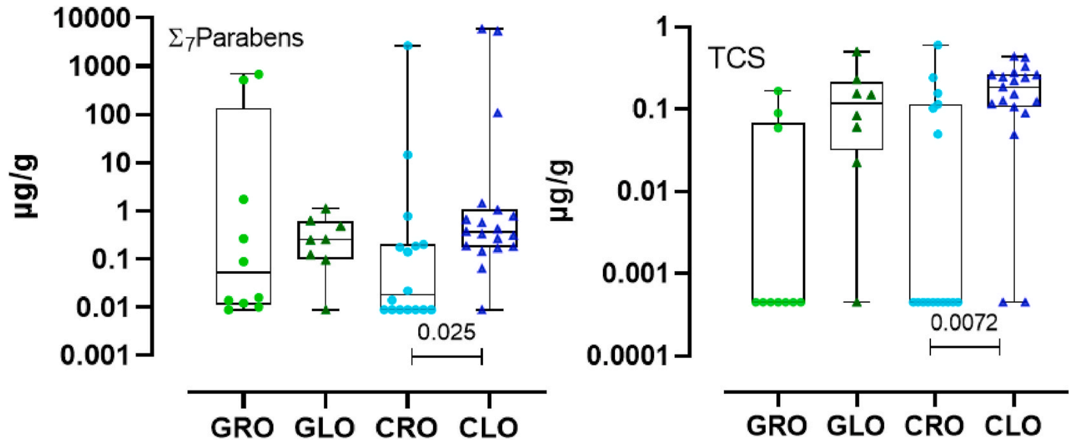

Fig. 1. Box-and-whisker plot (horizontal lines are medians, 95% confidence intervals, minima, and maxima) of the sum of parabens detected in all product groups. Different product groups are green rinse-off (GRO), green leave-on (GLO), conventional rinse-off (CRO), and conventional leave-on (CLO). The *p*-values of significant differences between product groups are indicated.

Table 5
Estimated daily intake (EDI) of parabens through conventional personal care products for men and women in the Czech Republic. An asterisk (*) indicates products that are included in the EDI calculation, but not included in the questionnaire of Figure S3.

	Product	Σparaben median (µg/g)	Application quantity[a] (g/application)	Application frequency[b] (application/day)	EDI (µg/kg-bw/day)
Green products Female use	Shampoo	0.012	12	0.7	0.000005
	Conditioner*	263	14	0.7	0.14
	Lotion	0.25	10.5	0.9	0.013
	Deodorant	0.17	0.5	1	0.00046
	Mascara	0.12	0.025	0.8	0.00001
	Toothpaste*	679	0.08	1	0.03
	Shower gel*	0.014	8.7	1	0.00007
			Cumulative EDI		**0.18**
Conventional products Female use	Shampoo	0.19	12	0.7	0.00009
	Conditioner*	1335	14	0.7	0.71
	Lotion	0.27	10.5	0.9	0.0014
	Deodorant	0.3	0.5	1	0.0008
	Mascara	2994	0.025	0.8	0.32
	Toothpaste*	0.0089	0.08	1	0.00000004
	Shower gel*	0.022	8.7	1	0.00001
			Cumulative EDI		**1.03**
Green products Male use	Shampoo	0.012	12	0.3	0.000002
	Conditioner*	263	14	0.3	0.048
	Lotion	0.25	10.5	0.1	0.0011
	Deodorant	0.17	0.5	0.5	0.00018
	Mascara	0.12	0.025	0	0
	Toothpaste*	679	0.08	1	0.0024
	Shower gel*	0.014	8.7	1	0.000005
			Cumulative EDI		**0.052**
Conventional products Male use	Shampoo	0.19	12	0.3	0.00003
	Conditioner*	1335	14	0.3	0.24
	Lotion	0.27	10.5	0.1	0.00013
	Deodorant	0.3	0.5	0.5	0.00033
	Mascara	2994	0.025	0	0
	Toothpaste*	0.0089	0.08	1	0.00000003
	Shower gel*	0.022	8.7	1	0.000008
			Cumulative EDI		**0.24**

The cumulative EDI values were determined by summing the individual EDIs from each category. The EDIs of parabens from the individual PCPs are very low (<1 µg/kg-bw/day). The highest EDI was 0.71 µg/kg-bw/day for conventional conditioners used by women.

According to the theoretical calculation, a reduction of 82% in paraben EDI can be expected if only green products are used *in lieu* of conventional products. This contrasts with the statistical comparisons between green and conventional products (Section 3.1), where there were no statistically significant differences in paraben concentrations between the product groups. It suggests that even if the concentrations of parabens in some individual green products do not significantly differ from conventional products, the cumulative effect of reduced paraben exposure may be significant if a consumer commits to a lifestyle of using green products exclusively.

Even though the cumulative EDIs for this study were found to be relatively low and no health risks were expected, it should be noted that the cumulative EDI only accounted for seven products. Typically, people use more PCPs on a regular basis, and will have other exposure sources such as diet and pharmaceuticals (Błędzka et al., 2014; Liao et al., 2013).

3.4. Consumer attitude to green products

Due to increased public awareness of certain chemicals compounds' potential health and environmental effects, many consumers gravitate towards alternative or green products (Dodson et al., 2020). In 2019, the sale of natural cosmetics brands accounted for $ 1.6 billion in sales in the United States (NPD Group, 2018). Hence, many companies produce and promote green cosmetic products to retain a competitive advantage in the market (Luo et al., 2020).

The practice of paraben avoidance is proven to be implementable and effective. A study by Dodson et al. (2020) revealed that cosmetic users are willing to avoid potentially hazardous compounds if they have prior knowledge. The participants that actively avoided products with harmful compounds by studying product ingredient lists had lower urinary concentrations of parabens than people who did not practice avoidance (Dodson et al., 2020). Similarly, a study by Harley et al. (2016) revealed that MeP and PrP in the urine of adolescent girls decreased by 43.9% after using products labeled as "paraben-free" for three days (researchers screened these products beforehand to confirm that they were paraben-free).

However, since most consumers are not familiar with technical terms or chemical nomenclature, ingredient lists are not ideal communicators, even if the producers are transparent (Marć and Martyn, 2019). Many consumers rely on social media to choose PCPs, leading to skewed perspectives (Luo et al., 2020). Consumers also fear "greenwashed" products, where producers intentionally label a product as green, but no effort has been put into making the product green (Urbański and ul Haque, 2020). The greatest danger of green products is the fact that the term "green," "bio-," "natural," and other similar labels are haphazardly communicated and currently unregulated, with no standards in place to determine ingredient content or concentrations of chemical compounds (Dodson et al., 2012; Rubin and Brod, 2019). The label "paraben-free" is not officially registered in the EU, and producers are under no legal obligation to remove all parabens from the products (Nowak et al., 2021).

4. Conclusion

The PCP industry is a big international business. Many synthetic compounds are included in the production of PCPs, including potential endocrine disrupting compounds such as parabens, TCS, and TCC. Due to growing public awareness of potential health risks of parabens and other synthetic compounds, more PCPs are being produced and marketed as "green," "alternative," or "natural." However, due to vague regulations regarding green products, it is difficult to determine whether products marketed as green contain lower concentrations of harmful chemical. After analyzing various green and conventional PCP products from a European store for seven parabens, TCC, and TCS, we found that there was no significant difference in the paraben concentrations between the product types, thus rejecting our initial proposed hypothesis. Methylparaben was the compound present at the highest concentration and detection frequency among all target analytes. Only four products included parabens in the list of ingredients. Except for one mascara, which can be considered a borderline or extreme cosmetic product, the concentrations of all compounds were below the maximum concentrations set by the EU Regulations. It was concerning that four banned paraben compounds were quantifiable in the majority of the PCP samples. The cumulative EDI for parabens was an order of magnitude higher for conventional products than for green PCPs. Even though the EDIs for individual products were very low, the cumulative effect indicates that consumers could be exposed to fewer parabens using predominantly green PCPs in their daily routine. The potential health risks of cumulated PCP use warrant further investigation. The lack of set parameters on product labels limits the ability of consumers to make informed decisions on product purchases and may pose a risk for the consumer".

Credit author statement

Veronica van der Schyff: drafting the manuscript, data interpretation; **Lenka Suchánková:** Acquisition of data, data interpretation, manuscript revision; **Katerina Kademoglou:** Acquisition of data, data interpretation, manuscript revision, study design; **Lisa Melymuk:** Study design, data interpretation, manuscript revision, Supervision; **Jana Klánová:** Supervision, Funding acquisition, manuscript revision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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