Identification of chemical ingredients in PCPs according to EU regulations that enter the sewerage system.

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1. INTRODUCTION

Council Directive 91/271/EEC is protecting both the environment and public health from the adverse effects of urban wastewater discharges. The Directive has been in force for more than 30 years while many changes have occurred: depletion of natural resources, palpable manifestations of climate change, as well as novel environmental threats and pressures (European Commission DG Environment, 2017). Throughout these 30 years, emerging pollutants have been added to the bulk of contaminants that should be treated at a wastewater treatment plant (WWTP). As such, nowadays research is focusing on the presence and persistence of pharmaceuticals and personal care products (PPCPs) in wastewater treatment plants because of their ubiquitous presence, their common use, and their adverse effects on aquatic biota. It seems that the highest concentrations of PPCPs are eliminated during the secondary treatment of influents, with the help of microorganisms found in activated sludge. However, there may be unsatisfactory performance of conventional activated sludge towards a lot of PPCPs, as such these substances may be released to the receiving waters intact or in the form of active metabolites. It is also implied that advanced tertiary treatment (i.e. membrane filtration, activated carbon use) is necessary for the removal of a variety of PPCPs, so that the effluents are free of these substances.

Besides human pharmaceuticals, PCPs are also consumed in bulk in westernized societies. In EU, **Regulation 1223/2009/EC** on cosmetic products is the main regulatory framework for finished cosmetic products placed on the EU market. It is a comprehensive legislative tool that safeguards the safety of cosmetic products and streamlines the framework for all operators in the sector. Safety requirements for cosmetic products are laid out in the Regulation's Annexes, and especially in Annex II, where the prohibited ingredients are reported, in Annex III, where the maximum concentrations for ingredients in specific products are reported, and in Annex V, where the maximum concentrations for allowed preservatives are reported.

The ingredients in Annex III are under restrictions, mainly because of their possible human toxicological concern in high doses. However, these restrictions may not be sufficient for their possible environmental effects after their release from WWTPs. Their presence is inversely proportional to their degradation in WWTPs to innocuous products; for example, parabens which have raised concern because of their endocrine disrupting properties are easily biodegradable in aerobic conditions and as such, can be effortlessly degraded in secondary biological treatment (Gonzales-Marino et al., 2011), reaching removal rates of up to 96.1% (Jonkers et al., 2009) at conventional WWTPs. On the other hand, ubiquitous parfums which are usually synthetic musks are not easily biodegradable due to their lipophilic nature, and they tend to accumulate (Schreurs, 2002; Simmons et al., 2010). These characteristics enhance their persistence in WWTP, which are not able to eliminate musks to a high extent (Vallecillos et al., 2014).

Table 1: Excerpt of Annex III of Regulation 1223/2009/EC

ANNEX III

LIST OF SUBSTANCES WHICH COSMETIC PRODUCTS MUST NOT CONTAIN EXCEPT SUBJECT TO THE RESTRICTIONS LAID DOWN

Reference number	Substance identification				Restrictions			Wording of conditions of use and warnings
	Chemical name/INN	Name of Common Ingredients Glossary	CAS number	EC number	Product type, body parts	Maximum concentration in ready for use preparation	Other	
a	b	c	d	e	f	g	h	i
1a	Boric acid, borates and tetraborates with the exception of substance No 1184 in Annex II	Boric acid	10043-35-3/ 11113-50-1	233-139-2/ 234-343-4	(a) Talc	(a) 5 % (as boric acid)	(a) Not to be used in products for children under 3 years of age Not to be used on peeling or irritated skin if the concentration of free soluble borates exceeds 1,5 % (as boric acid)	(a) Not to be used for children under 3 years of age Not to be used on peeling or irritated skin
					(b) Oral products	(b) 0,1 % (as boric acid)	(b) Not to be used in products for children under 3 years of age	(b) Not to be swallowed Not to be used for children under 3 years of age
					(c) Other products (excluding bath products and hair waving products)	(c) 3 % (as boric acid)	(c) Not to be used in products for children under 3 years of age Not to be used on peeling or irritated skin if the concentration of free soluble borates exceeds 1,5 % (as boric acid)	(c) Not to be used for children under 3 years of age Not to be used on peeling or irritated skin

2. AIMS AND SCOPE

Our research focuses on the quantification of consumption of primarily PCPs and secondly of pharmaceuticals, in a medium-sized city in Northern Greece. The frequency of the ingredients belonging to Annex III of 1223/2009/EC, as well as the use of the most common ingredients will be recorded, for massive consumer outlets of the city. Based on this input, the most important findings will be modelled, in a simulation of WWTP with similar characteristics to ours. Finally using these results and data on toxicology and biodegradability, several ingredients (parabens, phthalates, triclosan, BHA, BHT, propyle glycol, MEA, DEA, TEA, formaldehyde, PEG, SLS) will be sought in the WWTP influent and effluent, for different seasons of the year. Some preliminary results are shown here.

3. CASE STUDY OF WWTP OF FLORINA, NORTHERN GREECE

Our case study is the WWTP of Florina city that receives wastewater from the urban agglomeration of Florina (population equivalent of 26,000 inh.; actual population 17,000 inh.) with a maximum flowrate of 9000 m^3/d and a mean flowrate of 7500 m^3/d. The WWTP comprises primary sedimentation, activated sludge aeration, secondary sedimentation and chlorination. Nitrification-denitrification processes are also performed. The unit may accept 60 m^3/d of septic tank scum. The treated effluents are released to the non-sensitive Sakoulevas River.

Figure 1: View of some of the Florina WWTP tanks (grit chamber, activated sludge aeration, secondary sedimentation)

4. PCPs MARKET SURVEY

Approximately 200 distinct PCPs have been coded from the main consumer outlets of Florina and categorized (shampoos, body wash, soap bars, liquid soap, toothpaste, mouthwash). These categories have been identified as the most relevant because they are directly washed from the body, without significant skin penetration. 20 shampoos have been analyzed for the presence/absence of Annex III ingredients and the relative frequency of each Annex III ingredient found has been noted. Furthermore, the relative frequency of the rest of the ingredients (not included in Annex III or V) has also been recorded.

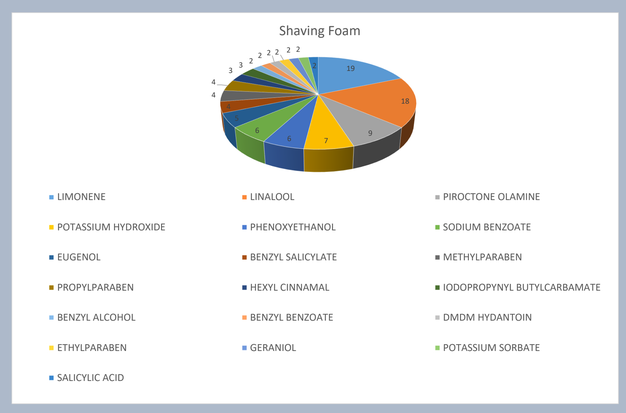

Figure 2: Shaving foam ingredients

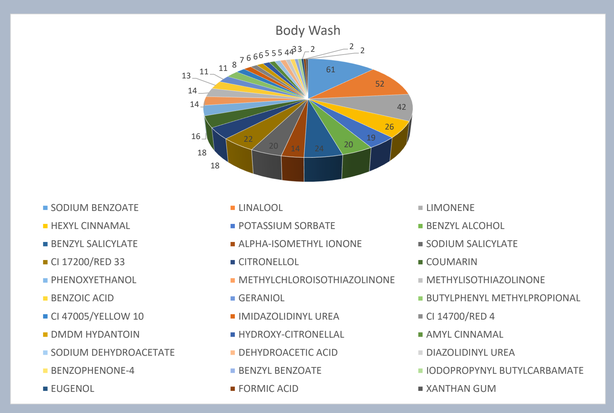

Figure 3: Body wash ingredients

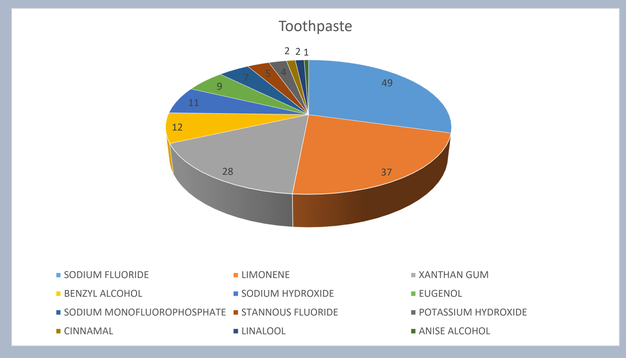

Figure 4: Toothpaste ingredients

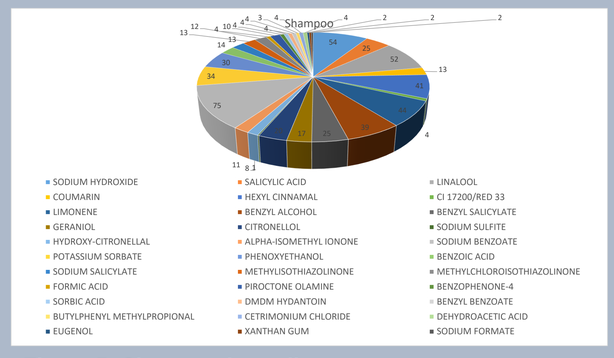

Figure 5: Shampoo ingredients

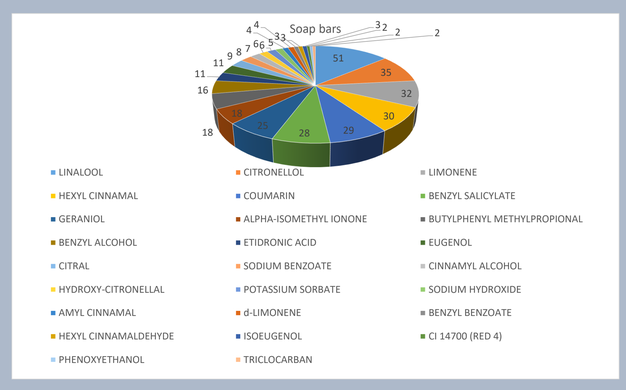

Figure 6: Soap bars ingredients

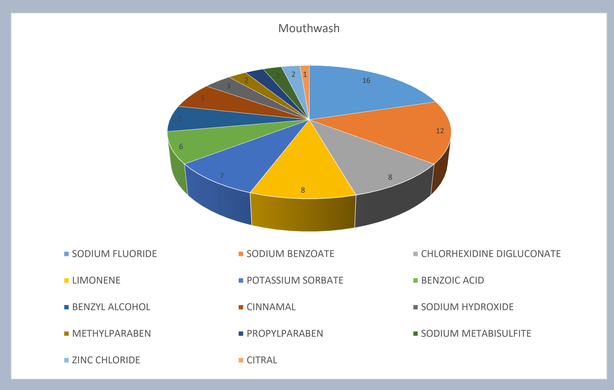

Figure 7: Mouthwash ingredients

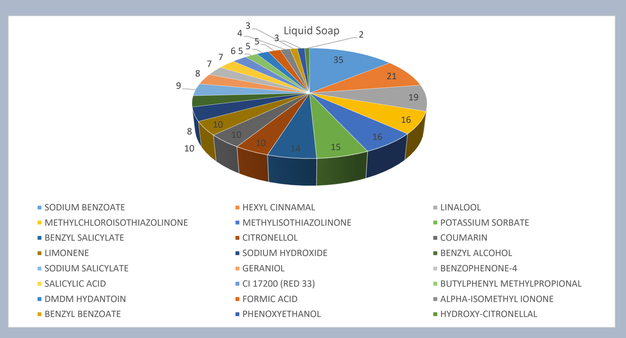

Figure 8: Liquid soap ingredients

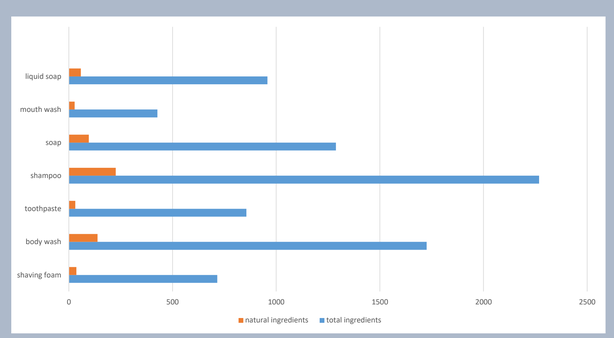

Figure 9: Percentage of natural ingredients out of the total ingredients of PCPs

5. SURVEY RESULTS

Many other ingredients have been found in the examined PCPs and some of them in percentages less than 5-25% (these ingredients are not shown). For the rest, it is interesting to note that *parfum* is found in all the examined products. As already mentioned, *parfum* is a broad term which mainly comprises synthetic musks. The proprietor is not obliged to state the exact parfum recipe, by law. Several toxicological and ecotoxicological findings have been attributed to nitro-musks. The polycyclic musk tonalide (AHTN) has shown estrogenic activity in MCF-7 cells (Bitsch et al., 2002), anti-estrogenic activity in 293HEK cells (Schreurs et al., 2005) and both tonalide and galaxolide have inhibited progesterone and cortisol production in H295R cells (Li et al., 2013). The "fourth generation of musks" (Eh 2004) (cyclomusk, helvetolide, romandolide) are not studied, but may be a promising alternative in the fragrance industry (Li et al., 2018).

Furthermore, oils, extracts, filtrates, waxes and juices of plant or animal (bees) origin as well as honey were also found in the examined PCPs. These ingredients are not supposed to be of significant toxicity or ecotoxicity. Nevertheless, physicochemical properties such as high lipophilicity of oils, may become an issue in a conventional WWTP at very high concentrations.

6. CONCLUSIONS AND SUGGESTIONS

- At least 200 distinct PCPs have been found in Florina market belonging to categories that are easily washed out from the body (shampoos, body wash, soap bars, liquid soap, toothpaste, mouthwash).
- 13 ingredients belonging to Annex III of 1223/2009/EC were found in 20 shampoos examined; highest frequencies were noted for linalool, hexyl cinnamal and limonene, which are allergens.
- Parfum was found in all 20 shampoos examined; no further information on what comprises this "parfum" is given.
- Some of the PPCPs of toxicological concern and/or low biodegradability (e.g. parabens, phthalates, triclosan, BHA, BHT) will be analytically sought at the WTTP under study.

References: European Commission DG Environment. 2017. Evaluation of the Urban Waste Treatment Directive 91/271/EC.; Regulation (EC) No 1223/2009 products; González-Mariño et al. R. Simultaneous determination of parabens, triclosan and triclocarban in water by liquid chromatography/electrospray ionisation tandem mass spectrometry. *Rapid Commun Mass Spectrom* 2009, 23, 1756–1766; Jonkers et al. Mass flows of endocrine disruptors in the Glatt River during varying weather conditions. Environ Pollut 2009, 157, 714–723; Schreurs et al.. Interaction of Polycyclic Musks and UV Filters with the Estrogen Receptor (ER), Androgen Receptor (AR), and Progesterone Receptor (PR) in Reporter Gene Bioassays. Toxicol Sci, 2005, 83, 264–272; Simmons, et al. Interaction of Galaxolide® with the human and trout estrogen receptor-α. Sci. Total Environ. 2010, 408, 6158–6164; Vallecillos et al. On-line coupling of solid-phase extraction to gas chromatography-mass spectrometry to determine musk fragrances in wastewater. J. Chromatogr. A 2014, 1364, 1–11; Environmental Working Group. 2019. Available online on: https://www.ewg.org/skindeep; WHO, 1998, Concise International Chemical Assessment Document 5 LIMONENE; Bitsch et al. Estrogenic activity of musk fragrances detected by the E-screen assay using human mcf-7 cells. Arch Environ Contam Toxicol. 2002, 43, 257-264; Eh M. New Alicyclic Musks: The Fourth Generation of Musk Odorants. Chem Biodivers. 2004, 1, 1975-84; Li et al. A Class of Commercial Fragrance Additives in Personal Care Products (PCPs) Causing Concern as Emerging Contaminants. Advances in Marine Biology, 2018, 81, 213–280. Academic Press. Li et al. Effects of polycyclic musks HHCB and AHTN on steroidogenesis in H295R cells. Chemosphere 2013 90, 1227-1235.