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Persistant Organic Pollutants and Lesser Known Problems in the Environment

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Abstract: **Surface-active compounds are an integral part of washing agents (powders) and are designed to used in water. One of the hazardous chemical classes for environment and human health are persistent organic pollutants (POPs).Substantial amounts of pyrene are solubilized through the use of household soaps and washing powders (the pyrene concentration varies from 4.6 -180 times). Surface-active compounds (SAC) are very active even in the low concentration range of 0.005 - 1%. Therefore, from a scientific viewpoint, the listed range of their concentration in washing agents is so broad (e.g. <5%; -15%; -30%) that meaningful results based on the concentration of these SAC cannot be obtained in laboratory experiments. Particular attention needs to be paid to the development of national policies for the control of surface-active chemicals in polluted washing waters and wastewaters. The first step would be an initiative to ensure that Latvian regulations and legislation are backed up with effective control systems for not only for "surface-active substances" as a whole, but also specifically for nonionic and cationic substances.**

Keywords: **Persistent organic pollutants, washing agents, surface active compounds, pyrene, solubility**

I. Introduction

Persistent organic pollutants have a number of specific properties: toxicity, persistence, bioaccumulation, volatility and the potential for long-range environmental travel. POPs are very dangerous substances because they have an adverse impact on human health, leading to various tumors and cancer formation, behavior disorders and reproductive health problems [1]. POPs have a tendency to travel in the direction from the equator to cooler climatic areas.Although a portion of the POPs in the atmosphere is produced during natural, incomplete combustion, the main source of these dangerous substances is from man-made activities [2]. Due to their mobility, POPs present problems in geographic areas that are not necessarily the key sources of these pollutants.

Climate change has lead to diverse fluctuations in the levels of POPs in open water bodies. Due to the sorption qualities of POPs, these substances accumulate in sediments. Any technical and/or natural activity that stirs up water can lead to the suspension of polluted sediments, which can become soluble in the water column. A number of investigations have been conducted into the solubilization of POPs by surfactants. Some studies have noted enhanced contaminant degradation rates [3,4] while others report no impact [5].

Through the increase of industrial development and through the improvement in the quality of life that people have experienced in many countries, the amount of detergents and cleaning agents used across the world has increased as well.

This article gives results obtained by focusing on the solubility experiments using household soaps and washing powders - to better understand the mechanism of interaction between the different surface active substances and pyrene.

II. Materials and methods

A Chemicals

The PAH used in this study was pyrene, ACROS, 98 %.

B Washing powders and soaps

The choice of samples was random. Persil [P] (content: 5-15% anionic, <5% non-ionic and <5% cationic substances), Henkel; Ariel [Ar] (content: 5-15% anionic, <5% non-ionic substances), Procter & Gamble, Poland; Laundry soap [SA] (content: 72 % anionic substances), Group 1, Aict, Russia.

C *Surface tension measurements*

The method described by Shaw (Shaw, 2000) was used for determining surface tension at 20ºC with a Traube surface tensiometer (stalagmometer). Surface tension is calculated using the formula:

$$\sigma_1 = \frac{\sigma_2 * N_2}{N_1},$$

where σ_1 – surface tension of the investigated liquid; σ_2 – surface tension of distilled water; N_1 – droplet count of the investigated liquid; N_2 – droplet count of the investigated liquid (certified value from the producer).

D The detecting concentration of pyrene

The concentration of pyrene was detected using a methodology that we elaborated and validated as described in [7].

E Pyrene solubilization experiments

Washing powders and soaps were dissolved into 500 ml of distilled water, comprising 0.1% by present weight. Pyrene was added to each vial in an amount exceeding its solubility. The vials were mixed on a platform shaker (PSU-20, 50-200 rpm, VEF-BIOSAN, Latvia) at 20^0 C in a thermo heater (WWT, Germany). The same amount of pyrene was introduced into each sample and the concentration of pyrene in each solution was then determined at a number of progressive time intervals. The solution was filtered through a 0.1-μm inorganic membrane filter (Whatman, UK) mounted on a 10-ml syringe to remove the undissolved pyrene. The concentration of pyrene in washing powders and soap

solutions was measured with a UV spectrophotometer (Jenway 6405 UV/VIS, UK). UV spectra were recorded in the range from 210 to 350 nm. Absorbance of the samples was measured at λ=273 nm.

The pyrene concentration was calculated after baseline corrections from a calibration curve (Stikans, 2005).

III. Results and discussions

Characteristics and measurements of surface-active compounds.

Surfactants are substances with both hydrophobic and hydrophilic properties. Due to their dual nature, surface-active substances are used as washing agents. Surfactants are the principal and essential ingredient in detergents. Regulation (EC) N 648/2004 regulates the manufacture of detergents in the European Union (EU). Under this Regulation, surfactants and detergents containing surfactants that meet the criteria for ultimate aerobic biodegradation as laid down in Annex III may be placed on the market without further limitations relating to biodegradability. According to the Article 11 of this Regulation, the producer must indicate on the label of the detergent only the group of ingredients (e.g. anionic, cationic, amphoteric or non-ionic surfactants) within a concentration range (e.g.< 5%; -15%; 15-30%; 30%), as specified in Annex VII.

The surface tension measurements for 0.1% water liquids of Persil (P), Ariel (Ar), and Soap SA are displayed in Figure 1. The investigated washing powders and soaps showed essentially decreased water surface tension. The most effective in the decreasing of surface tension is the soap SA (decreasing of water surface tension in the presence of investigated soap SA $\Delta A = 72{,}75 - 28{,}35 = 44{,}4$ N/m).

According to the surface tension measurements shown in Figure 1, one can conclude that substances in equal concentrations possess different surface-active properties, due to their varying composition and due to the presence of various other chemical compounds.

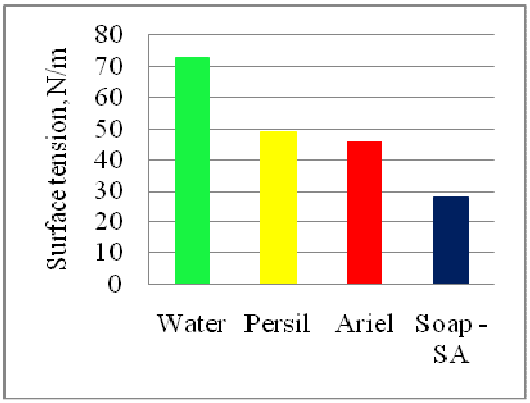

Fig. 1. Surface tension measurements for 0.1% water liquids of the washing powders Persil, Ariel and Soap SA.

It is evident that with regard to surface activity, as characterized by surface tension, the investigated soaps were more effective than the washing powders. This could be explained in the simplest way, which is that soaps contain more surface-active compounds on a weight basis than washing powders.

IV. Solubility experiments

In order to assess the influence of such complicated systems on the solubility of pyrene, 0.1% surface active substances aqua solutions were prepared. The same amount of pyrene was introduced into each sample and the concentration of pyrene in each solution was then determined at a number of progressive time intervals. Several attempts to assess the influence of such complicated systems as washing powder and soaps on increasing the solubility of pyrene were made.

The solubility of pyrene (c_0) at 20^0C is 0.16 mg/L [8]. During the first two days of the experiment, the increase in the solubility of pyrene was negligible and there were no major differences between the employed washing agents. The greatest differences could be seen on the 30th day after the introduction of the pyrene into the aqua solutions (Table 1). Substantial amounts of pyrene are solubilized through the use of household soaps and washing powders (the pyrene concentration varies from 4.6 -180 times).

TABLE 1.

Results of the pyrene content analysis of all samples after 30 days

Name	C/C_0
Soap - SA	180
Ariel	10,9
Persil	4,6

C - concentration of pyrene in water solution after 30 days,
C_0 - beginning concentration (solubility of pyrene)

From the table one can see that the solubility of pyrene grew noteworthy in the presence of the soap SA. Differences and similarities in the solubility results could be explained by the development of different micellar structures in solutions and this may increase the apparent aqueous solubility of pyrene. The results from this study indicate that washing powders containing different surface- active substances have a much smaller effect on pyrene solubility than soaps.

The anionic substances in soaps act as a sorbent (apparent solubility) for pyrene. Both the decrease in surface tension and the increase in solubilisation contribute to the facilitated transfer of hydrophobic pollutants into the aqueous phase. When interpreting the results, it should be kept in mind that an increase of pyrene solubility through the addition of a surfactant should not always would be correlated with bioavailability, for it is possible that microorganisms have no direct access to the PAHs if they are located in the micelles produced by the surfactants (9).

V. Situation with surfactants in Latvia

Data from the Central Statistical Bureau of Latvia (Figure 2). show that the amount of packaged detergents and soaps imported into the country has steadily increased. The increase has been even higher for nonionic substances.A less marked increase is also evident for cationic surfactants. In establishing how the pollution of water with surface-active substances is being controlled and regulated in Latvia, the study authors established that the country's legislative enactments require

Latvia's environment control institutions to assess merely the presence of "surface active substances" in wastewater that contains washing agents. In the opinion of the study authors, the broad and general nature of the term "surface-active substances" means that in practice, the uncontrolled pollution of water with nonionic and cationic substances can take place with impunity, for their concentration in water is not regulated by Latvian legislation. In To date, laboratory experiments have not permitted the study authors to determine the influence of nonionic surfactants, for the particular legislative situation regarding washing agents (the weight percentage ranges of the published ingredients may be kept confidential) prevents a full evaluation of the risks that arise (or may arise) when nonionic surface-active substances, alone or in combination with other surface-active substances, increase the solubility of persistent organic pollutants.

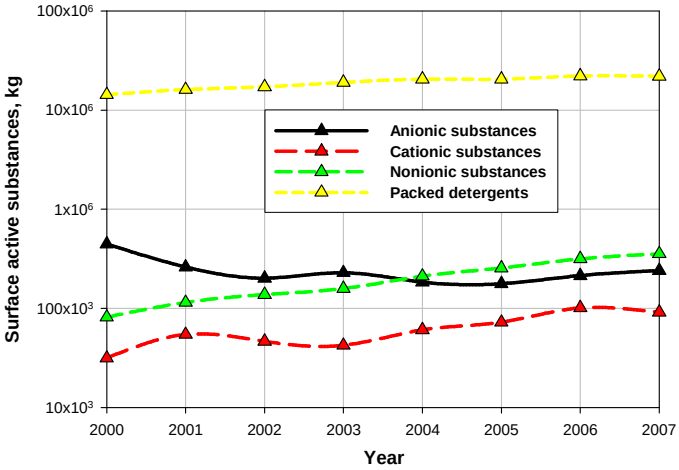

Fig. 2. Imported anionic substances, cationic substances, nonionic substances and packed detergents for the time period 2000-2007.

Surface-active compounds are very active even in the low concentration range of 0.005 %-1%. Therefore, from a scientific viewpoint, the listed range of their concentration in washing agents is so broad (e.g. <5%; 5-15%; 15-30%) that meaningful results based on the concentration of these SAS cannot be obtained in laboratory experiments. Particular attention needs to be paid to the development of national policies for the control of surface-active chemicals in polluted washing waters and wastewaters. The first step would be an initiative to ensure that Latvian regulations and legislation are backed up with effective control systems for not only for "surface-active substances" as a whole, but also specifically for anionic, nonionic and cationic substances. To achieve this goal, there is a need for continued and improved research, monitoring, investigation, and analysis to extend our knowledge regarding the effect of washing powder and soaps on persistent organic pollutants.

V. Conclusions

Laboratory experiments revealed that substantial amounts of pyrene are solubilized using household soaps and washing powders. Environmental conditions and water characteristics vary for each site and further research is required to understand fully the mechanism responsible for persistent chemicals solubility duty so complex system as soaps and washing powders.

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Indulis Stikāns, Daina Kalniņa, Linda Bušmane. Noturīgie organiskie piesārņotāji un mazāk zināmās to vidē radītās problēmas.
Ir vispārzināms fakts, ka noturīgie organiskie piesārņotāji ir ļoti mobīli, pārvietojas lielos attālumos un sorbējas gan uz augsnes daļiņām, gan uz sedimentiem. Šie savienojumi solubilizējas virsmas aktīvo savienojumu klātbūtnē. Darbā pētīts, kā ikdienā lietojamo dažādu mazgāšanas līdzekļu pārstāvju (ziepju un pulveru) klātbūtne ūdens šķīdumos ietekmē poliaromātisko savienojuma pārstāvja - pirēna šķīdību.
Virsmas aktīvie savienojumi ir pamatkomponents mazgāšanas līdzekļiem (pulveriem un ziepēm), kas paredzēti izmantošanai ūdens šķīdumos. Ievērojami pirēna daudzumi tiek solubilizēti saimniecības ziepju un veļas pulveru izmantošanas rezultātā (pirēna koncentrācijas pieaugums ir robežās no 4.6 līdz 181 reizēm). Virsmas aktīvie savienojumi uzrāda lielu virsmas aktivitāti pat pie mazām koncentrācijām (diapazons no 0,005 līdz 1 %). Tā kā mazgāšanas līdzekļos uzrādīto virsmas aktīvo savienojumu koncentrācijas ir ļoti dažādas (piem., <5%; 5-15%; 15-30%), tad balstoties uz šīm virsmas aktīvo savienojumu koncentrācijām, nav iespējams iegūt zinātniski korektus rezultātus laboratorijas apstākļos. Dažādu mazgāšanas līdzekļu izmantošanas apjoms, saskaņā ar Latvijas Statistikas pārvaldes datiem, ar katru gadu būtiski pieaug, sevišķi pieaug nejonogēno un katjonaktīvo virsmas aktīvo savienojumu daudzums.Ir jāvelta īpaša uzmanība nacionālo stratēģiju izstrādei virsmas aktīvo vielu kontrolei un ierobežošanai piesārņotos mazgāšanas ūdeņos un notekūdeņos. Kā pirmais solis tiek ierosināts nodrošināt Latvijas likumdošanu un normatīvos aktus ar efektīvām kontroles sistēmām, ne tikai kopējo virsmas aktīvo savienojumu noteikšanai, bet arī specifiski nejonogēnajiem un katjonaktīvajiem virsmas aktīvajiem savienojumiem.

Индулис Стиканс, Дайна Калныня, Линда Бушмане. Стойкие органические загрязнители и ими вызванные менее известные проблемы в окружающей среде.
Общеизвестным является факт, что полиароматические соединения в окружающей среде очень мобильны и перемещаются на большие расстояния, сорбируются на поверхности почвы и на седиментах. Эти соединения солюбизируются в присутствии поверхностно-активныхвеществ. В работе исследовано влияние отдельных моющих средств (порошков и мыл) на растворимость представителя полиароматического соединения пирена в воде. Поверхностно активные вещества являются основным компонентом моющих редств (порошков) используемых в водных растворах. Значительные обемы пирена солюбилизируются в результате использования озяиственных мыл и стиральных порошков (повышение концентрации пирена в 4.6 – 181 раз). Даже при низких концентрациях поверхностно активные вещества 0.005 – 1 % поверхностно активные вещества (ПАВ) проявляют высокую активность. По этому, с научной точки зрения, учитывая широкий диапазон заявленных кончентраций ПАВ в моющих средствах (на пример, <5%; 5-15%; 15-30%), основываясь на эти концентрации ПАВ нет возможности получить полноценные лобораторные данные.Объем использования отдельных моющих средств в соответствии с данными статического управления латвийской республики, существенно возрастает с каждым годом, особенно количество неионогенных и катионных поверхностно-активных веществ. Особое внимание необходимо уделить разработке государственной политике контроля ПАВ в загрязненных промывочных водах и сточных водах. Как первый шаг может послужить инициатива обеспечения законодатльства и нормативной базы Латвийской Республики инструментом систем ефективново контроля содержания не только общих поверхностно-активных веществ, но и отдельно неионогенных и катионных поверхностно-активных веществ