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Effects of water soluble perfluorinated pollutants on phospholipids in model soil decomposer membranes

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ABSTRACT

Water soluble perfluorinated compounds (PFCs) as perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA) and their shorter chain homologues are persistent organic pollutants widely distributed in the environment. PFCs accumulate in soils and sediments and because of their toxicity endanger the decomposer organisms. PFCs are toxic to a wide spectrum of soil bacteria and their biocide activity was related with their membrane activity; however, the exact mechanism of PFCs – bacterial membrane interactions is unknown. Therefore, to shed light on these questions we applied phospholipid Langmuir monolayers as simplified models of bacterial membranes and studied their interactions with selected environmentally relevant PFCs. The mechanical properties of the monolayers were characterized by surface pressure-mean molecular area isotherms and the analysis of compression modulus. The effects of PFC on the texture of the model membranes were studied with Brewster angle microscopy, whereas their influence on molecular packing in the 2D crystal lattice was searched by the Grazing Incidence X-ray diffraction technique. The effects of PFCs on the phospholipid polar headgroup conformation were studied by PM-IRRAS spectroscopy, whereas the effectiveness of the incorporation of PFCs into the model membrane was monitored in penetration tests. It turned out that the membranes rich in phosphatidylethanolamine typical to Gram negative bacteria are much PFCs susceptible than the cardiolipin rich membranes imitating Gram positive species. Moreover, the studies indicated that the switch from eight-carbon atom perfluorinated chains to shorter chain homologues is not necessarily environmentally benign as perfluorobutane sulfonate caused also significant structural changes in the model membranes.

1. Introduction

1.1. PFCs as persistent organic pollutants

Water soluble perfluorinated compounds (PFCs) are widely distributed in the environment persistent organic pollutants [1–4]. These compounds were and are applied in large quantities in different technologies due to their thermal and chemical durability, lipophobicity and excellent surface activity [5,6]. Perfluorinated compounds found also multiple medical applications as for example ocular endotamponades or blood surrogates [7,8]. Among the different homologues these with eight perfluorinated carbon atoms in the hydrophobic chain occurred most effective as surface active agents and repellents and were produced in larger quantities than their shorter or longer homologues [6]. Therefore, eight-carbon atom perfluorinated pollutants are determined in largest concentrations in different environmental matrices as compared with other fluorochemicals [6,9]. The

concern regarding the ubiquitous presence of perfluorinated compounds in the environment [10,11], their toxicity to different organisms and the possibility of their accumulation lead to the inclusion of perfluorooctanesulfonate (PFOS), the perfluorinated compound produced and applied in the largest quantities to the protocol B of Stockholm Convention and the cease of its production in many countries [11]. It is also well known that perfluorinated carboxylic acids (mainly perfluorooctanoic acid, PFOA) have similar properties and there is also a strong insist on their inclusion on the Stockholm Convention list [6]. The elimination of PFOS and PFOA in water treatment plants is very limited and they remain unchanged in the effluents and in the sludge [2,12]. With waters they can migrate to large distances and their presence in the oceans, also in the arctic regions, was proved by multiple scientific reports [10,11,13,14]. PFOS and PFOA are toxic to different water animals: fish [15,16], plankton organisms [17,18] and algae [19]. Being present in large concentrations in sludge, they contaminate arable soils and pastures, as water treatment biosolids are often applied

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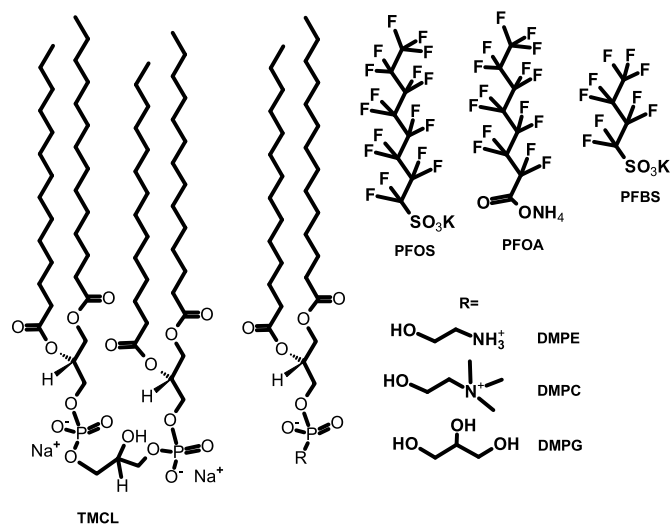
as fertilizers [3,20]. In the soils PFCs endanger the decomposer community being toxic to earthworms and other soil-living invertebrates [21,22].

1.2. Effect of PFCs on decomposer organisms

The persistence of PFC in the environment is connected with the limited biodegradability of such compounds [1,23]. The derivatives of long chain hydrocarbons are degraded mainly in the β -oxidation process, in which a two-carbon atom fragment is cut off as the active acetate. However, the soil bacteria and fungi do not possess the enzymatic apparatus enabling the elimination of the fluorine atom from the β -carbon in the perfluorinated chain which is connected with the high energy of the C–F bond. The presence of PFCs in the soils can lead to the lowering of the degradation of dead organic matter by decomposer organisms [24,25]. It was also stated that the effectiveness of the biodegradation of other organic pollutants and petroleum derived compounds is lowered in the presence of PFCs [26,27]. Thus, it can be stated that PFCs can be toxic to different soil bacteria and fungi and that these substances can act as biocides. The problem of the mechanisms of the adverse effects of water soluble PFCs on soil decomposer communities was practically not studied [28] and the exact mechanisms of PFCs toxicity on microorganisms are unknown. As far as mammals are concerned it was considered in multiple studies that PFCs toxicity can be connected with their membrane activity [29,30]. PFCs are lipophobic so their incorporation into the membranes should be limited [31,32]. On the other hand, PFCs are much more surface active than hydrocarbon surfactants so the incorporation of even a limited number of PFCs molecules into the membrane can lead to profound effects [5,33]. Moreover, multiple studies proved that the immiscibility observed between the hydrocarbons and perfluorocarbons in the bulk is not so obvious in the molecular scale and the interactions between phospholipid molecules and perfluorinated surfactants can be strong and specific [34].

1.3. Membrane activity of PFC and its modeling

At the beginning of our studies we propose a hypothesis that the PFCs toxicity toward soil microorganisms can also be membrane-related. To explore this subject we applied Langmuir monolayers formed by different phospholipids as model bacterial membranes. The monolayers were spread on pure water and on the solutions of perfluorinated substances, which enabled the comparison of the physical properties of such membranes. In our studies we applied phospholipids typical to microorganisms: phosphatidylethanolamine, as the main component of the inner membrane of multiple species of Gram-negative bacteria membranes [35], anionic phospholipids: cardiolipin and phosphatidylglycerol being main phospholipids of Gram positive bacteria membranes [36] and phosphatidylcholine typical to fungal membranes [37]. Regarding the PFCs we applied PFOS and PFOA as the substances of the highest environmental impact. Additionally perfluorobutanesulfonate (PFBS) was studied as there is a strong tendency to switch the perfluorochemical compounds to short perfluorinated chains, which are claimed to be less ecotoxic [6,38,39]. The mechanical properties of the model membranes were characterized by the monolayer compression and the recording of surface pressure (π) – mean molecular area (A) isotherms. The texture of the model membranes was monitored in-situ by Brewster angle microscopy (BAM), whereas the effects exerted by PFCs on the phospholipid headgroup were followed by the application of the surface-dedicated PM-IRRAS spectroscopy. To obtain the information about the two-dimensional crystal structure of the model membranes and its alteration after the contact with PFCs the Grazing Incidence X-ray diffraction technique was employed.



Scheme 1. Structural formulas of the phospholipids and PFCs applied in the studies.

2. Experimental

2.1. Materials

The phospholipids applied in our studies: 1,2-dimyristoyl-sn-glycero-3-phosphoethanolamine (DMPE), 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), 1,2-dimyristoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DMPG) and 1',3'-bis[1,2-dimyristoyl-sn-glycero-3-phospho]-glycerol (sodium salt) (cardiolipin, TMCL) were purchased from Avanti Polar Lipids as lyophilized powders of high (99%) purity. The samples were delivered under dry ice and stored refrigerated at -20°C . The water soluble perfluorinated chemicals: heptadecafluoro-1-octanesulfonic acid potassium salt 99% (PFOS), pentadecafluorooctanoic acid ammonium salt 99% (PFOA) and nonafluoro-1-butananesulfonic acid potassium salt 99% (PFBS) were bought from Sigma Aldrich. The solvents applied in the experiments: HPLC grade chloroform (99.9%) (stabilized by ethanol) and HPLC grade methanol (99.9%) were bought also from Sigma-Aldrich (Scheme 1). Ultrapure water of the resistivity of $18.2\text{ M}\Omega\text{cm}$ was produced in our laboratory with the application of the Synergy Merck-Millipore water purification system.

2.2. Preparation of the solutions

Samples of the investigated phospholipids were weighted on the Mettler-Toledo analytic scales (accuracy of 0.01 mg) and dissolved in class A 10 cm^3 volumetric flasks in the chloroform/methanol 9/1 v/v mixture. When not used the solutions were kept refrigerated at -20°C . Typically approx. 2 mg of a phospholipid were dissolved which gives the concentration of approx. $3 \cdot 10^{-4}\text{ M}$. The phospholipid solutions were applied for Langmuir monolayer preparation. The perfluorinated compounds PFOS, PFOA and PFBS were applied as components of the aqueous subphase. Thus, their samples were dissolved in 2 dm^3 class A glass volumetric flasks to achieve the required concentration of 10^{-4} M . The flasks were sonicated at the ultrasonic bath to achieve the complete dissolution of these substances. For the penetration tests more concentrated 0.05 M solutions of the investigated PFCs in 98% ethanol were prepared.

2.3. Techniques

2.3.1. Langmuir technique

Three different Langmuir troughs were applied depending on the technique of monolayer characterization. For the π -A isotherm

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