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Prediction of Persistent Organic Pollutants Biodegradation in Contaminated Marine Sediments Using Passive Sampling Probes

***E. Prokofyeva*[1] --- *E. Frapiccini*[2] --- *M. Marini*[3]--- *A. Bondarenko*[4]--- *M.L. Ruello*[5]**

[1]Lipetsk State Technical University, Moskovskaya St., Lipetsk, Russia
Università Politecnica delle Marche, SIMAU, Via Brecce Bianche, Ancona, Italy
[2,3]CNR-ISMAR, largo Fiera della Pesca, Ancona, Italy
[4]Lipetsk State Technical University, Moskovskaya St., Lipetsk, Russia
[5]Università Politecnica delle Marche, SIMAU, Via Brecce Bianche, Ancona, Italy

Abstract

The aim of this study is to evaluate a new configuration (new materials) of the commercial passive sampler Chemcatcher as probe for predicting the bioavailability of persistent organic pollutants in marine sediments. To predict the availability of pollutants to biota, it is important to understand both solution- and solid-phase processes in the sediment, including the kinetics of pollutants release from its binding agent (ligand and/or particle). The present study examined the kinetic of desorption and biodegradation of Polycyclic Aromatic Hydrocarbons (PAHs) in two different marine sediments sampled in the Adriatic Sea. The sediments were spiked with a standard mix of 16 PAHs in the range of 11-12 mg/Kg (dry sediment). Formaldehyde was added into the sediments to prevent biodegradation. After equilibration, the passive probes were placed in the specimens with prevented biodegradation, recovered and analyzed at prefixed time slots (in the range of 50 days) for the assessment of the accumulated PAHs; in parallel a little amount of sediments was collected and the residual concentration of PAHs was measured. Free PAHs in the sediment pore waters were also determined. The results suggest that the kinetically labile solid-phase pool of PAHs, which is included in the DGT measurement, played an important role in biodegradation processes along with the free PAHs in sediment pore water.

Keyword: Passive probe, Passive sampling, Persistent organic pollutants, Bioavailability, Biodegradation, Diffusive gradient in thin film (DGT), Chemcatcher.

1. Introduction

To predict the availability of pollutants to biota, it is important to understand both solution- and solid-phase processes in the sediment, including the kinetics of pollutants release from its binding agent (ligand and/or particle). Passive sampling could provide the solution to problems associated with costly and time consuming sampling programs and biomonitoring.

The diffusive gradient in thin film (DGT) technique is a passive sampling technique, which has been successfully applied for measuring inorganic contaminants in water, sediments and soils. This principle has been used for organic pollutants evaluation in soil. The research showed the developing of the method for environmental risk assessment of contaminated soils by using adsorptive equilibrium of pollutant in system soil matrix-soil solution. The technique was designed by adapting the DGT method, originally meant for heavy metals, to organic molecules [1, 2]. This method is able to measure PAHs concentration in sediments by perturbing the equilibrium between solid and liquid phases after diffusion through a thin deionized water layer. The aim of this study is to evaluate a new configuration (new materials) of the commercial passive sampler Chemcatcher as probe for predicting the bioavailability of PAHs in marine sediments.

2. Materials and Methods

2.1. Study Area

The marine sediments used in this study were collected from the Adriatic Sea close to Senigallia (AN), Marche Region, Italy. The geographical locations of the sampling sites are shown in Fig. 1. Two different sediment samples were chosen for the analysis.

2.2. Sampling and Preparation of the Samples

Shallow sediment samples (0-2 cm) of both study sites were collected using a box corer (17x10x24.5 cm). After collection, gross vegetable material, animal remains and shell residue were removed. Cleaned sediment samples were stored in closed jars of transparent glass, in the presence of oxygen and at room temperature. For two study sites, the particle-size values were classified by Shepard's scale [3] and the total organic carbon (TOC) were measured in silver capsules using a FISONS NA2000 Element Analyzer after removal of the carbonate fraction by dissolution in 1.5 N HCl [4]. The measured characteristics of the marine sediments collected in two areas of the Adriatic Sea are described in Table 1.

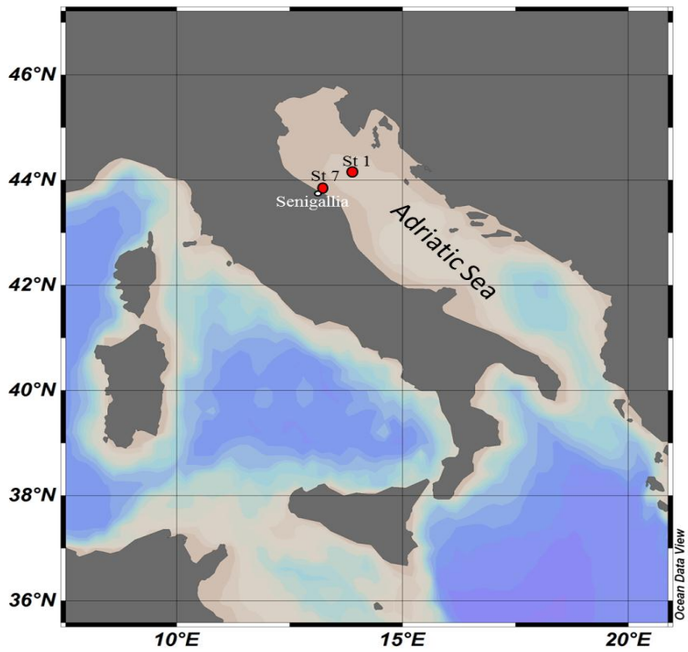


Figure-1. Geographical locations of the sampling sites: site 1; site 7.

Table-1. Characteristics of the marine sediments

Sample	Coordinates	Depth	Salinity	Ctot, %	Corg, %	Sandy fraction, %	Classification of sediment types
Site 1	44°02.96N 13°41.03E	70m	>38	4.89	0.30	34	Clay loam
Site 7	43°45.87N 13°13.03E	12.5m	30-35	4.41	0.29	60	Sandy clay loam

2.3. Chemicals

C18 Empore disks (47 mm diameter) were purchased from Supelco (part of the Sigma-Aldrich Corporation, Bellefonte, Pennsylvania, USA). Whatman glass microfiber filters grade GF/A (47 mm diameter) and the solvents (HPLC grade quality or equivalent), acetone; 2,2,4-trimethyl pentane; ethyl acetate; dichloromethane; acetonitrile; methanol and water were obtained from Supelco. Certified pure (purity >98% in all cases) reference standards of the test compounds (PAH solution EPA 610 PAH Mix) were obtained also from Supelco.

2.4. Sampler Design

The passive sampling device (Figure 2) consists of a C18 Empore disc as chromatographic receiving phase overlaid with a Whatman glass microfiber filter membrane (47 mm diameter). The water is added to the interstitial space between the receiving phase and membrane. The principle of measurement for the probe is based on Fick's first law as the traditional diffusion-adsorption technique [5]. The receptor material was separated from the specimen by a water chamber of thickness Δg (0,2 mm). This technique is named Diffusion Gradient Technique (DGT) because the gradient of concentrations produced by the water chamber of thickness 0,2 mm is the driving force of diffusion. Organic molecules diffuse through the water layer and are rapidly bound by the receptor material; hence, their concentration at the interface water-receptor is maintained at zero throughout the deployment. Water chamber and glass fiber membranes were chosen specifically in order not to interpose selective media for the pollutant diffusion process [6]. The probe measures the average flux of pollutant that diffuses through the water layer by accumulating a mass of pollutant over time through a well-defined area. In the DGT technique, solutes are dynamically removed by their diffusion through a membrane to a binding adsorbent material, so the sampled PAHs represent the labile pollutants pools. The PTFE Chemcatcher body [7] supported both the receiving phase and the diffusion membrane and sealed them in place.

Figure-2. The passive sampling device Chemcatcher

2.5. Preparation of the Samplers

C18 Empore disks were conditioned by soaking them in methanol for 20 min until translucent and then stored in methanol until required. The Empore disks were prepared in a 47 mm diameter disk vacuum manifold platform. Methanol (10 mL) was slowly passed through the disk, followed by 10 mL ultrapure water. The conditioned disks were placed in the Chemcatcher body, which was subsequently filled with purified water. The glass microfiber filter membrane was put on the top of the Empore disk. Any air bubbles were smoothed away from between the two layers by gently pressing the top surface of the membrane. The PTFE supporting disk was placed into the sampler body and fixed in place to form a watertight seal between the membrane and the top section of the sampler.

2.6. PAH Extraction for Bio/Degradation Parameters

The standard PAH solution EPA 610 was used as inoculum for the batch degradation test. An appropriate dilution of the standard solution EPA 610 in the ratio 1:50 was prepared with dichloromethane. Standard solution (1:1) contains a mixture of sixteen priority PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno [1,2,3-cd]pyrene and benzo[ghi]perylene, with a known total concentration of 5700 µg L-1. The collected sediments (about 200 g) were spiked with a diluted standard PAHs solution (2 mL). A known quantity of 40% formalin (200 µL) has been added to each sediment samples in order to observe in parallel the degradation kinetic without microbial activity. Both bio/degradation rates were studied after equilibration of one day for a period of 49 days. The extractions were conducted in prefixed time periods (1, 3, 5, 7, 14, 21, 28, 35, and 49 days) after inoculation and equilibration. For both degradation studies the U.S. EPA's 16 priority PAH were extracted from 10 g wet sediment samples. The PAH extraction from sediment was achieved by three 15 min cycles in an ultrasonic baths [8] using as solvent dichloromethane (20 mL) and a liquid-liquid separation was made. The PAH enriched solvent removed initially by rotary evaporation (T = ± 2 30°C) and later by gentle nitrogen flow [9]. The final volume of the analytical sample was adjusted to 300 µL with acetonitrile.

PAH quantification and PAH qualification were carried out by high performance liquid chromatography (HPLC Ultimate 3000, Thermo Scientific, USA) with fluorescence and diode array detectors (Thermo Scientific, USA). The sixteen PAHs were separated with a gradient program (1.5 mL min-1) on an analytical reverse-phase column C16 (4.6x150 mm, 3 µm 120Å). A mixture of acetonitrile and water (Mill-Q system, Billerica, MA, USA) was used as mobile phase [10]. Calibration solutions were prepared by serial dilutions from the standard PAH solution.

The wet weight of each sample of marine sediment was corrected to the dry weight, after the determination of the percentage of humidity in the sediment samples. Each concentration was expressed on a dry-weight basis.

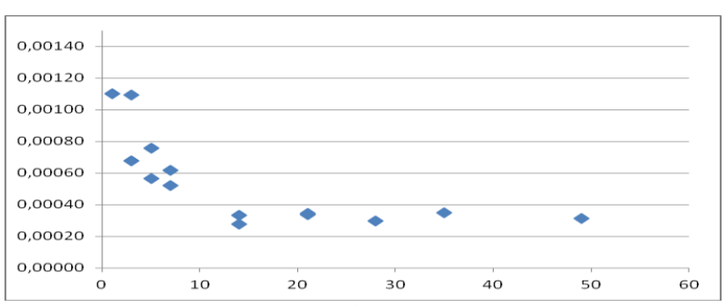
2.7. Extraction of Analytes from the Passive Samplers

After exposure (1, 3, 5, 7, 14, 21, 28, 35, and 49 days), the sampler was carefully disassembled and the membrane removed. Compounds were extracted from the Empore disks in an ultrasonic bath (5 min) using acetone (5 mL) followed by 5 min in 50 : 50 (v/v) ethyl acetate: 2,2,4-trimethylpentane (5 mL). The disks were removed and the solvent extracts combined. The solvent extract was gradually reduced under nitrogen. The reduced extract was transferred to 2 mL vials prior to analysis. The final volume was adjusted to 300 µL with acetonitrile.

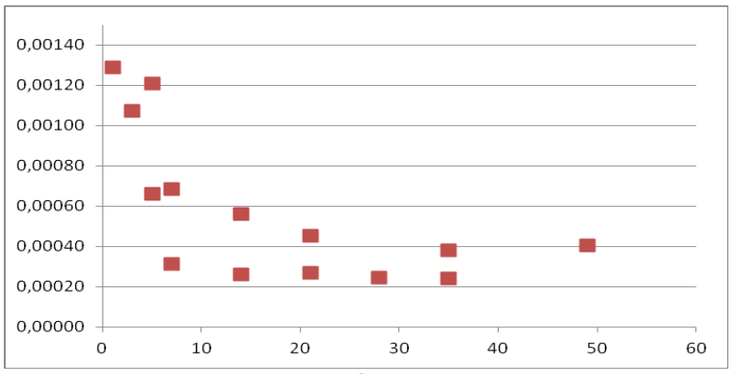
PAH quantification was carried with the same method described above.

3. Results and Discussion

The concentrations of PAHs as perceived by the passive sampler considered in the work are compared with the measured concentration in the pore water. Characteristic analyte uptake curves for benzo[a]pyrene in both the sediments are shown in Fig. 3a – 3b.



(a)



(b)

Figure-3. Ratio(R) between concentration of benzo[a]pyrene measured by passive probe and measured in the pore water for: a - Site 1, b – Site 7(x – days, y – R)

The graphs show that the ratio (R) between these concentrations quickly decreases in the first 14 days and then remains constant at very low values. This behavior is indicative of the low ability of the solid phase in sustain the pore water concentration. After 14 days this ability is so low that the concentration in solution is sustained only by diffusion and no more by resupply from the solid phase.

These results are supported by the high half-life of benzo[a]pyrene measured by the degradation test.

5. Conclusions

The present study describes the activities performed to test a new method for measuring the mobility of persistent organic pollutants in the solid phase of sediments within the context of environmental pollution risk assessment. The method is based on the design of a new probe for the passive sampling of organic pollutant in sediments (or in water saturated soils). This method in different configurations can be a useful tool for such studies and especially due to its cheap and simple investigation conditions.

6. Acknowledgements

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