

EXPERIMENTAL INVESTIGATIONS AND NUMERICAL MODELLING OF IN-SITU REACTIVE CAPS FOR PAH CONTAMINATED MARINE SEDIMENTS³

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Abstract

The present study compared numerical modelling and experimental investigations to evaluate the effectiveness of in-situ reactive capping for marine sediments contaminated by polycyclic aromatic hydrocarbons (PAHs). As a case study, sediment samples from Mar Piccolo (Italy) were analyzed and experiments were undertaken using batch columns. Two types of capping amendments were tested: AquaGate® + 5% of powdered activated carbon (AG PAC) and Organoclay Reactive Core Mat (OC RCM). The column tests were carried out for 20 days, obtaining a short-term PAH distribution for three cases analysed, which compared the application of the two caps with no intervention. In parallel, in order to evaluate the intervention long term efficacy, an ad-hoc multilayered model predicting PAH concentrations into the sediments and the overlying water column was developed and validated with the experimental results. Both capping systems considerably reduced PAH concentrations in the overlying water, with the highest performance seen in AG PAC for benzo[a]pyrene (99%) and anthracene (72%); results also confirmed in the model predictions. In addition, the numerical simulations indicated a good efficiency of both caps over time, obtaining PAH values below the threshold limit in the long term. Although further experiments need to be developed accounting for multiple contamination competitiveness.

Keywords: In-situ capping; marine sediments; adsorption; PAHs; predictive model.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent hydrophobic organic pollutants which are widespread in the environment, particularly in water and sediments (Luo et al., 2004). Their main threat is their recognized toxic, mutagenic and carcinogenic characteristics to human health and the natural environment (Gan et al., 2009).

Principal sources of PAH contamination are related to the development of coke-oven gas plants, refineries and other types of chemical industries, but are also due to incomplete combustion and pyrolysis of organic matter and natural processes. Furthermore, rapid urbanization and industrialization over the past five decades has contributed to the PAH contamination of several hundred thousand sites across the world (Moore et al., 2015).

PAH presence in aquatic environments is mainly a consequence of dry and wet atmospheric deposition, surface and roadway runoff, storms, municipal and industrial effluents and shipping. Once in superficial water, because of their low water solubility, hydrophobic nature and high persistency, PAHs tend to accumulate with inorganic and organic material in suspended solids and sediments, which implicates a long-term harmful impact on benthic organisms. Further to this, coastal environments affect PAH behavior, fate and transport due to sediment resuspension and bioturbation which contribute to their redistribution in the ecosystem (Dong et al., 2018).

Several remediation techniques have been developed and tested to either contain, clean up or restore coastal sediments contaminated by PAHs, including both *ex-situ* and *in-situ* technologies (Abdel-Shafy and Mansour, 2016; Ghosh et al., 2011). Of particular relevance is in-situ reactive capping (ISC), considered a valid alternative to ex situ remediation options, which require expensive dredging of the seabed and the subsequent transport of masses to appropriate treatment plants or disposal facilities (Samuelsson et al., 2015; De Gisi et al., 2017). ISC works as an isolation barrier, which could opt for a sand layer with gravel or silt or active/reactive layers containing a mixture of sand and reactive amendments such as organoclay (OC), activated carbon (AC), apatite, zeolite and zero-valent

iron. In particular, the use of reactive materials allows for a reduction of the thickness required for conventional sand caps (Lofrano et al., 2017). However, the effects of these materials on the different contaminant immobilization and availability are currently under investigation (Yang et al., 2019; Li et al., 2019). OC consists of a modified clay whose main constituent is “montmorillonite”, which has a large surface area, great cation exchange capacity, swelling comportment and high adsorption characteristics, especially with PAHs and chlorinated hydrocarbons (De Paiva et al., 2008). In contrast, AC is mainly obtained from fossil and biomass materials and can be produced as either a powder, granule or brittle material (Baker et al., 1992). It is a well-known and characterised adsorption media, used to remove organic and hydrophobic pollutants such as polychlorinated biphenyls (PCBs) and PAHs (Brändli et al., 2009; Oleszczuk et al., 2012). PAH adsorption occurs via the AC’s large internal specific surface and the intra-particle diffusion of PAH molecules in carbon macropores and micropores. Cornelissen et al. (2011) showed that powdered AC (PAC) has superior PAH sorption capacity than granular AC (GAC) because of faster kinetics and reduced fouling. Despite this, these ISC materials have demonstrated high efficiency, although there is little data available on their long-term use for PAH removal and, thus, on their effects on PAH fate and bioavailability. Several mathematical models have been developed to predict the fate, transport and sorption of PAHs within sediments and reactive caps (Go et al., 2009; Reible, 2014; Zhang et al., 2015; Silvani et al., 2017). The majority of these models were focused on describing the physical processes involved, such as advection, consolidation, dispersion and bioturbation, by simplifying the geochemical and solid-liquid interaction processes, and often relying on the assumption of local equilibrium and sorption phenomena simply described via a retardation factor, rather than considering time-varying kinetic properties of the different layer materials to represent contaminant partitioning and fate. As mentioned by Shen et al., (2018), sorption/desorption of some organic compounds could be slow and the local equilibrium assumption may be not sufficient to describe the rate of the sorption/desorption process, and mass transfer coefficients are required to represent the sorption kinetics. In addition, Minick and Anderson (2017) showed how the PAH dissolved concentration

gradient and compound-specific distribution coefficient can determine the flux occurring across the sediment/water interface, while Yan et al. (2019) highlighted the necessity to consider the effect of the mass transfer coefficient on contaminant transport through the contaminated sediment and the capping layer.

Driven by all these premises, in the present study, an ad-hoc multi-layered numerical laboratory model was developed to predict PAH concentration distribution into marine sediments and the upper water layer, by considering both physical, geochemical and reactive mechanisms. Site-specific parameters were used for the numerical solutions, which were validated by comparison with the experimental data. The case study examined marine sediments from Mar Piccolo (Italy), where several investigations were carried out in recent decades. The attention was concentrated on PAHs because of their mutagenicity, toxicity and the significant concentrations observed (Todaro et al., 2018). Specifically, the highest values among the PAHs were measured for pyrene, benzo[a]pyrene and anthracene. These three compounds are listed among the USEPA regulated PAH priority pollutants (OFR, 1982) to have been analyzed in aquatic and terrestrial ecosystems. In particular, benzo[a]pyrene is termed as index or gold standard of the whole group of PAHs due to its high carcinogenicity. It is considered a classic DNA-damaging carcinogen (Collins et al., 1991) causing mutations and eventually cancer. Although it is not as dangerous as benzo[a]pyrene, several studies on animals showed that pyrene is toxic to both kidneys and liver, and could affect some living functions in fish and algae. For anthracene, the main contamination pathways are through breathing, ingestion and direct contact, and it has also been shown to affect the kidneys, liver and skin (Krasnov et al., 2005; Oliveira et al., 2012).

In this context, two reactive capping materials were tested and compared to evaluate their sequestration efficacy for the three compounds considered. Laboratory column tests, representing the multi-layered system with and without a cap, were carried out in order to determine the short-term variation of the three compound concentrations in both the sediment and marine water layer. Prediction modelling of the contaminant profiles was conducted using COMSOL Multiphysics[®], a

finite element model where diffusion, advection and desorption/adsorption mechanisms were considered to simulate both flow and reactive processes occurring in the columns. This model was parameterized using the physical and chemical characteristics of both sediments and ISC systems and of the PAHs investigated.

2. Material and method

2.1 Site study

The marine sediments examined in this study were from Mar Piccolo, a part of the Gulf of Taranto, located in the Ionian Sea in the south of Italy (Figure 1). Mar Piccolo has a total surface area of approximately 21.7 km² and is comprised of two bays (or “seni”): an external bay, called “first bay”, connected to the open sea via an artificial channel named “Canale Navigabile” and the natural Porta Napoli channel, and an internal bay, called “second bay”, connected to the first via a subaqueous channel and the Punta Penna bridge (Labianca et al., 2018). The first bay and the second bay have respective depths of 13 m and 9 m.

In both bays, the hydrodynamic is strong due to several influences, which are depicted in Figure 1 and can be classified as: (i) some fresh water springs, called *citri*, located on the bottom of both bays; (ii) two main rivers, Galeso (with flowing rates of respectively 350 and 520 l/s) in the first bay and Aiedda Canal (1030 l/s) in the second bay, which also carries wastewater from sewage treatment plants; (iii) a tidal wave action in both bays; (iv) and a seawater intake pipe of a steel factory in the first bay (De Serio et al., 2007; Bellucci et al., 2016).

Mar Piccolo is on the Italian Priority List as a Site of National Interest (SIN) for environmental remediation, and is classified as a very extensive contaminated area, which is dangerous due to its highly compromised environmental status (De Serio et al., 2007). The industrial and anthropogenic impacts can be mainly attributed to the presence of the Italian Navy shipyard with its dry docks, located in the first bay, and to a steel factory and a petroleum refinery in the industrial area on the west side of the first bay (Figure 1). Furthermore, additional pollution sources have been identified

and in particular, nine sewage discharge pipes and some small rivers with surrounding agricultural activities all draining nutrients into the basin, which add to the extremely intensive mussel farm production (with 30.000 tons/y) and the fishing-boat activity in both bays (Cardellicchio et al., 2007).

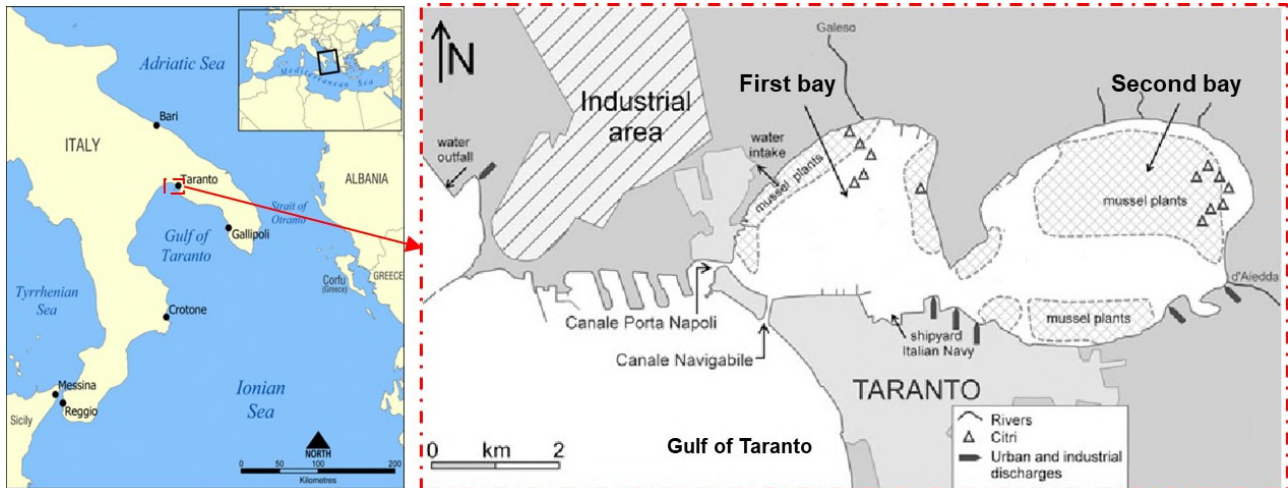


Figure 1. Sources of contamination individuated for Mar Piccolo of Taranto, south of Italy.

Numerous site investigations and research projects were carried out from 1995 to 2016 (ISPRA, 2010; Annicchiarico et al., 2011; ARPA Puglia, 2014; Vitone et al., 2016) showing the presence of numerous contaminants such as heavy metals (copper, zinc, mercury, lead, etc.) and several species of organic pollutants in the basin (Storelli and Marcotrigiano, 2000; Cardellicchio et., 2007, 2016). The most recent measurements were investigated in 2016, with the location of the boreholes shown in Figure 2 and described in detail in Todaro (2018).

In particular, high PAH concentrations were detected for a total of $6500 \mu\text{g kg}^{-1}$ and among them, pyrene, benzo[a]pyrene and anthracene showed the highest values in the sediments, with concentrations equal to 898, 519 and $695 \mu\text{g kg}^{-1}$, respectively. The values exceeded their respective regulatory threshold limits by over two order of magnitude (ICRAM, 2004; Ministerial Decree 56, 2009; Legislative Degree 152, 2006). The Italian regulatory threshold limit for pyrene is set to $5 \mu\text{g kg}^{-1}$ for soils in residential areas, while it is $50 \mu\text{g kg}^{-1}$ for industrial areas, also considered for

sediments (Legislative Decree 152, 2006). Benzo[a]pyrene, being more toxic, has lower limits corresponding to $0.1 \mu\text{g kg}^{-1}$ and $10 \mu\text{g kg}^{-1}$ for residential areas and industrial areas, while anthracene is not listed. In marine water bodies the threshold concentrations of the three PAHs are respectively equal to the limit indicated for benzo[a]pyrene correspondent to $0.05 \mu\text{g L}^{-1}$ (Ministerial Decree 56, 2009).

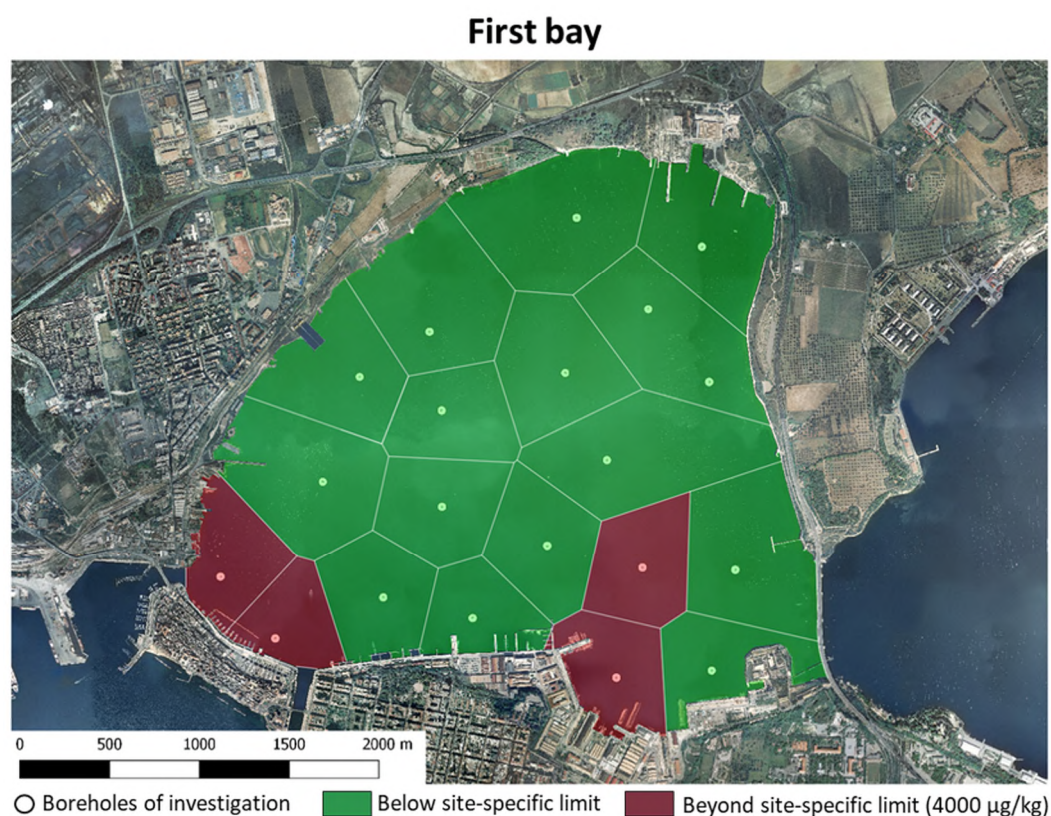


Figure 2. Area of investigation for the first bay in Mar Piccolo of Taranto, with representation of PAH concentration in the first 1.5 m below the seafloor, with reference to site-specific limits (ICRAM, 2004).

In recent years, PAH concentrations were also detected in mussels all over Mar Piccolo, ranging between 14.8 and $645.3 \mu\text{g kg}^{-1}$ wet weight. Among the compounds identified, there was a predominance of anthracene (peak of $501.0 \mu\text{g kg}^{-1}$ and average $64.7 \mu\text{g kg}^{-1}$ wet weight) and pyrene

(peak of $101.0 \mu\text{g kg}^{-1}$ and average of $18.4 \mu\text{g kg}^{-1}$ wet weight), while benzo[a]pyrene was detected in low concentrations that ranged from $3.1 \mu\text{g kg}^{-1}$ to $1.0 \mu\text{g kg}^{-1}$ (Storelli and Marcotrigiano, 2000).

2.2 Evaluation of short-term adsorption efficacy of two reactive materials

Lab-scale batch column tests were carried out to assess two reactive materials:

- a) AquaGate[®]+ 5% of Powdered Activated Carbon (AG PAC), made of composite particles coated with bentonite and PAC;
- b) Organophilic Clay Reactive Core Mat (OC RCM), a thin permeable composite mat with a layer of organophilic clay encapsulated between two geotextiles.

A control column with no cap (NC) was also tested to investigate how pollutants move through the sediment layer. AG PAC is a patented composite-aggregate consisting of small stones with a dense clay-sized aggregate core (10% by weight of sodium bentonite) and covered with fine-grained activated carbon additive (5% by weight) (AquaBlok Ltd., Toledo, Ohio). OC RCM is also a patented material commonly known as PM-199 (De Gisi et al., 2017).

Each column had a total height of 150 cm with an internal diameter of 15 cm and was made up of two sections of different length (50 cm and 100 cm) to facilitate the column handling and cleaning.

The thickness of the marine sediment layer from Mar Piccolo, h_{sed} , was 30 cm, with a marine water layer above, h_w , of 1 m for each test. A schematic representation of the columns is represented in Figure 2. The AG PAC column was capped with a 2 cm layer of Provect CH4[®] (Scalzi and Karachalios, 2013) and a 5 cm layer of AG PAC (h_{cap}) to increase the adsorption effectiveness of the ISC system. The 2 cm layer of Provect CH4 was used to inhibit the production of methane (Mueller and Booth, 2016). In contrast, the OC RCM column was capped with a single 0.6 cm layer of PM-199 (Figure 3). The thickness of both capping systems was calculated by reference to the target dose

recommended in the reactive product technical sheets and a literature review of the main case studies (Lofrano et al., 2017).

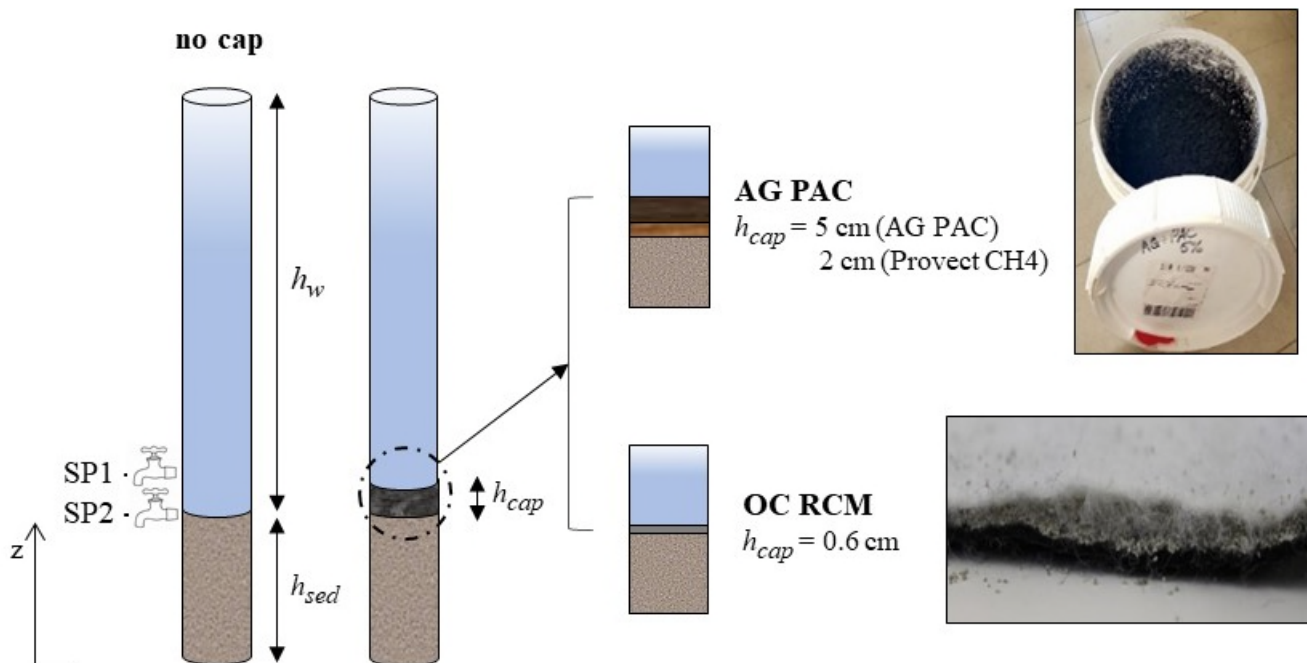


Figure 3. Schematization of experimental columns with the cap layer thicknesses (note: faucets represent the sampling points).

Prior to use, the wet sediments were homogenized after the removal of large debris and shells (particles larger than 2 cm) and transferred to an airtight container where they were stored in the dark at +4 °C. The experimental tests of the current study have been performed on a representative sediment sample made by mixing the most polluted specimens in the first bay of Mar Piccolo (Figure 2). Both sediments and seawater samples were chemically characterized with EPA standard method 8275A. The column experiments were set up following the same methods used by U.S. Army Corps of Engineers (1987) and several researchers (Gidley et al., 2012; Dixon and Knox 2012; Silvani et al., 2017). Pyrene, benzo[a]pyrene and anthracene concentrations were equal respectively to 898, 519 and 695 $\mu\text{g kg}^{-1}$ in sediments, and to 0.032, 0.005 and 0.039 $\mu\text{g L}^{-1}$ in seawater. For the determination of the total PAH concentrations, as well as each compound or homologue group, a Gas

Chromatograph - Mass Spectrometer (GC-MS, Thermo Scientific TRACE 1300) and EPA method 8275A were used. Furthermore, the sediment physical properties were measured and resulted in 19% of sand fraction, 43% of silt fraction, and 38% of clay fraction (ASTM D422) while the porosity was equal to 0.67, calculated from the void ratio (ASTM 2216). Once in the column, the water was added very slowly, in particular 0.02 L min⁻¹ for the first two liters and 2 L min⁻¹ for the rest of the column (Harris, 2005). This was achieved by using a peristaltic pump so as not to disturb the contaminated sediment, and carefully positioning the caps. Experiments have been carried out at ambient temperature.

Two sampling ports were inserted along the column height to sample the sediments and water which were located respectively at the sediment/water interface (z=30cm) (SP2) and at 40 cm from the bottom (SP1) (Figure 3). After a first characterization (t=0 days), PAH concentrations were measured after 5, 10 and 20 days, via SP1, while sediments were sampled at the end of the experiment, after 20 days. Further information is available in the study carried out by Todaro et al. (2018).

2.3 Numerical Model development

The numerical model has been parameterized and developed by following the experimental set up. The main equation, used to describe the transport of PAH dissolved pore water concentration in porous media over the time t , can be written as (Bear, 1979):

$$\varepsilon \frac{\delta C}{\delta t} = -\varepsilon \cdot v \frac{\delta C}{\delta z} + \varepsilon \cdot D_{eff} \frac{\delta^2 C}{\delta z^2} \pm R \quad (1)$$

where $C(z,t)$ represents the solute contaminant concentration ($\mu\text{g L}^{-1}$), ε is the sediment porosity (-), v is the pore water velocity (m s^{-1}), D_{eff} represents the effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) and R is the reaction term (Bortone et al., 2018). The adsorption/desorption phenomena occurring both in the sediments and the cap layers were described by substituting the reaction term, R , in Eq. (1) with the

kinetics of soil - liquid interaction, as shown in Eq. (2). (Di Natale et al., 2015, Minick and Anderson, 2017).

$$R = (1 - \varepsilon)\rho_s \frac{\delta C_s}{\delta t} = k_c a (C - C_{eq}(C_{sed})) \quad (2)$$

In Eq. (2), $C_{sed}(z, t)$ represents the concentration onto the sediments, ρ_s is the sediment density, k_c (m s^{-1}) is the mass transfer coefficient between water and particles, $C_{eq}(C_{sed})$ is the concentration in the pore water which is at equilibrium with the amount of sorbent uptake C_{sed} , a is the specific area of the sorbent particles and is equal to $6/dp$, where dp is the particle average diameter (mm).

The equilibrium concentration C_{eq} between solid and liquid phases can be described by several multicomponent adsorption models, whose complexity depends on the physical adsorption mechanism assumed. For the three conditions investigated in this study, the adsorption phenomena and C_{sed} were described by a linear and Freundlich isotherms, Eq. (3) and Eq. (4), respectively.

$$C_{sed} = K_D C_{eq} \quad (3)$$

$$C_{sed} = K_f C_{eq}^{1/n} \quad (4)$$

where K_D (L kg^{-1}) is the partition coefficient, while K_f (mg g^{-1}) and $1/n$ are respectively the Freundlich constant and exponent, whose values are listed in Table 2.

As described in Eqs. (2)-(4), the PAH adsorptive/desorptive flux over the time is a function of the mass transfer coefficient, k_c , and is driven by the dissolved concentration gradient between solid and liquid ($C - C_{eq}(C_{sed})$).

The computational domain was schematized as a 1-D multilayered system, taking into account the influence of gravity to describe the hydrostatic pressure in the column of water. Eq. (1) and Eq. (2)

were solved by considering the schematization in Figure 2 and assuming the following initial conditions in Eq. (5):

Initial conditions in the pore water and sediments

$$C(z; t = 0) = C_0 \quad 0 \leq z \leq h_{sed} \text{ and } z = h_w$$

$$C_{sed}(z; t = 0) = C_{PAH} \quad 0 \leq z \leq h_{sed}$$

Initial conditions in the cap layer

(5)

$$C_{cap}(z; t = 0) = 0 \quad z = h_{cap}$$

where the subscripts *w*, *cap* and *sed* denote parameters for the pore water and cap and sediment layers, respectively.

As shown in Eq. (5) a uniformly contaminated sediment layer was considered underneath the cap layer with no contaminant assumed in the cap. While the boundary conditions are listed in Eq. (6) (Reible, 2014).

Boundary conditions

$$\left. \frac{dC(z, t)}{dz} \right|_{z=0} = 0$$

$$-D_{cap} \left. \frac{dC(z, t)}{dz} \right|_{z=h_{sed}} = -D_{sed} \left. \frac{dC(z, t)}{dz} \right|_{z=h_{sed}} \quad (6)$$

$$-D_{sed} \left. \frac{dC(z, t)}{dz} \right|_{z=h_{sed}+h_{cap}} = k \cdot C(z, t)|_{z=h_{sed}+h_{cap}}$$

In particular, a no flux condition was assumed at the bottom of the sediments ($z=0$), while a continuous flux was considered through the layers, although different effective diffusion coefficients D_{eff} were assumed in h_{sed} and h_{cap} equal to D_{sed} and D_{cap} , respectively. At the top of the sediment layer

($z=h_{sed}$), in the no cap scenario, and the cap layers ($z=h_{sed}+h_{cap}$), respectively for the two capping scenarios analyzed, the flux was assumed to be dependent to the parameter k , which represents the boundary layer mass transfer coefficient ($m\ s^{-1}$), equal, in this case, to the pore water velocity, v .

For the scope, the fate and transport of PAHs within the cap system were investigated through numerical simulations by using COMSOL Multiphysics® as herein described.

The numerical solution of Eqs. (1)-(6) was performed using pre-defined modules respectively called “Free and porous media flow” and “Solute Transport” describing the advective/diffusive flow of contaminants into sediments, also under the gravity effect. In particular, Eqs. (2) and (3) were implemented via an *ad-hoc* user-defined physic adding the adsorption and desorption phenomena. All the parameters used in the simulations respectively for the sediments and water layer, and the two ISC scenarios analyzed, in case of pyrene, benzo[a]pyrene and anthracene, are listed in Tables 1 and 2. Specifically, Table 1 summarises the density ρ , permeability K and thicknesses h used for each layer, while Table 2 shows the values, for all layers in all scenarios, of the effective diffusion coefficient, D_{eff} , the partition coefficients, K_D , and the mass transfer coefficient multiplied by the specific area of the sorbent particles, $k_c a$.

The effective diffusion coefficient, D_{eff} , of pyrene in water was determined from Kim and Kwon (2018), while for both benzo[a]pyrene and anthracene from values listed in Eek et al. (2008).

The partitioning coefficients, K_D , for the sediment layer and each of the PAHs considered were calculated via the following equation Eq. (7).

$$K_D = K_{oc} f_{oc} \quad (7)$$

where K_{oc} (L/kg) is the organic carbon equilibrium coefficient and f_{oc} is the fraction of organic carbon. $\log K_{oc}$ values for each contaminant were obtained from US EPA (1996; 2012) while f_{oc} was equal to 5% and it was calculated by taking into account the sediments organic matter (OM) (Brady, 1984; Todaro, 2018).

Table 1. Sediment and cap geo-physical parameters for the three scenarios.

	ρ [kg m ⁻³]	K [m ²]	h [cm]
Water	1000	[-]	100
Sediments	1563.8	1.43E-17	30
AG PAC	1281	8.9E-11	7
OC RCM	500	8.9E-10	0.6

The mass transfer coefficient k_c , used to describe the desorption processes into the sediments as in Eq. (2), was calculated by using the equation suggested by Minick and Anderson (2017), dependent on a boundary layer δL (m) and a specific diffusion coefficient in water D_w (m²s⁻¹), which is function of the molar volume of the chemical V (cm³mol⁻¹) and the viscosity of water μ (equal to 10⁻² g cm⁻¹s⁻¹). Based on the study carried out by Minick and Anderson (2017), a δL of 2cm thickness was considered in this study for the calculations.

Table 2. Sediment and cap chemical parameters for the three scenarios tested.

	Compound	Water	Sediments	AG PAC	OC RCM
D_{eff} [m ² s ⁻¹]	Pyrene	6.62E-10	3.88E-10	7.74E-11	7.74E-11
	Benzo[a]pyrene	3.57E-10	2.09E-10	4.18E-11	4.18E-11
	Anthracene	4.57E-10	2.68E-10	5.35E-11	5.35E-11
K_D [L kg ⁻¹]	Pyrene	[-]	4769.75	$1/n=0.33$ $K_f=7.5E-3$ [μg kg ⁻¹]	286000
	Benzo[a]pyrene	[-]	19157.88	$1/n=0.44$ $K_f=0.0336$ [mg g ⁻¹]	3500
	Anthracene	[-]	974.48	$1/n=0.70$ $K_f=0.376$ [mg g ⁻¹]	36000
$k_c \cdot a$ [s ⁻¹]	Pyrene	[-]	6.4	[-]	[-]
	Benzo[a]pyrene	[-]	6.3	[-]	[-]
	Anthracene	[-]	7.7	[-]	[-]

3. Results and discussion

3.1 Experimental results

The measurement of the evolution of pyrene, benzo[a]pyrene and anthracene over the time in the three experimental columns, investigating a no intervention scenario (no cap) and in the case of using OC RCM cap and AG PAC cap, are presented both for concentration values in sediments (C_{sed} , μg kg⁻¹) and in water (C , μg L⁻¹), by also comparing them with the Italian regulatory threshold limits indicated in the case study description. Pyrene, benzo[a]pyrene and anthracene concentrations into sediments were measured for the three case scenarios, at t=0 and after 20 days, from the lower valve at the interface water/sediments (SP2) (Figure 5), whose values are listed in Table 3.

Measurements of the three PAHs into water were conducted, instead, from the upper valve of the column (SP1), respectively after 0, 5, 10, 15 and 20 days (in triplicates), whose average concentration values are shown in Figure 4. Specifically, in Figure 4, results were represented in blue in the case of no cap, and respectively in yellow and red for the AG PAC and OC RCM scenarios. The standard deviations of the concentration values were not reported in the figures, due to the potential

overlapping of the error bars. However, it is worth considering $\pm 5\%$ as an instrumental measurement uncertainty. Comparison of normalized concentrations (to the initial concentration C_0 , at $t=0$) obtained from both sediments and water sample measurements are summarized in Figure 5.

Table 3. Pyrene, benzo[a]pyrene and anthracene concentrations into sediments measured after a time of 20 days for the three scenarios tested.

PAH compound	unit	no cap		AG PAC	OC RCM
		t=0 day	t=20 days	t=20 days	t=20 days
Pyrene		898	770	743	288
Benzo[a]pyrene	$[\mu\text{g kg}^{-1}]$	519	597	315	236
Anthracene		695	376	279	149

As shown in Table 2 and Figure 4, in the case of no cap, 14% of pyrene sediment concentration (C_{sed}) was released into water after 20 days, determining an increment of the pyrene concentration in the pore water, which ranged from an initial value of $0.032 \mu\text{g L}^{-1}$ to a concentration of $0.053 \mu\text{g L}^{-1}$ (Figure 4a). Anthracene, also, increased from $0.039 \mu\text{g L}^{-1}$ to $0.079 \mu\text{g L}^{-1}$, while benzo[a]pyrene concentrations slightly varied to approximately $0.01 \mu\text{g L}^{-1}$. This is probably due to its reactivity to oxygen species, with the creation of its diol epoxides, the ultimate carcinogenic metabolites which bind to DNA, which were not measured.

With the use of both capping amendments tested, AG PAC and OC RMC, a significant reduction of concentrations into the upper water layer was detected, in the period observed, for all PAHs analyzed. Thanks to the combination of both physical and reactive barrier of both capping systems, pyrene, benzo[a]pyrene and anthracene were effectively adsorbed, by maintaining their concentrations lower than the regulatory threshold limit set at $0.05 \mu\text{g L}^{-1}$.

In particular, the highest reduction of contamination in water percentage was obtained with the AG PAC for benzo[a]pyrene (99%) and anthracene (72%), probably due to the higher specific surface of PAC and high pore availability, and because of the mixing with the inert material.

By considering contamination in sediments, OC RCM was the sorbent with the highest level of performance for all of the targets investigated, reducing sediment concentrations of pyrene by 68%, benzo[a]pyrene by approximately 32% and anthracene by 61%, respectively. These outcomes confirm the results in Knox et al. (2007) identifying OC material as among the best performers for organic compound control, which appears to be more effective for longer chain hydrocarbons. In addition, OC RCM's biggest advantage is the design, which provides a simpler placing method, also helping to preserve the sediment's natural ecosystem.

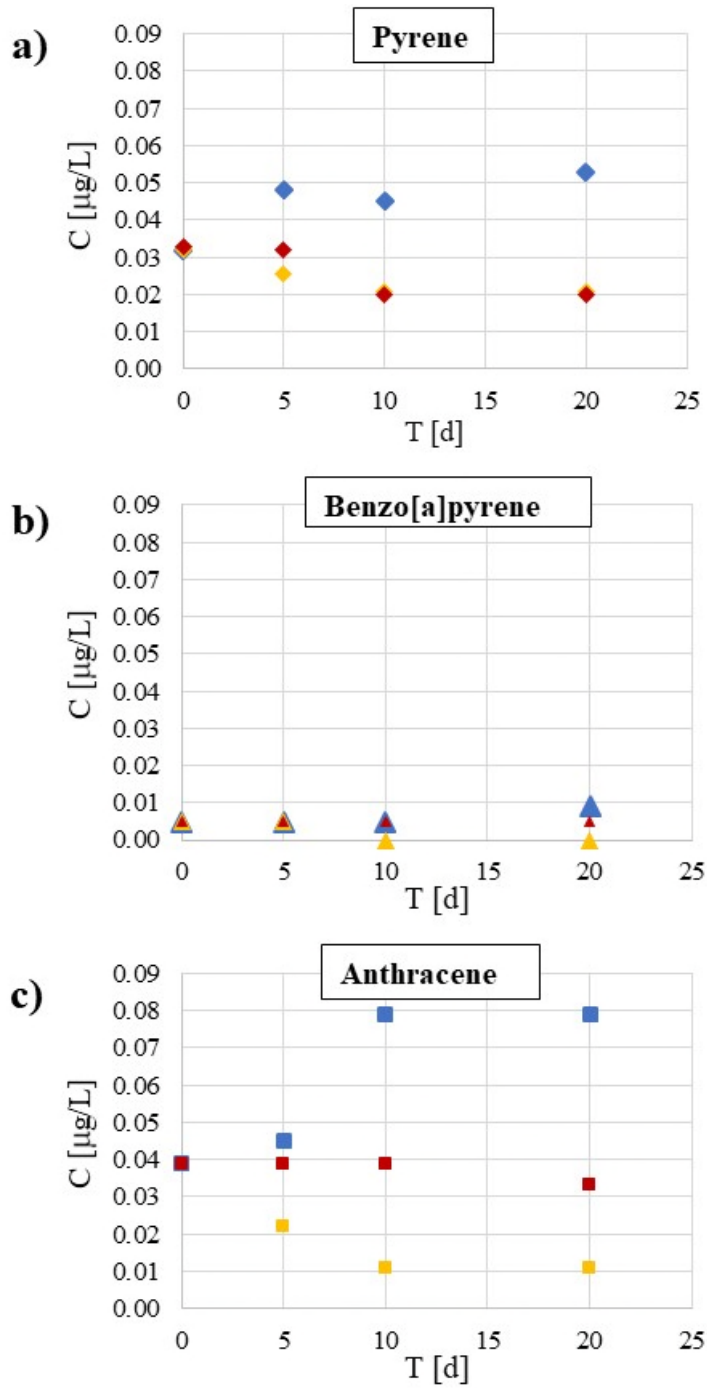


Figure 4. Pyrene, benzo[a]pyrene and anthracene concentrations into the water column measured after a time $t=0, 5, 10, 20$ days respectively in case of no cap (■), AG PAC (■) and OC RCM (■).

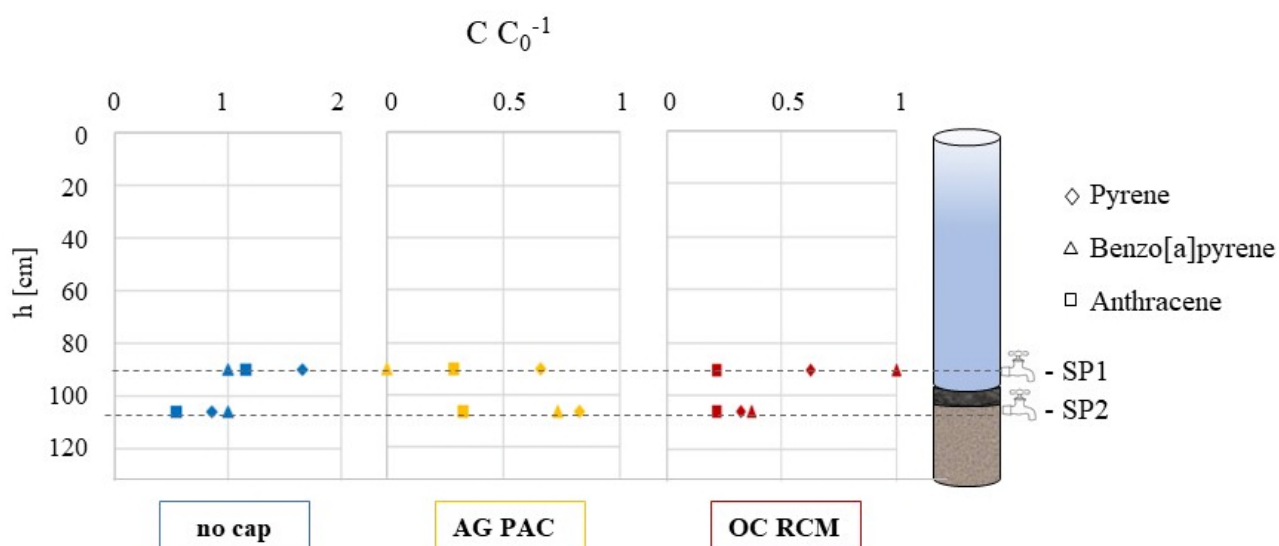


Figure 5. Comparison of pyrene, benzo[a]pyrene and anthracene normalized concentrations measured at the two sampling ports (SP1 and SP2) after a time of 20 days, respectively in case of no cap (■), AG PAC (■) and OC RCM (■).

3.2 Numerical results

A model in COMSOL Multiphysics® was set up to reproduce the results from the column experiments as closely as possible, by considering as input values the physic-chemical properties measured during the experimental tests, and taken from literature as described in Section 2.3.

The transport of the PAHs concentrations, from the multi-layered model to the upper water layer, was predicted by considering the phenomena of diffusion, advection and desorption in the sediments for all scenarios, and by adding the adsorption processes in the two cap materials tested, AG PAC and OC RCM. Based on the evidence of the experimental data, the diffusive/sorptive model was used to simulate the transient flux for the target PAHs over the time, both in the short and long term. A period of 20 days (short term) to model the long-term (≥ 12 months) behaviour of the different capping systems is in line with similar investigations (Silvani et al., 2017).

The advective pore-water flow was induced by a variation of the sediment layers, Δh , in the experimental columns for all scenarios, the effect of the consolidation of the contaminated sediment layer under the weight of an applied capping layer, h_{cap} or through the sediment adjustment in the

column (Kodikara and Rahman, 2002). The consequent velocity field was calculated according to the different Δh observed during the experimental tests (Table 3). The variations of the sediment layer measured in the columns for all scenarios are summarized in Table 4, where the consequent consolidation-induced advective velocities, v , are listed too. In particular, a total Δh of 0.8 cm in the case of the scenario testing AG PAC cap was observed, while the lighter weight of the OC RCM cap brought a reduction in the h_{sed} of 0.5cm.

Table 4. Depth variation of the sediment layer measured in the columns and porewater velocities for the three scenarios.

	time [days]	Δh [cm]	v [m s ⁻¹]
no cap lab	0-5	0.1	2.3E-09
	6-20	1E-7	1E-15
AG PAC lab	0-5	0.7	1.60E-08
	6-20	0.13	1E-09
OC RCM lab	0-5	0.5	1.35E-08
	6-20	1E-7	1E-15

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Results of the numerical simulations are depicted in Figure 6, where also a comparison with the experimental measurements are shown. The model outcomes were generated via a probe located at the same height of the sampling port into the water (SP1), i.e. $z = 40\text{cm}$ from the bottom of the column, consistent with the experimental activity (Figure 5). It was essential for the models to be calibrated in order to be considered reliable.

In order to assess the accuracy of the modelling process, the measured PAH concentrations and those predicted, of all scenarios, were compared by calculating their mean absolute errors (MAE), chosen as best fitting descriptor (Eq. (8)). MAE can be defined as follows:

$$\text{MAE} = \frac{1}{N} \sum_{n=1}^N |X - f| \quad (8)$$

where X is the actual outcome value at period t and f is the forecast value at period t . MAE values obtained are listed in Table 5.

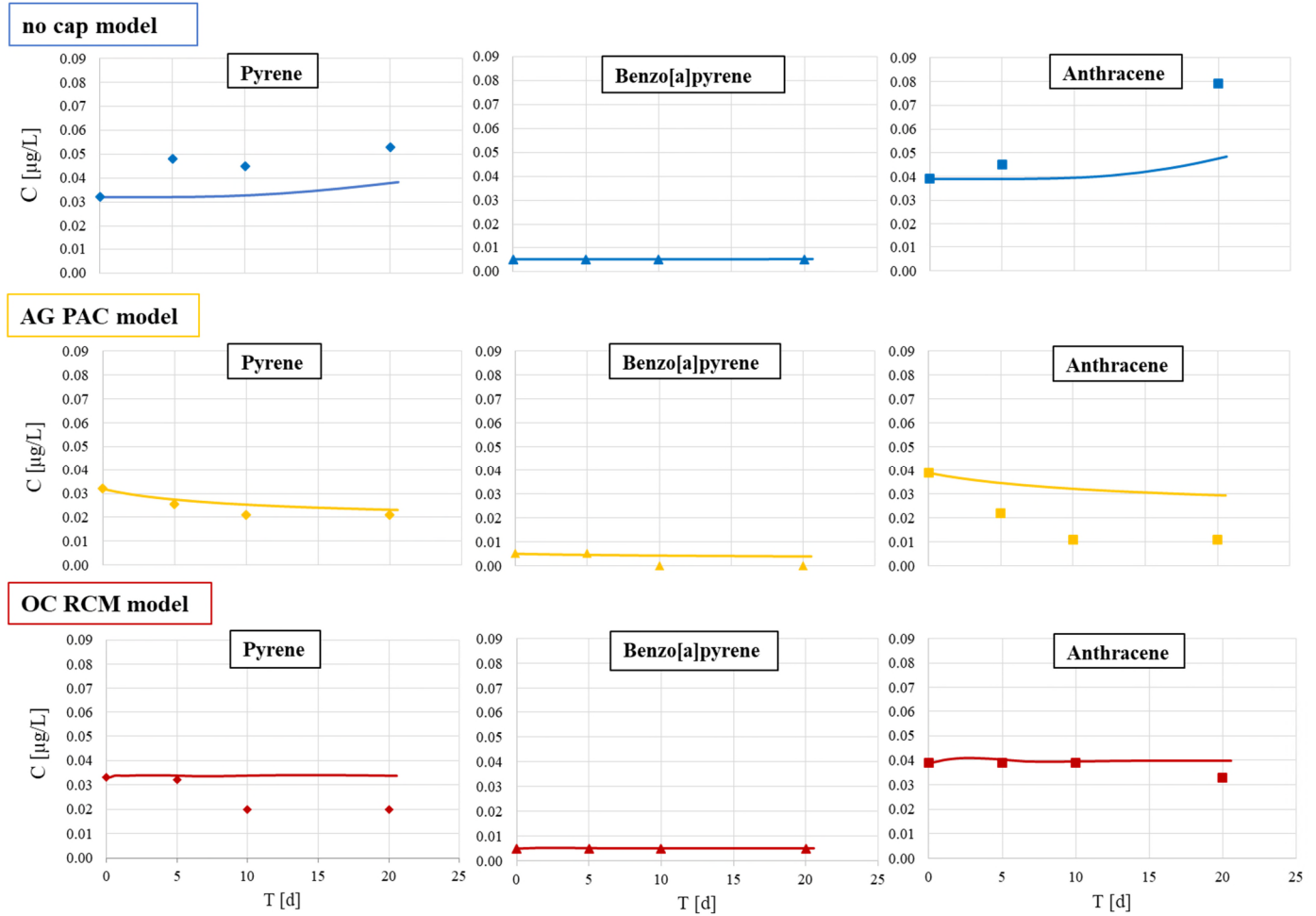


Figure 6. Experimental (points) and simulated (solid line) outputs for the three target PAH compounds investigated (no cap (■), AG PAC (■) and OC RCM (■)).

Table 5. Statistical indicator for the fitting quality evaluation between experimental and modelling data for the three conditions tested and for the different target PAHs.

	Scenario	Pyrene	Benzo[a]pyrene	Anthracene
MAE ($C \cdot C_0^{-1}$)	no cap	0.33	0.006	0.48
	AG PAC	0.06	0.43	0.33
	OC RCM	0.15	0.09	0.03

As can be seen from Figure 6 and Table 5, good agreements between the measured and the calculated concentrations were obtained, with MAEs equal to $\pm 10\%$, for all three PAHs in the case of OC RCM cap, pyrene in the case of AG PAC cap and benzo[a]pyrene in the case of no cap. Higher errors were instead collected for the remaining cases showing a lower accuracy of the numerical models compared to the experimental tests. This was possibly due to the competition and different PAH behavior occurring when more than two PAHs are present in a system, which has been shown to affect sorption of less hydrophobic PAHs (Wang et al., 2006; Khan et al., 2007), and to the necessity of a site-specific mass transfer coefficient (Yan et al., 2019). There has been no published experiment or paper showing the variation of both AG PAC and OC RCM adsorption parameters in presence of multiple contamination and PAH competitiveness. Consequently, future studies are required, in order to investigate Mar Piccolo's microscopic mechanisms and hydrodynamic phenomena influencing PAH desorption/sorption into sediments and their competitive behavior, and also when testing capping materials, such as AG PAC and OC RCM.

Finally, long term modelling was performed, in order to evaluate the transport of the three analyzed PAHs in the case of no cap and to guarantee the long-term efficiency of the ISC technologies tested. To this aim a 1-year simulation was carried out, whose profiles are shown in Figure 7. Results demonstrated that in the no cap scenario, as expected, PAH concentrations for all three compounds increase over the time, reaching high levels of contamination far in excess of the Italian regulatory limits in water. Conversely, both conditions with capping showed a long-term effectiveness over the time, guaranteeing the level of the threshold limit set at $0.05 \mu\text{g L}^{-1}$. Further experimental investigation is needed to determine if parameter-specific studies may influence differently the long-term effect of the intervention.

Figure 7. Concentration profiles, predicted via numerical simulations, after 1 year for the three target PAHs (no cap (■), AG PAC (■) and OC RCM (■)).

4. Conclusions

In this study, experimental column investigations and numerical modelling were developed in order to evaluate the effectiveness of different capping materials for PAH contaminated sediments. As a case study, sediments from a marine bay in the south of Italy were examined, where pyrene, benzo[a]pyrene and anthracene showed the highest concentrations among all the PAHs measured. Three scenarios were evaluated by comparing a “no cap” condition with the use of two different cap materials, and respectively, AquaGate® + 5% PAC (AG PAC) and CETCO PM-199 (OC RCM). The results demonstrated a good effectiveness of both AG PAC and OC RCM for PAH contamination treatment over the time. The best performance, in terms of higher contamination reduction in the water column, was given by AquaGate® + 5% PAC for the cases of benzo[a]pyrene and pyrene. In addition, a site-specific diffusive and advective pore water transport model was developed to describe the PAH flux and the desorption/adsorption phenomena occurring from the sediments through the multi-layered system to the water column. This was used to simulate the cap efficiency both over a short term of 20 days, validated by comparing the experimental tests, and in a longer term scenario of 1 year. The numerical modelling provided a decent fitting to the experimental data, indicating that the model assumptions were close to the experimental procedures. Although, for some cases, the curve fitting showed itself as being less accurate when the simulation period was increased. Conclusions of this research are as follows:

- Lab-scale experimental investigations, with site-specific matrices, seawater and sediments combined with numerical modelling are crucial to investigate capping efficiency for marine contaminated sediments.
- The physical and geochemical site-specific parameters have a significant effect on the calibration of the numerical model and representation of the capping performance over the long term.
- Mass transfer coefficients through the sediment and capping layers, obtained via specific field-studies, should be considered to properly describe and predict the contaminant release and capture.
- Possible PAHs competitive behavior or inhibition of adsorption occurs when testing ISC technologies in the presence of multiple contamination which needs to be accounted for and further investigated.
- Field observations and experiments investigating the PAH partitioning and concentration variation through the sediments and the cap layer in a long observation period (≥ 10 months) should be developed for a more accurate evaluation of the intervention performance and validation via numerical simulations.

It should be noted that this study has certain limitations: important factors, such as hydrodynamic phenomena, bioturbation, solute dispersion, degradation processes, site-specific solute sediment kinetics, temperature and pH effect and multiple contaminant competition were neglected in this study, which will be our aim in future studies. This would also allow a more accurate recreation of the site environment under investigation, and a better understanding of the PAH transport into sediments.

Acknowledgements

The experimental activities described were funded by the Special Commissioner of the Italian government for urgent measures of reclamation, environmental improvements and redevelopment of the Taranto area (South of Italy).

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Experimental investigations and numerical modelling of in-situ reactive caps for PAH contaminated marine sediments

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2019-11-21

Elsevier

<https://doi.org/10.1016/j.jhazmat.2019.121724>

Bortone I, Labianca C, Todaro F, et al., (2020) Experimental investigations and numerical modelling of in-situ reactive caps for PAH contaminated marine sediments. Journal of Hazardous Materials, Volume 387, April 2020, Article number 121724