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Simulating the fate of selected PAHs in Saronikos Gulf, Eastern Mediterranean, using a far-field water-quality model.

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Abstract: The aim of this study is to investigate the distribution of selected Polycyclic Aromatic Hydrocarbons (PAHs) and predict their fate in the marine area of Saronikos Gulf. A three-dimensional model (Delft3D-FLOW) was used to simulate sea circulation and hydrographic variables (salinity, temperature), for a 365-day simulation time period (year 2018). A water-quality model (Delft3D-WAQ), set at the same grid as the circulation model, was used to model biogeochemical variables and as a next step, simulate the occurrence and distribution of selected PAHs in the water column. The main pathways for PAHs entering the marine environment of Saronikos have been determined and set as discharges in the modelling area. The dispersion and transformation of PAHs has been simulated, and the predicted concentrations have been compared with published observational studies. The main processes determining the fate of target compounds have been evaluated regarding their contribution to the annual mass balances.

Keywords: PAHs, marine pollution, coastal environmental modelling, Delft3D, Saronikos Gulf

1. Introduction

Saronikos Gulf is situated in the Aegean Sea, enclosed by the north coast of the Peloponnese and the peninsula of Attica. It is adjacent to the capital of Greece, Athens, and is under high environmental pressure over the last decades, mainly due to the highly populated urban area, the industrial area of Thriassion Plain (oil refineries, shipyards, smaller scale factories), the wastewater treatment plant (WWTP) of Psyttaleia, and intense marine traffic (Paraskevopoulou et al., 2014). A large part of the area is subject to EU Directives (e.g. 2000/60/EC, 2008/56/EC, 2008/105/EC and 2013/39/EU), requiring measures and actions for the protection of the aquatic ecosystem and surveillance of chemical pollution. As a result of human activity, a number of chemical organic contaminants can be found at trace concentrations, in the marine area of Saronikos. In the present study, PAHs were selected to be the class under investigation, as they are a group of pollutants occurring from various activities (e.g. transportation) and constitute a hazard to human health and aquatic ecosystems (Terzi and Samara, 2005). The aim of this study was to create a modelling tool, able to reproduce levels of PAHs pollution and estimate the fate of target compounds, in the marine environment of Saronikos Gulf.

2. Materials and Methods

2.1 Target compounds

The following PAHs were chosen for simulation (see Table 1), Benzo(a)pyrene (BaP), Fluoranthene (Flu), Pyrene (Py) and Anthracene (Ant).

Table 1. Description of target compounds

Compound	Formula	M_r	Rings No
BaP	$C_{20}H_{12}$	252	5
Flu	$C_{16}H_{10}$	202	4
Py	$C_{16}H_{10}$	202	4
Ant	$C_{14}H_{10}$	178	3

2.2 Simulation area and time-period

The marine area of Saronikos Gulf was selected due to location, importance, and vulnerability to pollution. The year 2018 was selected (365 days of simulation, 6-hour timestep), as there are monitoring studies investigating PAHs distribution in seawater available for this time period. It is worth mentioning that most studies investigate the concentration of PAHs in the seabed sediment but not in the water column (dissolved phase). Therefore, field data for the validation of a model investigating distribution of target compounds in the water column are scarce.

2.3 Model description and implementation

To simulate the fate of the selected compounds in Saronikos Gulf, a three-dimensional hydrodynamic module (Delft3D-FLOW) was coupled offline with a water quality module (Delft3D-WAQ), both developed by Deltares.

2.3.1 Hydrodynamics

The implementation of the Delft3D-FLOW module (Deltares 2023) started with the definition of the computational domain. A curvilinear grid was developed (Figure 1), with a horizontal resolution varying from approximately 1400 m (at open boundaries) to less than 300 m (at Piraeus coastal area). Vertical discretization in the water column is achieved by 20 σ-layers. Hourly data from the ECMWF ERA5 database were used as atmospheric forcing fields: air temperature, air pressure, relative humidity, precipitation, cloudiness, net shortwave radiation and x- and y- components of wind velocity on a 0.25° x 0.25° grid (Copernicus Climate Climate Data Store). To determine the lateral oceanic boundary conditions (temperature, salinity, sea surface elevation), data from an implementation of the Regional Ocean Modelling System (ROMS) covering the Central - North Aegean were used (Mamoutos et al., article under preparation). The following freshwater sources were considered: i) Kifisos river, ii) Mandra and Sarantapotamos intermittent water streams (Elefsis Gulf), iii) WWTP discharges (Psittaleia and Thriassio). Their annual flow was determined using real time measurements (HIMIOFoTs), prediction tools (SMHI, platform Hypeweb) and open data (WWTPs online Monitoring Database).

2.3.2 Water Quality and Ecology

Making use of the WAQ module (Deltares, 2020a), the water quality and ecology of the selected area were estimated by simulating dissolved oxygen (DO), organic matter (POC, DOC, DON, DOP), dissolved nutrients (NH_4^+, NO_3^-, PO_4^{-3}, Si) and phytoplankton (Diatoms, non-diatoms). For the above-mentioned variables, the relevant processes were selected (Deltares, 2020b) and parameter values were determined according to the simulation area properties (oligotrophic, coastal seawater). Apart from internal processes that directly affect the levels of simulated variables, external sources were also taken into consideration. Nutrients and organic matter discharged by rivers and WWTPs were computed, by introducing the relevant concentrations in freshwater discharge streams. Atmospheric deposition as well as open-boundary interactions were taken into consideration. All fluxes were determined utilizing a large amount of information retrieved from publications, online databases (Copernicus Marine Data Store, WWTPs monitoring database, National Water Monitoring Network), and monitoring studies (HCMR). An article describing the methodology in detail is under preparation for publication.

2.3.3 Pollution

Once the water quality and ecology of the area has been adequately simulated, the selected PAHs (Table 1) have been introduced in the modelling study. The WAQ module has been used and each PAH has been modelled as an Organic Micro Pollutant (OMP), by determining its chemical properties accordingly (Deltares, 2020a; Deltares, 2020b). From the WAQ module, the following processes were selected as they strongly influence and determine the fate of PAHs in Saronikos Gulf: i) degradation (loss due to photolysis and biodegradation), ii) sorption to suspended matter and sedimentation, and iii) volatilization. To determine degradation rate, the following equation was solved for each computing cell of the grid in every time step.

$R_{deg} = k_1 deg_{20} \times k_t deg^{(T-20)} \times C_{PAH}$ (Deltares, 2020b)

where:

R_{deg} : degradation rate [g m^{-3} d^{-1}]

$k_1 deg_{20}$: first order degradation rate at 20ºC [d^{-1}]

$k_t deg$: temperature coefficient for degradation [-]

T : temperature [ºC]

C_{PAH} : concentration of selected PAH [g m^{-3}]

First order degradation rate was determined by taking into consideration that photolysis occurs in the first 2 m of the water column (Vaiopoulou et al., 2020), while biodegradation occurs in the whole water column (Table 2). Sorption to suspended organic matter was computed by providing the relevant partition coefficient (K_p) for each PAH (Table 2), while the settling of suspended matter was determined by WAQ (section 2.3.2).

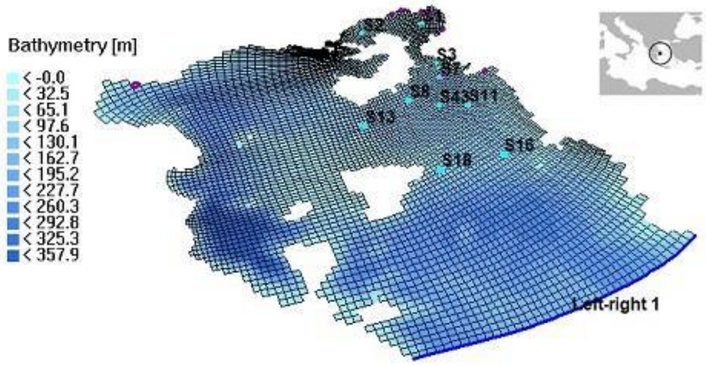

Figure 1. Saronikos Gulf computational domain, model bathymetry, Hellenic Center for Marine Research sampling stations network (cyan points) and locations of freshwater and/or pollution input (magenta points).

Volatilization rate was estimated by WAQ, using i) the concentration of each PAH, ii) the chemical properties of each compound (water/air partitioning coefficient) and iii) the temperature of water. Due to lack of data regarding the actual concentration of PAHs in the atmosphere, a background value was selected according to Terzi and Samara (2005). The transport of each pollutant was computed by FLOW output (2.3.1).

Table 2. Coefficient values related to process parameters.

PAH	K_1deg_{20} [a] <2m depth	K_1deg_{20} [a] >2m depth	Log K_p (l/kgC)[b]
BaP	2.11	0.0016	5.86
Flu	0.09	0.0036	5.10
Py	0.67	0.0024	5.04
Ant	3.94	0.0056	4.74

[a] Vaiopoulou et al. (2020), [b] Li et al. (2006)

The determination of pollution sources is crucial for the simulation of the fate of PAHs. As real emission data from the land (to the water or air) were not available, the possible pollution sources were determined through literature. The following point sources were introduced in the modelling area: WWTPs (Psittaleia and Thriassio), rivers and streams (Kifisos, Mandra and Sarantapotamos), and oil refineries (three oil refining complexes). Regarding WWTPs, the outflow concentration of each PAH was set according to measurements performed in similar plants (Wlodarczyk-Makula, 2005). River concentrations were set according to results from monitoring campaigns performed for Kifisos (National Water Monitoring Network). PAH mass loads occurring from oil refineries were determined according to permitted emission levels (Directive 2010/75/EU), as well as relevant literature (Hjort et al., 2021). Finally, mass loads occurring from atmospheric deposition were introduced, according to relevant studies (Terzi and Samara, 2005). As initial conditions for the simulation, a single value was used for the concentration of each PAH in the modelling area. This value was within the low range of recorded concentrations (Parinos et al., 2019). After a one-year spin-up, the spatially varying concentrations recorded on the last time-step of the simulation were used as the initial conditions for the next simulation.

3. Results

3.1. Model Performance

To ensure numerical correctness and stability, the associated error was quantified, and it was found to be lower than 1%, indicating very good model performance. The hydrodynamic simulation successfully reproduced the temperature and salinity fields (Kolovoyiannis et al., 2023). Additionally, water quality and ecological variables were within the range and fluctuation of field values.

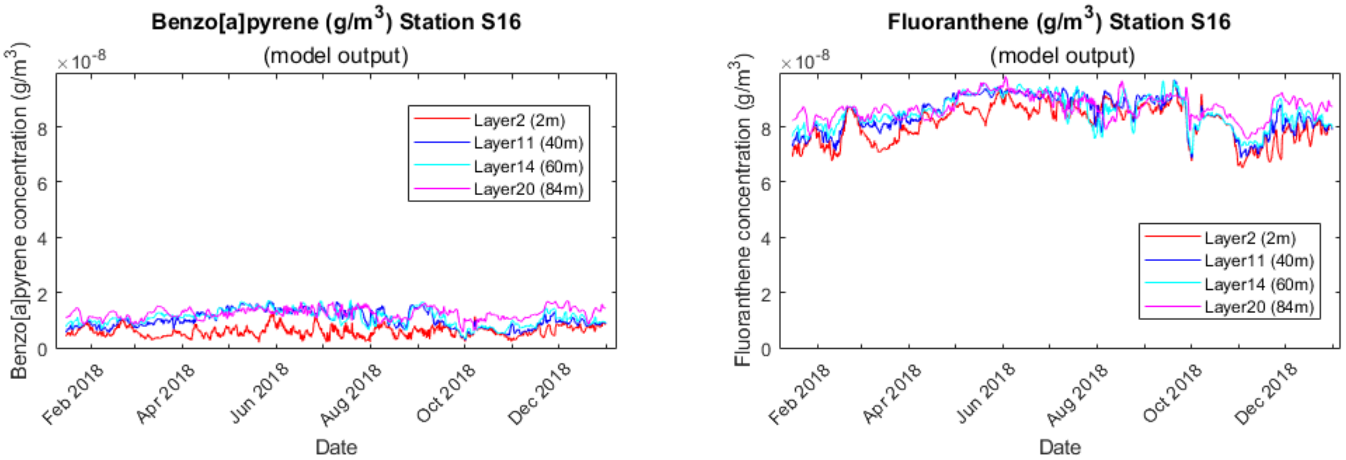

Figure 2. PAHs modeled concentration (g/m^3) at station S16 and four different depths (red line: 2m, blue line: 40m, cyan line: 60m, magenta line: 84 meters) for the year 2018, on the left for Benzo[a]pyrene and on the rigth for Fluoranthene.

3.2 PAH distribution and fate

Simulated concentrations of PAHs were higher in Elefsis (S1, S2), close to Psittaleia (S7) and Keratsini Bay (S3). Regarding vertical distribution, the concentration of each compound was slightly lower in the top layers (L1 and L2) and increased in the bottom layer (L20). Despite that, the vertical concentration was within the same range for each station and compound (see BaP and Flu at S16, Figure 2). For all monitoring stations and depths, the level of each PAH was below the level measured by Parinos et al. (2019), following the Agia Zoni II shipwreck (Figure 3, Station S11). The only exception was the bottom layer, for some cases, where Parinos et al. (2019) reported much higher concentrations. This could be attributed to higher pollution loads caused by the oil spill incident, or resuspension of surficial sediments, which was not taken into consideration in this simulation. Unfortunately, to the best of our knowledge, no further data for validation of the simulation are available. Regarding the fate of target compounds, the main process determining their concentration was degradation, with more than 80% of the mass being removed from the domain due to this process. Through the sedimentation process, a very small fraction of the total annual mass load ended up at the sediment layer (less than 1%). Volatilization seemed to play a minor role but for accurate prediction additional data are needed (e.g. atmospheric concentrations) in order to better simulate air/water interactions.

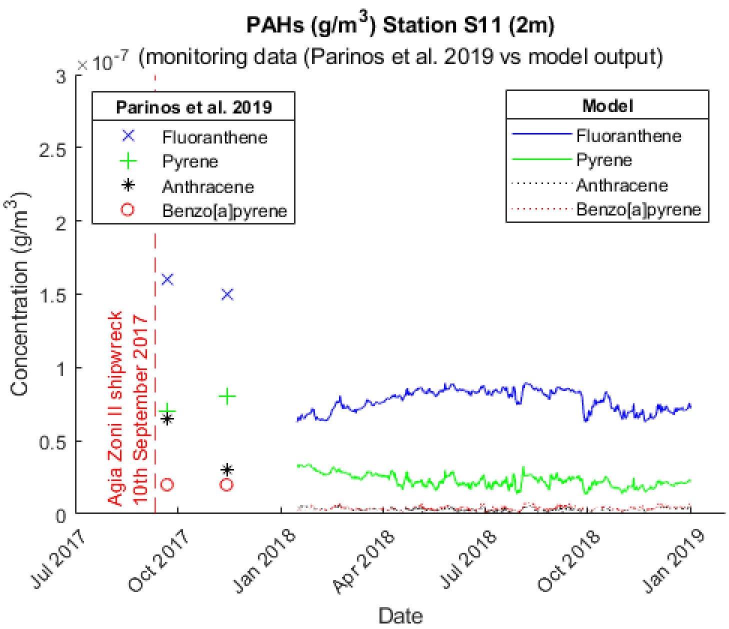

Figure 3. PAHs at station S11 (2 m). On the right side of the graph, the modeled concentrations (g/m^3) are displayed with a line, while on the left, monitoring values reported by Parinos et al. (2019) are displayed with a symbol. A dashed vertical red line indicates the date of Agia Zoni II shipwreck.

4. Conclusions

The present study describes a coupled hydrodynamic - water quality modelling approach for the simulation of selected PAHs in the marine area of Saronikos Gulf. With the present configuration, a baseline concentration for each compound is realistically reproduced, permitting the investigation of the cumulative effect of possible pollution scenarios (shipping pollution accident, land point source, increased shipping emissions). With the use of the presented modelling tools, and appropriate observational data, the fate of other pollutants can be predicted.

Acknowledgements

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