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PAH Modelling in the Niger Delta

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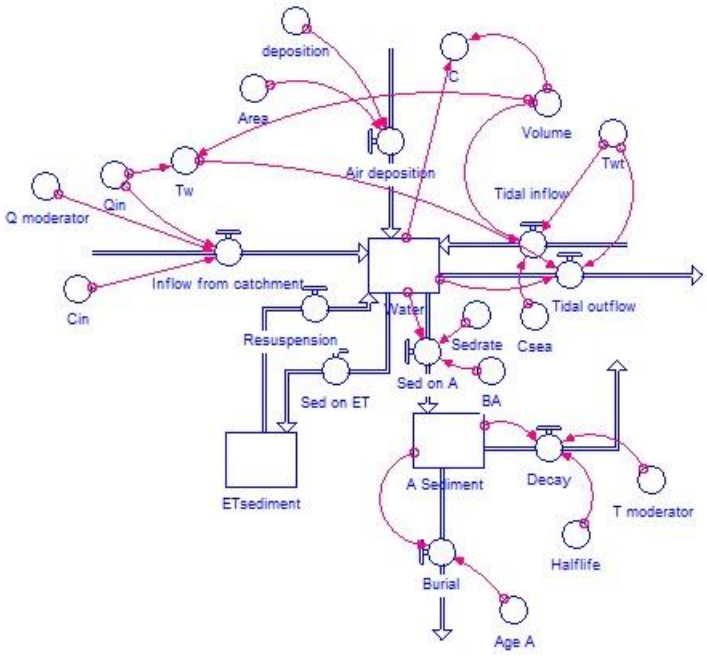

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Summary

Ogoniland in southern Nigeria has been subject to pollution from various oil activities for decades, leading to negative effects on human health and the environment, partly due to contamination of polycyclic aromatic hydrocarbons (PAH).

In the current study, we used a general process-based dynamic modelling approach to estimate the response time for the Niger Delta sediments to recover from previous contamination, by simulating a scenario where the upstream inflow from oil leakage ceased. The results imply that it would take about 15 years (Figure 3) for the system to reach a new steady state level reflecting the input solely depending on atmospheric deposition. The new steady state level corresponds to an average content of PAHs in the sediments of approximately 250 µg/kg dw, which can be considered as a naturally occurring background level. For PAH-compounds with higher molecular weight the decay rate is slower and the elimination time could be up to 35 years.

The results also show that in order to fulfil the mass-balance criteria for the chosen study area there must be a significant inflow of PAHs to the system of approximately 150 kg/month, most likely emanating from oil leakage from upstream the river delta and from the drainage basin. A major part of the PAHs entering the delta will be exported to the adjacent Gulf of Guinea, with a fraction of PAHs settling on the river bed. The present average PAH-contencentration in the top 10 cm level of the sediments of around 1 mg/kg dw corresponds to a standing stock of approximately 150 kg of PAHs in the sediment accumulation areas of the delta.

The results of our modelling efforts are uncertain due to the underlying assumptions and simplifications made and should thus only be regarded as indicative. However, they give an order of magnitude of the most important PAH-fluxes to, from and within the Ogoniland part of the Niger River Delta.

1 Introduction

As a result of decades of oil exploitation, Ogoniland in southern Nigeria has been subject to pollution from oil spills and oil well fires. This has had large impact on the regional environment, including soil contamination from crude oil, effects on vegetation (e.g. important habitats (mangroves, wetlands) and crops where invasive species take over), effects on the aquatic environment and on public health (e.g. contamination of drinking water, air pollution and dermal contact with contaminated matrices). In particular, the previous oil activities has resulted in contamination of hydrocarbons, including polycyclic aromatic hydrocarbons (PAH), some of them encompassing carcinogenic properties, which may pose long-term effects on the local environment and on human health (UNEP, 2011).

Apart from being components of crude oil, PAHs are also formed during incomplete combustion processes as well as during some industrial processes, and they are ubiquitous in the atmosphere as well as in aquatic environments. PAHs all consist of two or more ring structures, where at least one ring has the structure of benzene. Four examples of common PAHs are shown in Figure 1.

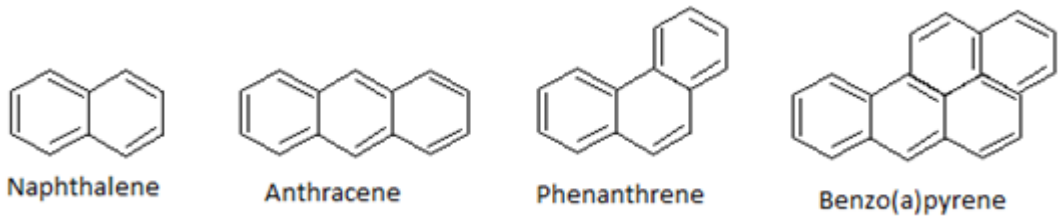

Figure 1. Molecular structures of four common PAHs.

PAHs in general are semivolatile, meaning that in air, they exist both in the gaseous and particle phase, the relative proportions being determined by the substance specific vapour pressure and the environmental properties. The 16 PAHs prioritized by USEPA are also among the most commonly monitored in the environment and include naphthalene (Nap), acenaphthylene, acenaphthene (Act), fluorene (Fln), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), fluoranthene (Fl), benzo[a]anthracene (BaA),

chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (IcdP) and benzo[ghi]perylene (BghiP), which have log K_{OW}-values between 3.4 and 6.5 (Mackay et al., 2006). Thus they are moderately to highly hydrophobic and will settle in sediments when released to the aquatic environment. As a consequence, a large part of the PAHs residing in the area (i.e. amounts remaining after the dominant transport to the Gulf of Guinea) due to release in connection with oil activities in Ogoniland are likely to reside in the delta sediments, where they may degrade or temporarily reside and be re-released to the surface water phase e.g. in connection with tidal flooding and/or heavy rains. To this date, no comprehensive picture has been gained regarding the extent of the PAH pollution and the ultimate fate of these substances in the aquatic environment of the Niger Delta, which is needed in order to make proper decisions on measures.

The current study aims to predict the elimination rates of PAHs in the Niger Delta by using a mass-balance model.

2 Material and Methods

2.1 Area description

The study area, Ogoniland is situated in the eastern part of the Niger River delta. Ogoniland covers approximately 10 % of the of the Niger delta area. The average discharge in the Niger River is around 5 600 m^3/s (Frenken & Faure's, 1997). Ogoniland covers around 1 000 km^2 of which roughly 20 % is water (UNEP, 2011). The tidal amplitude in the delta is around 1.5 meters. Physical characteristics of the study area are summarised in Table 1.

Table 1. Physical characteristics of the Niger delta in Ogoniland.

Parameter	Value	Source
Ogoniland area (km^2)	1000	UNEP, 2011
Area water (%)	20	UNEP, 2011
Average flow (Q) Niger River (m^3/s)	5600	Frenken and Faurès (1997)
Flow through Ogoniland (%)	10	Estimation
Average depth (m)	1	Estimation
Water residence time (days)	4	Calculated
Water volume (Mm^3)	200	Calculated
Water tidal residence time (days)	0.5	Calculated
Proportion of accumulation (A) areas (%)	15	Estimation

2.2 The model

We used a general process-based dynamic modelling approach originally derived and tested for organic matter dynamics in forested streams of British Columbia, Canada (Karlsson et al., 2005), which was further elaborated in Baltic coastal areas to mirror the turnover of dioxins (Karlsson et al., 2010). The first-order ordinary differential equations (ODE) that arise from the mass-balance were solved numerically with a time step of 36 hours using the modelling software Stella®. An outline of the model applied for the Niger Delta is given in Figure 2.

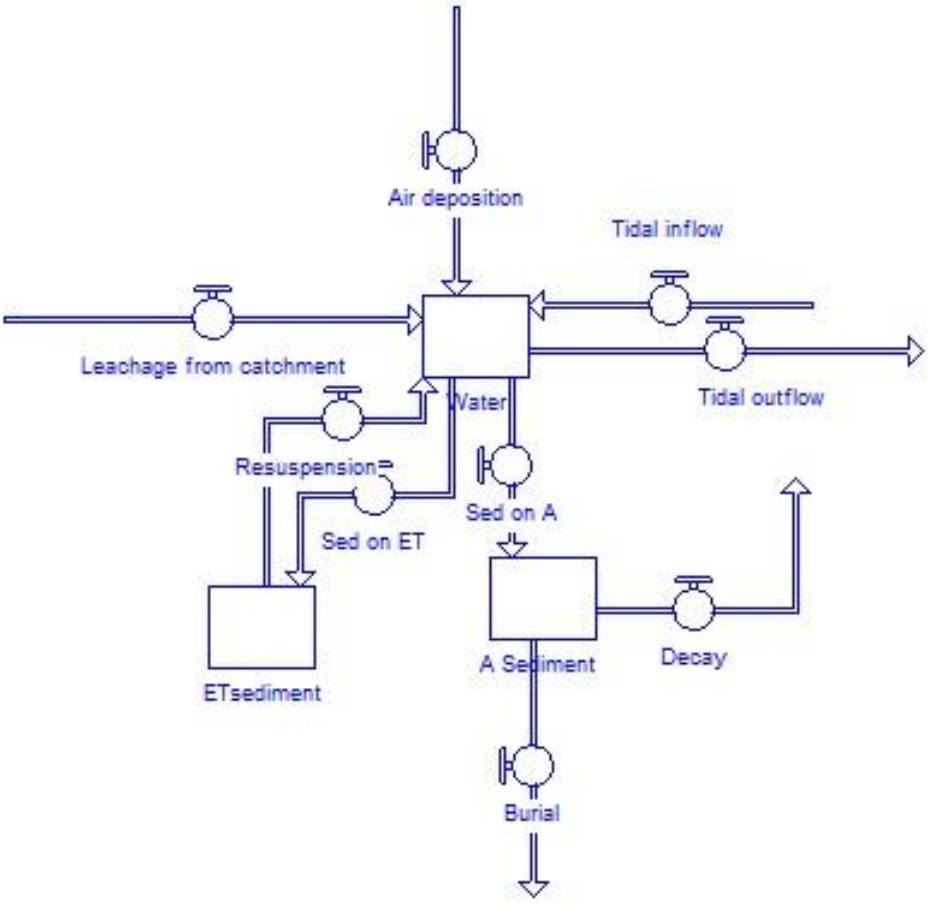

Figure 2. Outline of the model, where "Water" represents the total volume of the water body of the river delta in Ogoniland. "ET-sediment" represents erosion and transport areas where settling fine matter, by time will be resuspended. "A-sediment" represents accumulation areas with a net deposition of fine matter.

Fluxes of PAHs to the water body are assumed to emanate from oil spills in the catchment and from atmospheric deposition on the water surface. The daily water level fluctuations from tidal currents lead to water exchange between the delta and the adjacent sea, which creates a net outflow of PAHs.

PAHs, like many organic pollutants, have a strong affinity to particles. Due to gravity particles sink through the water column and may be deposited on the bed and banks of the delta (Lidén et al., 2001). In terms of sediment dynamics, the study area is subdivided into ET (erosion and transportation) and A (accumulation)-areas. ET-sediment represents erosion and transport areas where settling fine matter by time will

be resuspended. A-sediment represents accumulation areas with a net deposition of fine matter. Burial is the transport of PAHs from surficial A-sediments to sediment layers deeper than 10 cm. Decay represents the degradation of PAHs.

2.3 Parameterisation and model calibration

Lindén and Pålsson (2013) carried out extensive field measurements of water and sediment concentrations of PAHs in Ogoniland during 2010. These data were used to calibrate the model for the site specific conditions. Broman et al. (1991) measured background concentrations of PAHs in remote parts of the Baltic Sea. The levels from these measurements were used to estimate the background concentrations of PAHs in the sea adjacent to the Niger Delta and thereby the advection of PAHs through tidal water exchange. Atmospheric deposition fluxes were estimated based on observed deposition rates in Turkey, Taiwan and North America (Bozlaker et al., 2008; Fang et al., 2004; Franz et al., 1998; Odabasi et al., 1999), where a median deposition rate of 16 000 ng/m² day or 4.8×10^{-4} g/m² month for $\sum_{15}$PAH was applied.

Degradative reactions can be of several types; abiotic oxidation by e.g. ozone, photolysis, microbial degradation and metabolism by animals and plants (Neff, 1985). For modelling purposes, degradation rates are conveniently expressed as environmental half-lives (τ). The general picture is that the lower molecular weight PAH:s (e.g. naphthalene) have τ of days in the atmosphere, weeks in water, months in soils and about a year in sediments (Mackay and Callcott, 1998). The larger PAHs are quite persistent and thus have longer half-lives. Mackay et al. (1992) have suggested half-lives in sediments of three groups of PAHs (

Table 2). Table 3 summarises the numeric values of certain variables that was used in the model.

Table 2.Suggested half-lives (months) of three groups PAHs in sediments. Modified from Mackay and Callcott (1998).

PAH	Abbreviation	Half-life (months)
Naphthalene 1-Metylnaphthalene 2,3-Dimetylnaphthalene 1,4,5-Trimetylnaphthalene	Nap 1-MNap 2,3-DMNap 1,4,5-TMNap	4-14 Mean: 8
Acenaphthene Fluorene Phenanthrene Anthracene	Act Fln Phe Ant	14-42 Mean: 24
Pyrene Fluoranthene Chrysene Benz[*a*]anthracene Benz[k]fluoranthene Benzo[*a*]pyrene Perylene Dibenz[*a*,*h*]anthracene	Pyr Fl Chr BaA BkF BaP Per DahA	42-140 Mean: 80

Table 3. Numeric default values of model driving variables. Refers to sum of 16 PAHs as defined in chapter 1, unless otherwise noted.

Variable/process/rate	Value	Unit	Source
PAH average concentration in the Niger delta water (sum of 16 PAHs)	0.06	µg/L	Lindén and Pålsson (2013)
PAH average background concentration in sea water (sum of 16 PAHs)	0.0015	µg/L	Broman et al. (1991)
PAH average content in sediment (sum of 16 PAHs)	982	µg/kg dw	Lindén and Pålsson (2013)
Atmospheric deposition (sum of 14 PAHs[1])	4.8×10^{-4}	g/m^2 month	Estimated median based on Bozlaker et al. (2008); Fang et al. (2004); Franz et al. (1998); Odabasi et al. (1999)
Average half-life in sediment	24	months	Mackay and Callcott (1998)

[1]Includes Act, Fln, Phe, Ant, Fl, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, DahA, BghiP

Weather statistics including seasonal variation in precipitation and temperature (www.yr.no/place/Nigeria/Rivers/Port_Harcourt/statistics) were implemented in the model. However, since the impact on model performance was negligible when seasonal variation was taken into account this parameterisation was omitted from the final analysis. The model was calibrated following an iterative scheme assuming steady-state conditions and initial conditions from data presented by Lindén and Pålsson (2013).

3 Results

The results from the model simulations are shown in Table 4, where the calculated fluxes of PAHs to and from the Niger Delta in Ogoniland are presented, assuming the initial conditions given in Table 3 and steady state conditions.

Table 4. Calculated fluxes of PAHs to and from the Niger Delta in Ogoniland.

Flux	Value (kg/month)
Import	
Leakage from catchment	145
Atmospheric deposition	96
Tidal inflow	18
Export	
Tidal outflow	253
Sediment burial	1.3
Degradation	4.5

Figure 3 illustrates a simulated elimination of PAHs from the sediments in the Ogoniland part of the Niger Delta. The simulation is built up so that the leakage from the catchment ends at month 60 (5 years). A new steady state level is reached at approximately month 192 (year 18) reflecting the conditions when the import only consists of atmospheric deposition. Hence, one may conclude from Figure 3 that it would take approximately 13 years to fully eliminate the amount of PAHs in the sediments originating from oil spills.

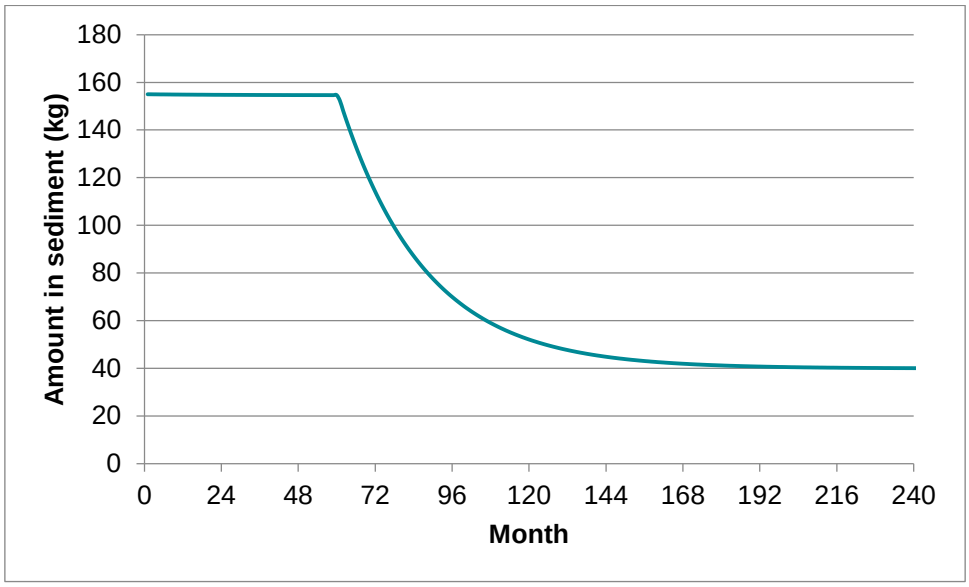

Figure 3.Simulated elimination of PAHs from the sediments assuming that the leakage of oil from he catchment ends at month 60.

It is apparent from

Table 2 that the degradation rate may vary for different compounds of PAHs. In Table 5 we estimate the time to eliminate different PAH compounds from the sediments. We also present the uncertainty around the prediction of elimination time based on the range of half-lives given in Mackay and Callcott (1998).

Table 5.Estimated time (years) to eliminate different compounds of PAHs from the sediments due to degradation and sediment burial. Values in brackets are estimated uncertainty intervals.

PAH	Elimination time (years).
Naphthalene 1-Metylnaphthalene 2,3-Dimetylnaphthalene 1,4,5 Trimetylnaphthalene	5 (4-8)
Acenaphthalene Fluorene Phenanthrene Anthracene	13 (8-17)
Pyrene Fluoranthene Chrysene Benz[*a*]anthracene Benzo[*a*]pyrene Perylene Dibenz[*a*,*h*]anthracene	20 (15-35)

4 Discussion

To estimate the response time for the Niger Delta sediments to recover from previous contamination, we have simulated a scenario where the inflow from oil leakage ceased. On average it would take about 15 years (Figure 3) for the system to reach a new steady state level reflecting the input solely depending on atmospheric deposition. The new steady state level corresponds to an average content of PAHs in the sediments of approximately 250 µg/kg dw, which can be considered as a naturally occurring background level (CCME, 1999). However, one must keep in mind that the degradation process not necessarily leads to a complete elimination of potential harmful substances since toxic metabolites may be formed (Neilson & Allard, 1998). For PAH-compounds with higher molecular weight (Table 5) the decay rate is slower and the elimination time could be up to 35 years. On the other hand, a study on PAH-contamination of

mangrove wetlands in China (Li, 2010) suggests a faster degradation in mangrove sediments compared to other environments due to high microbial activity.

The model was calibrated with initial conditions reflecting the PAH-levels in the delta that were found in the sampling campaign of 2010 (Lindén and Pålsson, 2013). The results show that in order to fulfil the mass-balance criteria for the chosen study area there must be a significant inflow of PAHs to the system of approximately 150 kg/month. It is reasonable to assume that this inflow emanates from oil leakage from upstream the river delta and from the drainage basin. A major part of the PAHs entering the delta will, through advection from water exchange, be exported to the adjacent Gulf of Guinea. However, a fraction of PAHs entering the system will settle on the river bed. The average PAH-content in the top 10 cm level of the sediments of around 1 mg/kg dw (Table 3) corresponds to a standing stock of approximately 150 kg of PAHs in the sediment accumulation areas of the delta.

The results of our modelling efforts are uncertain due to the underlying assumptions and simplifications made and should thus only be regarded as indicative. However, they give an order of magnitude of the most important PAH-fluxes to, from and within the Ogoniland part of the Niger River Delta.

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