

Polycyclic aromatic hydrocarbons (PAHs) in sediments of the amazon coast: Evidence for localized sources in contrast to massive regional biomass burning

Nikola Pichler, Fernanda Maria de Souza, Valdenira Ferreira dos Santos, and César C. Martins

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Michaela Vandermey

Literature Assignment

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Goal of research and analytical question:

The goal of the presented article is to evaluate the baseline concentrations of PAHs in a pristine Amazon coast zone in order to monitor anthropogenic activities such as deforestation, human occupation and mining. Therefore, the following analytical question was asked: What are the concentrations and major sources of 16 PAHs in sediment samples spanning the Oyapock estuary?

Introduction:

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds comprised of benzene rings arranged in linear and clustered arrangements. PAHs in general are volatile, have high melting points and low aqueous solubility, however they are very soluble in organic solvents (Abdel-Shafy and Mansour 2016). They are a group of environmentally ubiquitous and persistent compounds with various toxicities that impact both the human population and the environment. PAHs are formed during the incomplete combustion of organic materials, from both man-made and natural combustion sources (Abdel-Shafy and Mansour 2016) and are associated with pyrogenic sources (coal) as well as petrogenic sources, such as oil exploitation, oil spills and boat traffic emissions. Therefore, these compounds are easily detected in the air, soil and water and present a general concern to the global biogeochemical carbon cycle and to marine and terrestrial life.

Analytical method:

Sampling:

- Two sampling seasons were established at 23 sites along the estuarian gradient between French Guiana and Amapa Brazil: a wet season in May and a dry season in October. Samples were taken at each sampling site during both seasons. This sampling plan allows for discrete sediment samples to be collected at specific points and times.
- Sediment samples were considered to be any undisturbed surface sediment, the top 2 cm layer. Samples were acquired using a stainless-steel Ekman grab. This instrument allowed for consistent sampling of soft sediment free from any plants.
- The sediment samples were kept at -20°C and in sterile aluminum boxes to preserve the samples during transport to the lab.

Physiochemical parameters of the surface water:

- A number of parameters, including the pH, salinity, temperature and dissolved oxygen of the surface water, were analyzed at the time and place of sampling during each sampling season using a multimeter probe. This was done in order to classify and group the regions where each sample was taken and to note any differences in PAHs deposits in the sediment between the two sampling seasons.

Sample preliminary procedures:

- Sediment samples were freeze dried in order to remove all of the water present.

- Freeze dried samples were grinded using a mortar and pestle to get a fine, homogenous form for analysis.
- Ground samples were stored in clean glass bottles as the analyte of interest is organic and were kept at room temperature so that all samples were all kept in the same conditions until the next steps in the analytical method.

Sample preparation:

- A Soxhlet-extraction was carried out on the ground sediment samples for 8 hours using a dichloromethane (DCM) and n-hexane mixture (3:7, v/v). This was done in order to extract the organic layer in which the PAHs were in.
- A surrogate standards mixture comprised of deuterated PAHs was added to each sample as a quality check in order to determine the extraction efficiency of the method.
- The organic extracts were concentrated to approximately 2 mL by roto-evaporation to remove some of the solvent from the sample (reduce volume of solution).
- The concentrated extracts were submitted to a clean-up procedure in order to remove any interferences in the sample matrix that would cause problems for future steps.
- The analyte extracts were fractioned in glass columns with 15 mL of a DCM/n-hexane mixture (3:7, v/v), resulting in the elution of the PAH fraction.
- Before gas chromatography analysis, an internal standard was added to each sample for calibration and in order to quantify the analytes.

Instrumental analysis:

- PAHs were analyzed using an Agilent GC 7890A gas chromatograph coupled with a mass spectrometer with a triple-axis detector and capillary fused-silica chromatographic column.
- PAHs were identified based on the mass-per-charge ratio of the ion fragment from the mass spectrometer as well as from the retention times obtained from the standard mixtures.
- PAHs were quantified based on integrating the peak area of each individual PAH and a calibration curve.

Quality assurance:

- The quality assurance was based on extraction blanks and recoveries of the surrogate standard solutions.
- Procedural blanks were performed for each series of 7-8 samples.
- Extraction of three replicates of a standard reference material for sediments, supplied by the International Atomic Energy Agency, were performed in order to examine the method accuracy.

Critique of method:

The analytical question to be answered put forth by this paper was what are the concentrations and major sources of 16 individual PAHs in sediment samples spanning the Oyapock estuary?

The proposed analytical method accomplished the paper's goal as researchers were able to determine the concentrations of the 16 PAHs of interest as well as the main sources of the PAHs found in the sediment of the Oyapock estuary. These included petroleum, wood, oil and coal combustion as well as boat traffic emission and biogenic sources. In addition, it was concluded that as the concentrations of PAHs were very low, the Oyapock estuary was not contaminated with PAHs present in the sediment and thereby could be used as a reference site for monitoring other estuaries. The method also incorporated several green analytical chemistry principles. As PAHs are volatile and the proposed method used GC-MS, there was no need for derivatization. Additionally, in situ measurements of the sampling site's surface water were performed in order to determine whether the different sampling seasons had an impact on the concentrations of the PAHs and their distribution. Furthermore, the method's accuracy and quality control steps showed that the surrogate standard solution recoveries were within an acceptable range for extraction efficiencies and the results from the standard extractions were within range of certified values.

Although not specified, it appears that researchers may have used a judgmental sampling plan in order to select the 23 sampling sites as some were close to cities, while others were along the channel and closer to the open ocean. This was shown in the results as the sum of the individual PAHs were different between the identified inner, middle and outer sections of the area of study as well as between seasons. However, the researchers did not specify the sampling strategy used or the number of sediment samples collected at each site. It would make sense to

do grab samples and collect at regular intervals according to a predetermined plan (systematic sampling plan) in relation to the analytical question being asked. Moreover, there was no mention of any field, trip, method or instrument blanks, which could have been performed at the time of sampling, travel, sample preparation and GC-MS analysis. As well, the method did not enumerate any sieving or sub-sampling to achieve a smaller sample size in the lab after grinding. However, these missing steps may have been performed and not mentioned.

References:

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