

Using a biosensor to measure PAH concentrations in near real-time at the Money Point dredging site in the Elizabeth River, VA.

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Summary

An antibody-based biosensor for measuring dissolved polycyclic aromatic hydrocarbon (PAH) concentrations was used to monitor a PAH plume associated with a dredging project in the Elizabeth River, Virginia on June 9, 2009. PAH concentrations were very low (<10ppb) but the biosensor was able to document the gradient of PAH concentrations and the results were in good agreement with laboratory GC-MS data obtained from split samples. This validation exercise documented the successful PAH control measures, which limited PAH dispersal and also demonstrated the potential utility of this new analytical technology.

Background

The Elizabeth River Project (ERP) has targeted the Money Point area of the Elizabeth River for a remediation effort, beginning in 2009, to remove the most severely PAH contaminated sediments¹. This effort includes dredging of contaminated sediments, capping and wetland restoration. During the initial dredging portion of the restoration plan, phase 1, we planned to measure PAH concentrations in the water column near the dredging activity to monitor the effectiveness of suspended sediment and PAH control measures. VIMS has been developing a PAH biosensor as part of NOAA-CICEET funded research. This biosensor incorporates a PAH specific monoclonal antibody (mAb) developed at VIMS² and utilizes an advanced fluidics and UV detection system, the KinExA Inline Biosensor developed by Sapidyne Instruments Inc. (Boise, ID). This antibody-based technology has been used previously to quantify other contaminants at low concentrations in environmental water samples³. On June 9, 2009 the dredging project began and the PAH biosensor was employed to monitor dissolved PAH concentrations in the Elizabeth River (Figures 1-3.). A second monitoring effort took place on June 24, 2009 to evaluate PAH concentrations in the water column post dredging (Figure 4).

Methods

The KinExA Inline Biosensor was used on board the 21 foot VIMS research vessel, Oystercatcher. The biosensor was kept in the front cabin area and powered by 12 V car type batteries with an 110V power inverter (Figure 2). Testing has shown that this power source will provide enough power for a full day of remote sampling. The biosensor instrument was calibrated with standard solutions made up in advance with measured concentrations of the 3-ring PAH, phenanthrene. The mAb used for this field study

recognizes 3-5 ring PAH molecules. The range of detection for the biosensor is 0.3-10ug/L and when samples exceed 10ug/L, they must be diluted prior to assessment.

All sampling locations were determined by GPS and recorded in the field log. For biosensor analysis, water samples were collected using a 10ml syringe, immediately filtered (0.45 μm Teflon[®]) and transferred to a 30 mL amber glass vial. At seven of the sampling locations, additional water samples were collected in pre-cleaned 4L brown glass bottles and stored on ice in the dark. These samples were brought back to the environmental chemistry laboratory at VIMS and analyzed for PAHs by gas chromatography-mass spectrometry (GC-MS). Aliquots of the samples were filtered (47 mm, 0.45 μm Teflon[®]) and both a dissolved phase and an unfiltered “total” fraction were extracted and analyzed for a wide range of PAHs as well as benzene, alkylated benzenes and heterocyclic aromatic hydrocarbons.

Results

The biosensor was able to detect and quantify PAHs in all of the samples analyzed. The high temperatures (>95°F) on board the vessel during the June 9th sampling caused some problems with baseline drift on the instrument but it was still operational only with less precision. Samples were reanalyzed once back in the lab to verify field data. Cooling the reagents with ice during later field-testing alleviated this problem. The instrument is very sensitive with a detection limit below 1 $\mu\text{g/L}$ total PAH. Samples above 10 $\mu\text{g/L}$ 3-5 ring PAH require diluting. None of the samples analyzed on June 9 were above 10 $\mu\text{g/L}$ for dissolved 3-5 ring PAH so they were analyzed directly.

Subsequent GC-MS analysis of replicate samples at seven of the stations showed excellent agreement ($r^2=0.92$) between the biosensor and the six 3-5 ring PAH chosen for correlation (phenanthrene, anthracene, fluorene, chrysene, pyrene, and fluoranthrene). Total PAH concentrations (2-6 ring) also correlated ($r^2=0.91$) directly to the 3-5 ring PAH analyzed by the biosensor (Figure 5). Unfiltered and filtered samples were extracted and analyzed by GC-MS and were highly correlated to total suspended solids (TSS, Figure 6). PAH concentrations measured by the biosensor after dredging was completed (June 24) showed that no PAH gradient was detectable and that concentrations had returned to background levels (Fig 4).

Discussion

Overall, we have shown that the biosensor provided near real-time, on-site, dissolved PAH measurements during a dredging of PAH contaminated sediments at the Money Point area. The biosensor-determined PAH concentrations correlate extremely well ($r^2>0.9$) with total PAH and the 6 PAH determined by GC-MS. The strong correlations to both values are due to the weathered nature of these samples and therefore lack of 2-ring PAHs, which was confirmed by the GC-MS analysis. The lower molecular weight 2-ring PAHs are not detected by the biosensor, but if they were present, would contribute to higher total PAH concentrations. Therefore, the biosensor can be reliably used to estimate total PAH concentrations in weathered samples such as these.

By assessing total PAHs from filtered and unfiltered samples with varying TSS loads, it was demonstrated that the amount of PAHs dissolved in the water column was related to, but consistently lower ($40\% \pm 6\%$), than total PAH concentrations. Moreover, this demonstrates that by controlling the dispersal of resuspended sediment it is possible to limit the dispersal of particulate and dissolved PAHs during dredging. The installed underwater curtains that extended down to the riverbed contained the majority of TSS to within the curtained area, reducing the amount of PAHs entering the river.

Acknowledgments

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References

- 1) The River of the Future, Elizabeth River Restoration and Conservation: A Watershed Action Plan. 2008. 16 pp. The Elizabeth River Project, Portsmouth, VA 23704. www.elizabethriver.org
- 2) Spier, C. R., E. S. Bromage, T. M. Harris, M. A. Unger and S. L. Kaattari. 2009. The development and evaluation of monoclonal antibodies for the detection of polycyclic aromatic hydrocarbons. *Analytical Biochemistry*, 387, 287-293.
- 3) Bromage, E.S., G. G. Vadas, E. Harvey, M. A. Unger, S. L. Kaattari. 2007. Validation of an antibody-based biosensor for the rapid quantification of 2,4,6-trinitrotoluene (TNT) contamination in ground water and river water. *Environ. Sci. Technol.* 41, 7067-7072.



Figure 1. An overview of the Money Point dredging site on the morning of June 9, 2009. The dredge crane and barge are inside the orange oil boom/sediment curtain and the VIMS sampling vessel is outside the boom collecting water samples. Work on the constructed wetland is also visible.



Figure 2. PAH Biosensor on board the VIMS vessel analyzing water samples. Battery power was sufficient to run the biosensor all day. Very high temperatures on board ($>95^{\circ}\text{F}$) caused some baseline stability problems but cooling of the reagents with ice alleviated this problem.

Money Point Sampling (during dredging) – 9 June 09

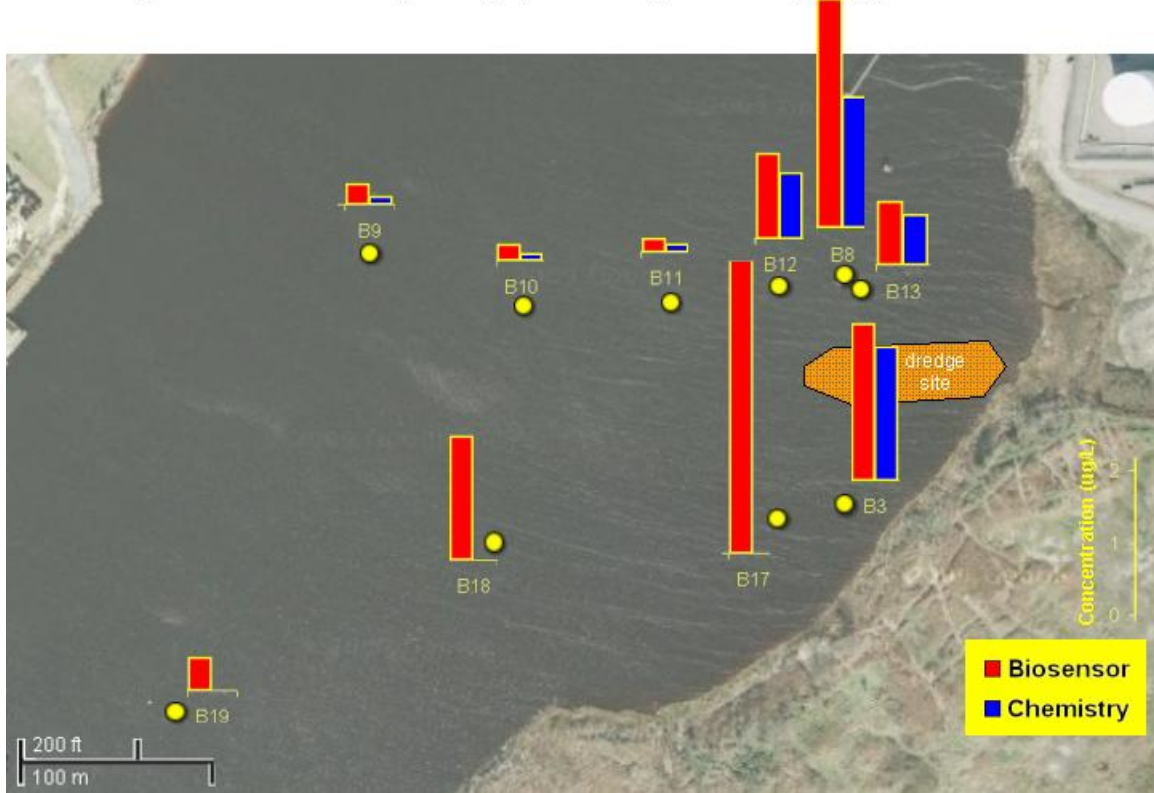


Figure 3. Real-time Monitoring of the PAH Plume with the Biosensor. The PAH concentrations determined by the VIMS antibody-based biosensor were able to define the plume of dissolved PAH (3-5 ring) associated with the remedial dredging project at Money Point in the Elizabeth River, VA. Data were available within minutes after sample collection and was reported to project engineers on shore via cell phone by scientists sampling in a boat. Biosensor data (red bars) correlated well with validation samples collected at 7 stations and analyzed by GC-MS (blue bars) for 3-5 ring PAH (also see Figure 5). The measured PAH concentrations were low (below 10 ppb) and demonstrated the success of control measures to reduce PAH releases. The biosensor was still sensitive enough to define a low concentration gradient in the water associated with the dredging of PAH contaminated sediments.

Money Point Sampling (after dredging) – 24 June 09

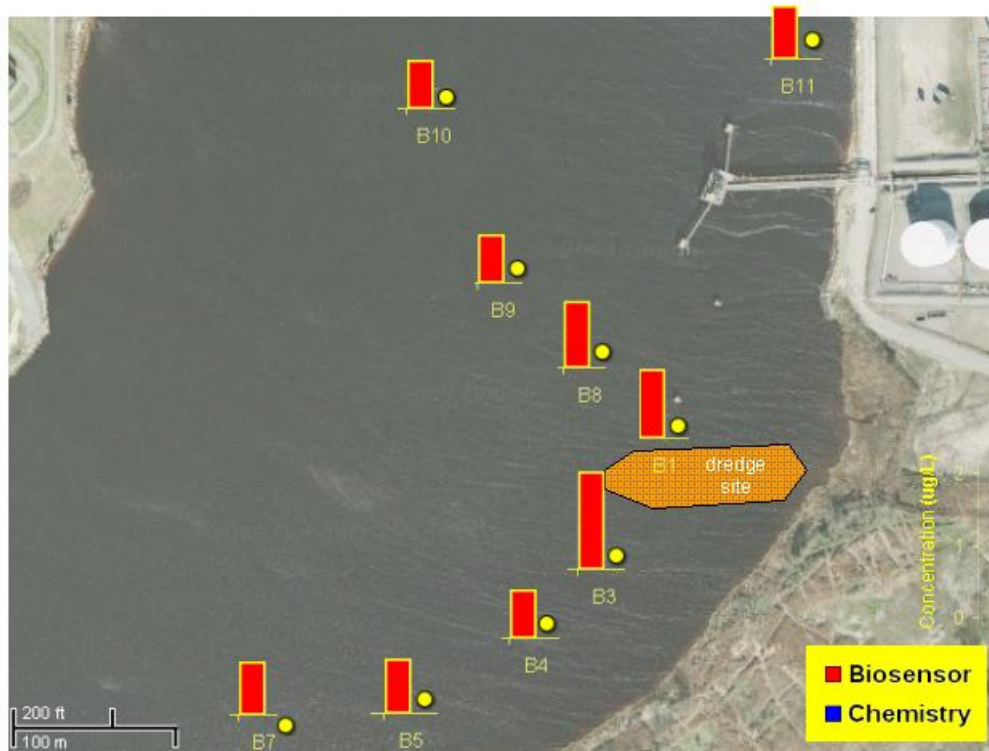


Figure 4. Real-time Monitoring of the PAH in the Elizabeth River at Money Point. Two weeks after the beginning of the remediation project (June 24, 2009), dredging was finished and the Biosensor monitoring showed the PAH concentrations at the dredge site were now equivalent to ambient concentrations in the southern branch of the E. River.

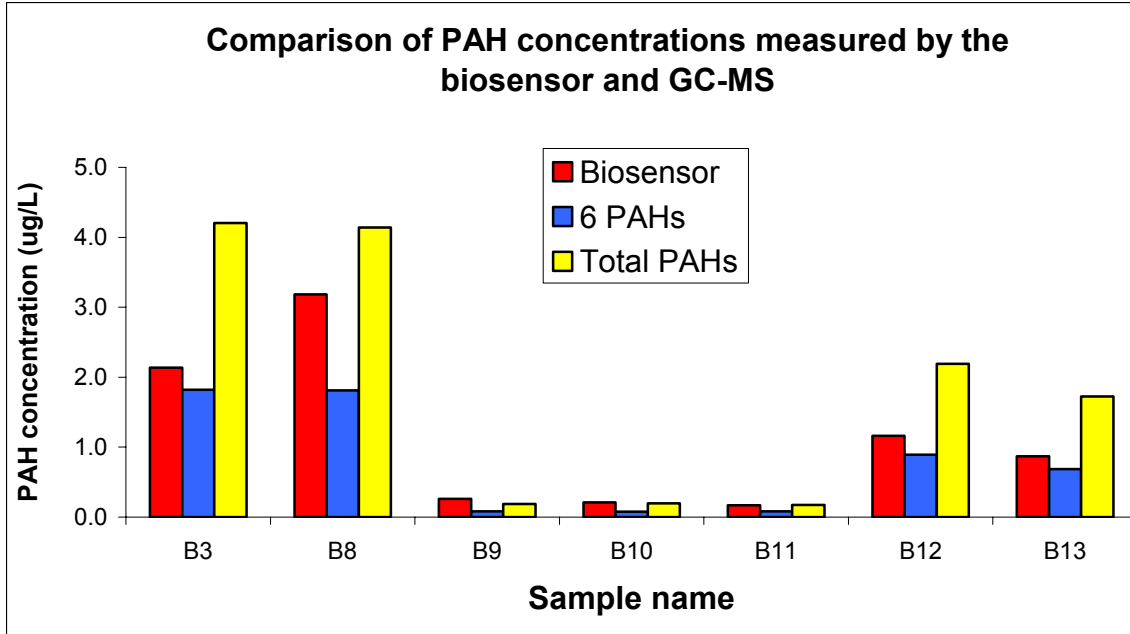


Figure 5. A comparison of PAH concentrations measured by the biosensor and GC-MS. There was good agreement between the dissolved PAH concentrations measured by the biosensor (3-5 ring) and six 3-4 ring PAH (phenanthrene, anthracene, fluorene, chrysene, pyrene, and fluoranthrene) summed from GC-MS results. This accounted for approximately half of the summed total dissolved PAH calculated from GC-MS data.

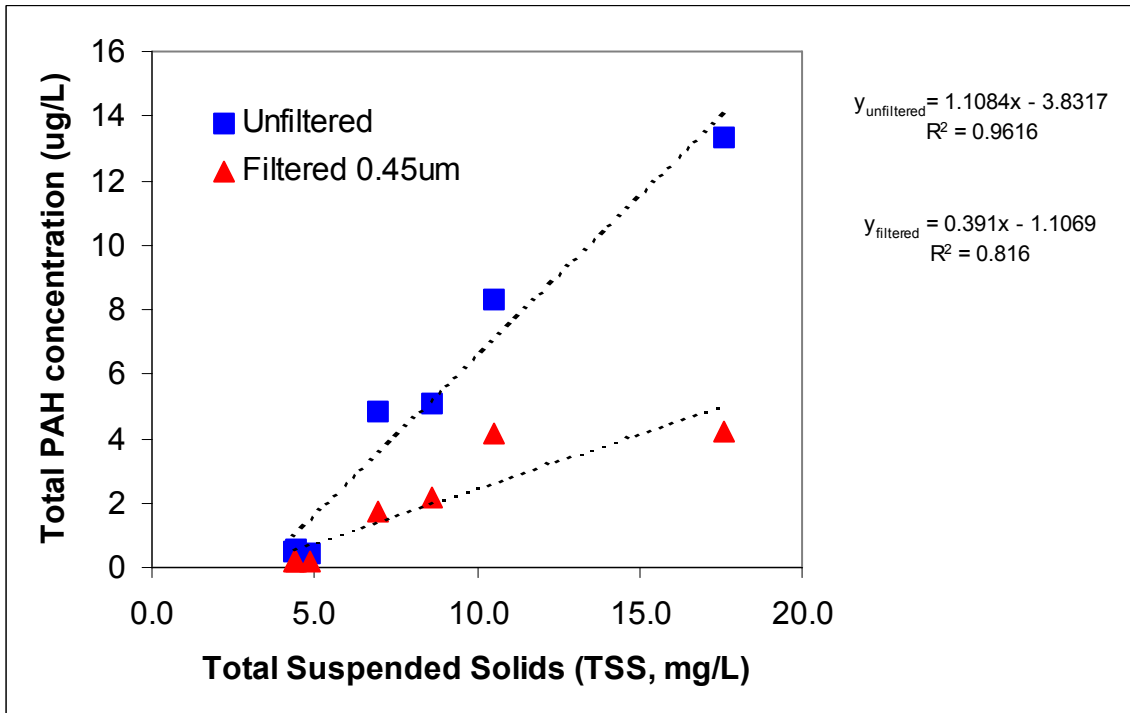


Figure 6. Relationship between TSS concentration and total PAH measured by GC-MS in filtered and unfiltered samples. Total TSS ranged from 4.4-17.6 mg/L at the 7 stations where high volume samples were collected for GC-MS analysis. Filtered and unfiltered total PAH concentrations were highly correlated to TSS. This demonstrates that sediment control measures will help to reduce the spread of PAH from the dredging area. Dissolved (< 0.45 μm) PAH concentrations averaged 40%(±6%) of the total PAH concentrations.