Development of an arrayed hydrocarbon sensing system for the detection of seeped hydrocarbons

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Hydrocarbon seeps in the marine environment are used as proxies for subsurface accumulations. Typically marine surveys to delineate these subsea features us a verity of techniques, which generally do not allow timely chemical identification of hydrocarbons. This paper outlines current research on the development of an integrated underway arrayed hydrocarbon sensing system that can be used on a variety of vessels to detect seeped hydrocarbons. The aim of the research is to increase the number of successful surveys through the deployment of this equipment. Field trials of the system have demonstrated its successful operation in the marine environment and testing of the hydrocarbon sensors have shown that the majority of the sensors used can detect dissolved hydrocarbons at ppb levels. Laboratory experiments using 23 oil-in-synthetic sea water extracts has shown that the sensor array has the potential to differentiate between oils (refined and unrefined) from different sources, based upon their seawater extracts.

I. INTRODUCTION

Hydrocarbon seeps can act as a direct indication of sub-surface hydrocarbon accumulations [1-3]. Marine surveys for the detection of hydrocarbon seeps typically use echo sounders, side scan sonar, multi-beam swath bathymetry, sub-bottom profiling, conductivity temperature depth (CTD) water sampling casts and sediment coring [4,5] to map and sample these features for exploration purposes. Water samples collected via CTD casts over areas identified as seepage features are subjected to analytical methods to distinguish thermogenic hydrocarbons from other hydrocarbon sources in marine waters. These include the use of headspace gas sampling or liquid-liquid extraction of hydrocarbons from waters, followed by gas chromatography and mass spectroscopy [6]. These methods can provide a detailed hydrocarbon fingerprint of the dissolved hydrocarbons present and when a distinct film is present the full range of petroleum compounds including petroleum biomarker compounds. These analyses are either performed onboard or post-survey in the laboratory. During water sampling there is often no chemical information available to verify that a valid sample has been captured and the analytical results are often acquired well after the survey vessel has left the survey area.

There are currently a number of commercially available hydrocarbon sensors for varied applications, including for the detection of PAH (polyaromatic hydrocarbons), BTX (benzene, toluene and xylene) and general volatile hydrocarbons [7] (Table 1). These devices use a number of detection strategies and vary in detection limits, response times and sensitivity to different hydrocarbon compound classes (Table 1).

Each of the hydrocarbon sensors alone cannot be used to fully reveal the composition of complex mixtures of dissolved hydrocarbons in the marine environment. By integrating sensors that are sensitive to different analytes, a more complete understanding of the composition of different classes of chemical compound can be obtained. Because the relative concentration of the dissolved hydrocarbon components can be correlated with the physical and chemical property of the oil (i.e., a high viscosity oil has higher proportions of volatile compounds and a low viscosity oil tends to contain more poly aromatic components), differentiation and identification of the oils and other hydrocarbon sources becomes possible based on sensor array's response patterns [8]. These instruments have the potential to provide timely and specific information on the hydrocarbons present in marine waters allowing valid water samples to be taken.

The use of such commercial sensors in concert with existing exploration techniques will allow potential seeps to be targeted for further detailed analysis, thus increasing the number of successful surveys acquired over areas of active seafloor hydrocarbon seepage. This paper outlines current research on the development of an integrated underway hydrocarbon sensing system that can be used on a variety of vessels.

TABLE I
HYDROCARBON SENSOR TYPES AND ATRIBUTES

Sensor	S1	S2	S3	S4	S5a,b	S6	S7
Application	PAH in marine waters			BTX in streams & ground water	Volatile hydrocarbons in water		Storage tank fuel alarm
Detection method	Fluorescence based measurement			Semi-conductor with partitioning membrane		Near-IR fibre optic probe	Hydrocarbon -sensitive conductive polymer
Detection limits*	10 ppt	100 ppt	100 ppt	0.5 ppm	0.5 ppm	1 ppm	Surface oil film

* Based on calibrant compounds. Analytes used (carbazole for S1 to S3, Toluene for S4 to S6)

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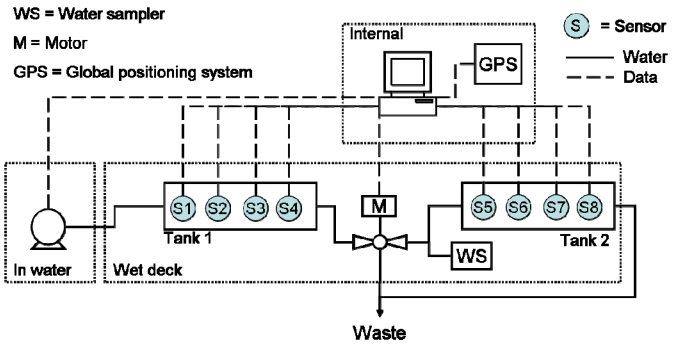
II. SYSTEM DESIGN AND INTEGRATION

The schematic representation of the system is outlined in figure 1. The hydrocarbon sensor arrayed system has been specifically designed to incorporate a large dynamic range in

Figure 1. *Simple schematic representation of arrayed hydrocarbon sensor system*



measurements and also to incorporate multiple detection methods. The sensor system comprises an array of three groups of hydrocarbon sensors that target volatile mono-aromatic hydrocarbons and poly-aromatic hydrocarbons at low concentrations, and oil films. These sensors are divided between two flow tanks based upon their response time; each sensor number corresponds to that found in table 1. The primary tank contains rapidly responding (within seconds) fluorometers and a gas semiconductor sensor with a partitioning membrane, whereas the secondary tank contains sensors with response times typically minutes in length. These sensors include a semiconductor with partitioning membrane, near infra red (NIR) fibre optic probe and a hydrocarbon sensitive conductive polymer sensor. The second tank is filled once the primary tank sensors reach a threshold value or can be manually triggered via the user interface. A water sample for conventional chemical analysis is also automatically collected during this operation.

In normal operation the flow tanks are continually supplied with water throughout the survey via a towed submersible pump connected to the tank by a chemically inert hose or can be connected directly to a ships seawater supply in the case of research vessels. An electrically-actuated valve is used to control water flow between the tanks.

Hydrocarbon sensor data is acquired with GPS coordinates and displayed in real time through an integrated graphical user interface. The software also includes georeferenced datalogging, diagnostics, pump and tank control. The software can be run on a laptop which can be situated at a distance from the flow through system which may be operated from deck of the survey vessel.

III. SYSTEM TESTING

The research activities were performed in three parallel phases to assess the performance of the system. For all of the testing stages the sensors were calibrated in the laboratory following manufacturers' specifications. Sources of organic contamination were kept to a practical minimum through the use of stainless steel components. The tank and fittings before each test were thoroughly cleaned with deionised water followed by wiping with ethanol. The ethanol was removed by either drying in the oven at 120ºC for a minimum of 1 hour or through the use of a heat gun to drive off any volatile organics from the surface of the tank. The synthetic seawater used in the experiments was prepared using the method of [9].

A. Phase 1 testing

A review and comparison of individual sensor was carried out in the laboratory by testing their responses to toluene or carbazole aqueous solution. The calibration results indicate under controlled operating conditions all VOC sensors selected have detection limits of sub ppm levels of toluene and all fluorometers used have sub ppb detection limits with carbazole (results not shown here).

B. Phase 2 testing

This phase of the testing was designed to evaluate the performance of the sensor array to detect and discriminate between hydrocarbon sources. All glassware used was where possible fired in a furnace at 500ºC or subjected to acid-base bath soaking overnight followed by drying in an oven for a minimum of 1 hour oven set to 120ºC. The tests were performed in a static measurement tank by exposing the sensor probes to diluted solutions of twenty three oil-in-synthetic sea water extracts in random sequence. Nineteen of those were produced from crude oils and four from refined oil products. The extracts were prepared using a method adapted from that of reference [10] which comprises the following:

A narrow neck 300 ml bottle is fitted with a length of 2mm id stainless steel tube and a magnetic stir-bar and positioned on a magnetic stirrer plate. The tube must be bent in a fashion that allows it to touch the bottom of the bottle, pass through the opening of the bottle and curve over the rim. The bottle is filled with 240 ml of synthetic seawater, onto which an aliquot of 16 ml of oil is carefully pipetted making sure that no oil forms droplets within the synthetic seawater. The bottle is then sealed with a pierced rubber septum (suba-seal) through which the 2mm stainless steel tube has been fitted. The exposed end of the steel pipe is also wrapped with parafilm to prevent gas exchange through the tube. The synthetic seawater is then gently stirred by the magnetic stirrer bar at a speed that does not cause any perturbation of the oil-water interface. Once this

has been set, the bottle is wrapped in aluminum foil to prevent photooxidation of hydrocarbon compounds. After 48 hours the magnetic stirrer is stopped and the now hydrocarbon saturated seawater extract is siphoned into a smaller 250 ml screw cap vial. The extract is siphoned to the second bottle by piercing the septum with a syringe needle and applying a positive headspace pressure to force the water through the stainless steel tube. Care must be taken that no oil is carried over into the second vial so only 210 ml of extract is removed from the first bottle. The oil-in-synthetic seawater extracts prepared in this way generally contain ppm to ppb level of dissolved low molecular weight hydrocarbons released to the lower water phase from the top oil phase as confirmed by previous GC analysis.

Sensors S1, S2, (S3 sensor response the same as S2) S4, S5a,b S6, S7 (S8 not available at time of testing) were placed in a sealed tank filled with 8L of synthetic sea water, equipped with a mixer to ensure the contents of the tank were instantaneously homogenized after each addition of liquid. 20-40 ml aliquots of the extracts were added at a time, with two 20 ml samples taken two minutes after each addition; one for subsequent liquid-liquid extraction with dichloromethane (DCM) followed by gas chromatographic analysis; the second for total scanning florescence and UV/Vis spectroscopy. The purpose of these sub-samples was to verify the actual concentration of hydrocarbons present in the tank after each addition of extract. The system was allowed to equilibrate for 30 minutes before proceeding to the next addition.

The same procedure was repeated until a total of 140 ml of the extracted solution was added to the 8 L tank. The sensor responses were recorded during the whole process. Several typical response curves are shown in figure 2. Following each addition of the extracted solution, most sensors showed stepwise increases and then reach the response plateau with response time varied from seconds to minutes.

Sensor S7 does not respond to hydrocarbon solutions at low concentrations but only to oil films. Sensor S6 based on NIR detection only gave a predictable response to pure toluene solution and petrol solution. This may be due to its relative high noise level and competitive adsorption of multiple analytes on the sensor membrane. Due to the lack of a reliable response the data generated from these sensors were excluded from subsequent data analysis.

Preliminary data analysis has been performed using Principle Component Analysis (PCA) (The Unscrambler, CAMO Inc.) to characterize the extract samples and find the relationship between sensor output and the oils. Sensor data was preprocessed with baseline correction, data centering and normalization prior to analysis. The resultant variance curve indicates that four Principal Components (PCs) are required to explain 93% of the variance in the data, with PC1 = 48 % variance; PC2 = 36 % variance; PC3 = 5 % variance; PC4 = 4 % variance. The score plot of principal component 1 and 2 illustrates the similarities and differences between oils and refined oil products (Figure 3).

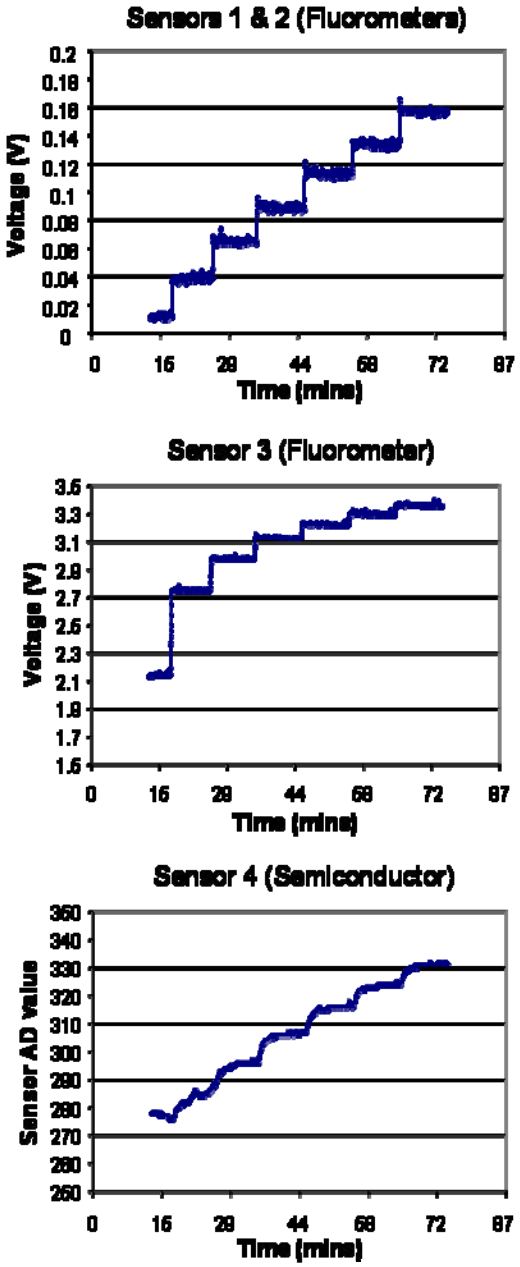


Figure 2. *Serial additions of 20 ml aliquots of dissolved crude oil extracts in synthetic seawater solutions into a 9 litre tank (equivalent to 9 ppb additions of dissolved hydrocarbons).*

Figure 3 shows that for PC1 & PC2 scores the refined oil values occur toward the extreme edges in of the scores plot. In particular petrol forms a distinct cluster that can be clearly distinguished from the other oils. Similar plots of PC1 and P3 results show a similar relationship (not shown).

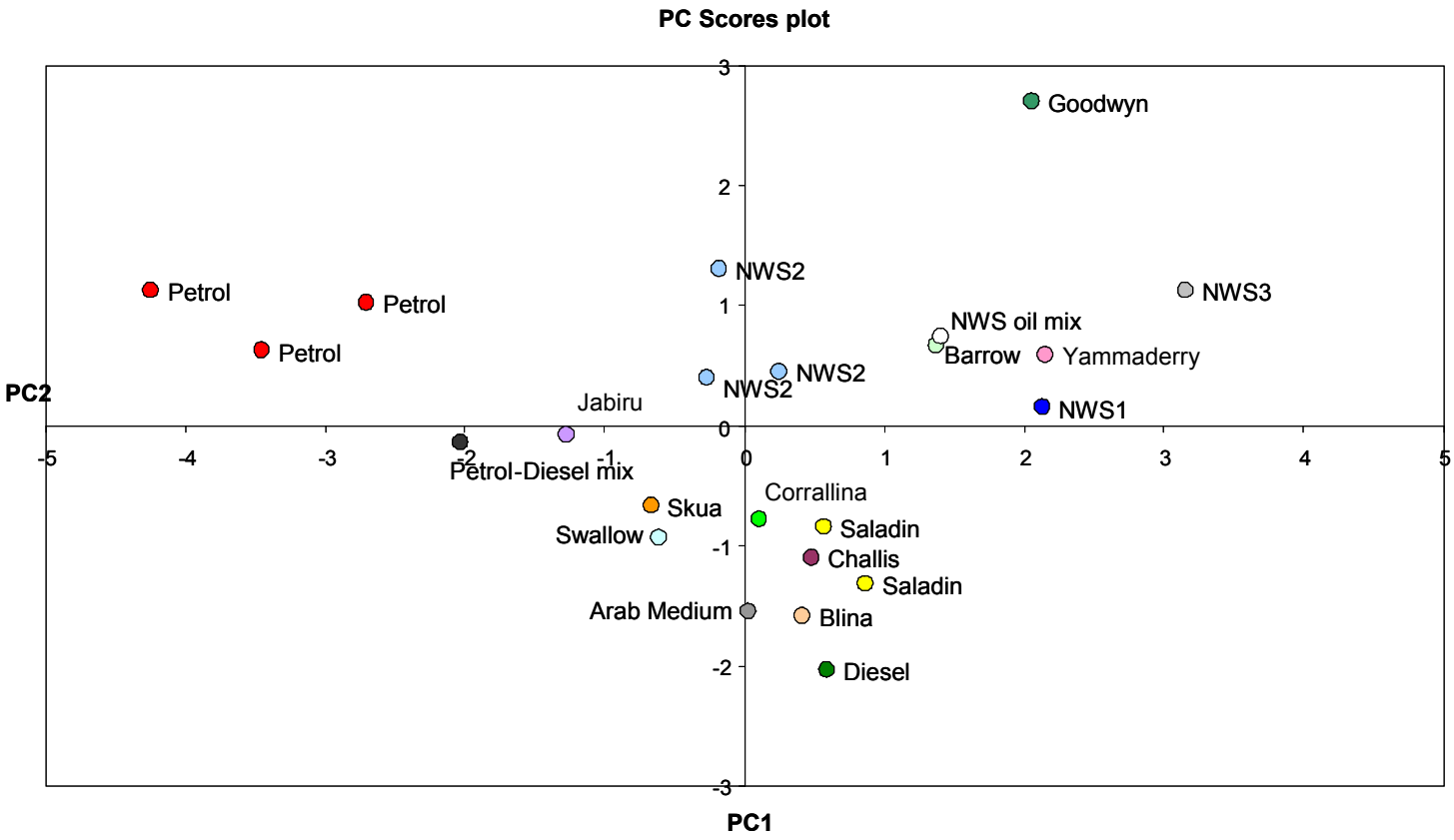


Figure 3. *PC1 and PC2 (84% variance) scores data for the 23 oil and refined oil products. Petro-1,-2,-3 are repeats of petrol extract experiments. NWS2-1, -2, -3 are repeats on an unaltered Australian North West Shelf oil.*

There is a relatively wide spread in the repeat values obtained for both the refined (petrol) and also a representative Australian North West Shelf oil (NWS2). This is attributed to sensor drift over the duration of the experiment.

The loadings principal component plot (Figure 4) shows the various weighting of each sensor contribution to each principal components variance. The figure shows that for PC2 all of the sensors appear to be affected nearly equally, however PC1, PC3 and PC4 are all differentially affected by either particular sensors or sensor types. For PC1 the loadings are dominated by the response of the flourometers over the semi-conductor sensor responses. This would suggest that this PC is partially reflecting the poly-aromatic hydrocarbon composition of the oil extracts. PC3 and PC4 are dominated by the response of particular semiconductor sensors and this may partially reflect the interaction between these sensors and particular volatile or BTX hydrocarbons within the extracts that are partitioning across the sensor membranes, however further work is required to fully understand the interactions.

C. Phase 3 testing

Three field investigations were conducted in the Perth coastal waters aiming to test the system stability, make further improvements and establish the baseline levels.

These tests were successful with over 10 hours of sensor data logged and consistent cruising speeds, in calm waters, of 8 knots were achieved. As a result of these tests improvements have been made on data synchronization, sensor auto initialization, GPS output format and display, to enhance user operability.

The only minor problems occurred when the borehole pump was lifted to the sea surface and the pump inlet was no longer submerged. Improvements to the weight and towing position have been suggested for improved sampling of surface water in the future.

A marine survey in collaboration with Australia's Marine National Facilities Southern Surveyor vessel was scheduled in late March with the aim to approach some potential seep sites in the Great Australian Bight and operate the system

continuously for 9 days. Early results will be presented at the conference.

IV. Conclusions

The detection of hydrocarbon seeps is of interest to the oil and gas industry as it provides evidence of subsurface accumulations. The development of an underway arrayed sensor system has the potential to efficiently identify these sites in order that more detailed surveying and analyses can occur.

The hydrocarbon sensor array system that has been developed has demonstrated long term operational stability in field trials in both, Perth Coastal Waters and the Great Australian Bight, for detection of hydrocarbons in water. The sensor responses have been characterised for the dissolved hydrocarbons for both oils and commonly occurring contaminant refined oils, and the dissolved hydrocarbons can typically be detected within the ppb range of concentration for the more sensitive instrumentation.

Preliminary PCA data analysis of twenty three oil-in-synthetic sea water extracts serial addition experiments has shown the potential for the sensor array to distinguish between natural oils and common contaminants and has defined importance of particular sensors within the array, however further research is required to fully understand the system capabilities and performance.

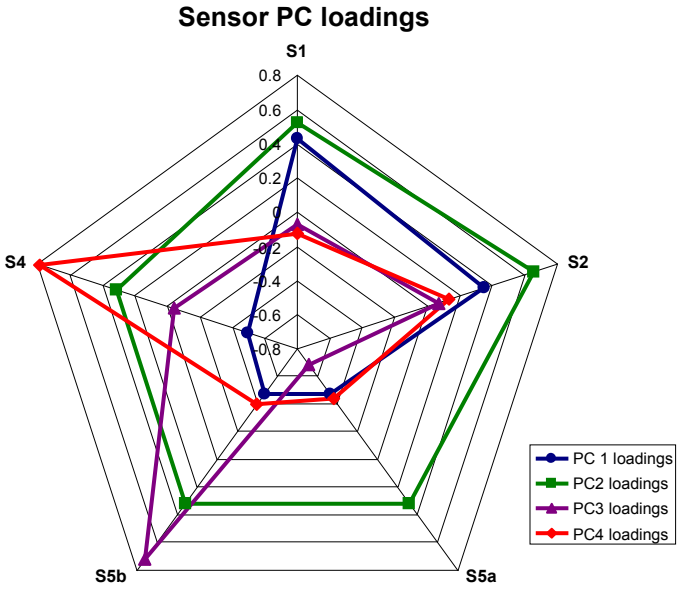


Figure 4. PCA loadings *data for S1, S2,S4 S5a,b sensors showing the relative weightings of each sensor response on each of the principal components.*

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