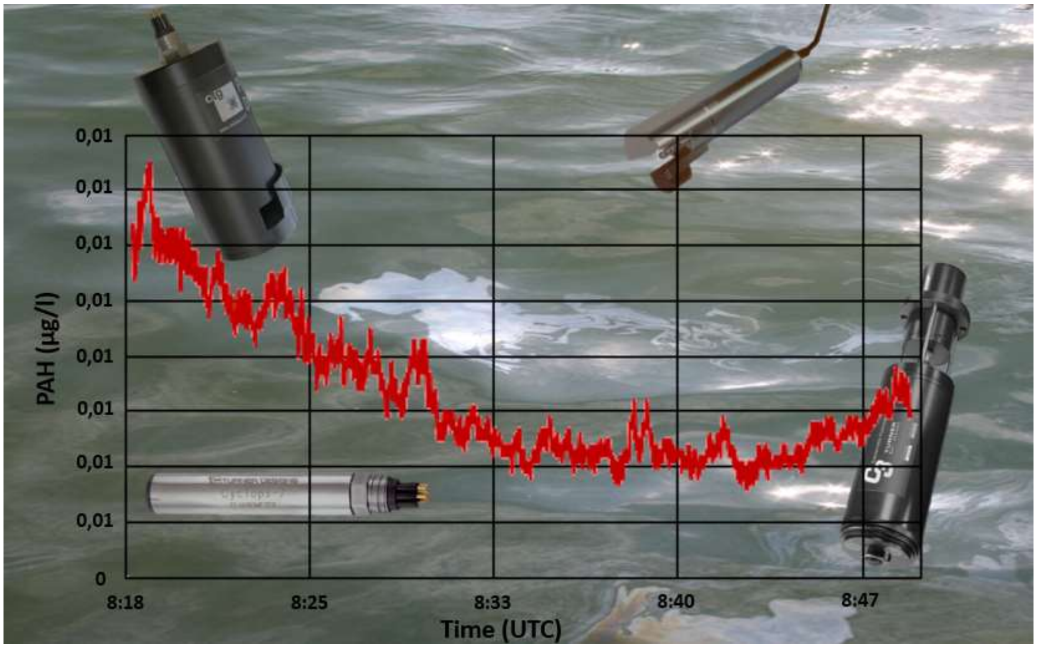
GRACE grant no 679266

In-situ oil detection sensor – technology overview and experiment design

D1.1

WP1: Oil spill detection, monitoring, fate and distribution



Prepared under contract from the European Commission
Contract n° 679266
Research and Innovation Action
Innovation and Networks Executive Agency
Horizon 2020 BG-2014-2015/BG2015-2

Project acronym:	GRACE
Project full title:	Integrated oil spill response actions and environmental effects
Start of the project:	01 March 2016
Duration:	42 months
Project coordinator:	Finnish Environment Institute (SYKE)
Project website	http://www.grace-oil-project.eu

Deliverable title:	In-situ oil detection sensor – technology overview and experiment design
Deliverable n°:	D1.1
Nature of the deliverable:	Report
Dissemination level:	PU
WP responsible:	WP1
Lead beneficiary:	Tallinn University of Technology
Due date of deliverable:	31.10.2016
Actual submission date:	31.10.2016

Deliverable status:

Version	Status	Date	Author	Approved by
1.1	Draft	21.10.2016	Siim Pärt and Tarmo Kõuts, TUT	WP1 members 24.10.2016
1.2	Final	24.10.2016	Siim Pärt and Tarmo Kõuts, TUT	Steering group 28.10.2016

Table of Content

Executive Summary

Deliverable 1.1 describes the basic hydrocarbon chemistry and oil in water sensing technologies generally. As UV fluorescence is nowadays becoming the main technology for online and quick analysis of oil in water, it focuses on the different applications of the UV fluorometers and gives review of the seonsors on the market. Experiments were done with the selected flurometer to verify manufacturer claims on the performance characteristics of the sensors, when applied to laboratory tests and real world utilization. In addition, overview of the planned experimentl design with the chosen UviLux fluorometer is given.

Oil in water is essentially petroleum compounds in water. Petroleum compounds can be divided into two main groups: hydrocarbons and heteroatom compounds. Hydrocarbons are in general grouped into three categories: saturated, unsaturated and aromatics.

Measurements are always method-dependent. Using different methods will almost certainly result in different resulting values. The reference methods for the analysis of oil in water are mainly based on three principles – infrared absorption, gravimetry and gas chromatography. For online monitoring UV fluorescence is nowadays becoming the main technology for analysis of oil in water. Fluorescence detection or fluorometry and is by no means new technology and has been used for many different applications during last four decades.

Nowadays there are many oil in water sensors on the market – suitable for in-situ field measurements. Such as: UviLux fluorometer, Turner C3 Submersible Fluorometer, Turner CYCLOPS-7 Submersible Fluorometer, FP 360 sc Oil-in-Water Sensor, UV AquaTracka, Seapoint Ultraviolet Fluorometer, enviroFlu-HC, SeaOWL UV-A™.

The objectives of the performance study of the chosen UviLux sensor are to verify manufacturer claims on the performance characteristics of the UviLux sensor, when tested in a controlled laboratory setting and in real field applications in a diverse range of coastal environments. For testing, the UviLux sensor was integrated with portable modem/datalogger system and a battery, allowing autonomous operations. In laboratory testing two experiments were made - one with clean water and one with mixture of motor oil. Both showed quite good sensitivity and stability but also some problems with senor “noise”. During field tests, the UviLux sensor was deployed in five different harbors around Estonian coast, where due shipping and other industrial operations may have higher concentration of PAH-s in water, to see if there is differences between the concentrations of PAH-s between those harbors. These field experiments showed good data quality and differences between harbors could be seen.

As the UviLux sensor will be later used on a FerryBox system, a closed-loop experimental system will be set up. In which a pump and tubing will be used to draw water from a vessel, containing water through the sample chamber of the fluorometer and then return the water to the original vessel. At noted time intervals, a known amount of oil, oil and dispersant mixture or premix, will be added to the vessel. The fluorometer values will be recorded and a samples of water will be collected, which will undergo a detailed chemical analysis to determine the TPH using reference method(s).

In conclusion, determining the amount of oil dispersed or dissolved in water is always a concern at major oil spills, but also traces of oils spills in seawater. Many different technologies and methods have been used to determine that, but UV fluorescence is nowadays becoming the main technology for online and quick analysis of oil in water. There are many UV sensors on the market now and further experiments should be conducted to test their stability and data quality in different conditions and compare their data with reference processes for better results.

Introduction

Following deliverable describes oil in water sensing technologies generally and as the UV fluorescence is becoming the main technology for online analysis of oil in water overview of the literature and different applications of these sensors are given.
Second part of this deliverable focuses on the commercially available UV fluorometers as their performance and applications vary to large extent.
Third part consists of experiments done with the selected flurometer to verify manufacturer claims on the performance characteristics of the sensors, when applied to laboratory tests and real world utilization. Also gives overview of the planned experimental design with the fluorometer.

1. Oil sensing technology

1.1 Definition of oil in water

There are two broad types of oil in water:
Dispersed oil – usually means oil in water in the form of small droplets, which may range from sub-microns to hundreds of microns. Dispersed oil will contain both aliphatic and aromatic hydrocarbons. [1]

Dissolved oil – usually means oil in water in a soluble form. Aliphatic hydrocarbons in general have very low solubility in water. It is the aromatic hydrocarbons, together with things like organic acid that form the bulk of dissolved oil. [1]

1.2 Basics of hydrocarbon chemistry

Oil in water is essentially petroleum compounds in water. Petroleum compounds can be divided into two main groups: hydrocarbons and heteroatom compounds. Hydrocarbons are usually measured as Total Petroleum Hydrocarbons (TPHs). These molecules only contain carbon and hydrogen. The heteroatom compounds are those that contain not only carbon and hydrogen but also heteroatoms such as sulphur, nitrogen and oxygen. Hydrocarbons are in general grouped into three categories: saturated, unsaturated and aromatics.

Saturated hydrocarbons are characterized by single C–C bonds with all other remaining bonds saturated by H atoms. This group can be subdivided into aliphatic and alicyclic.

Aliphatic hydrocarbons are straight or branched with a general molecular formula: $CnH2n+2$. The common names for these types of compounds are alkanes and isoalkanes, which are often referred to by the petroleum industry as paraffins and isoparaffins respectively.

Alicyclic hydrocarbons are saturated hydrocarbons containing one or more rings with a general molecular formula: $CnH2n$. They are also called cycloalkanes, naphthenes, or cycloparaffins by the petroleum industry.

Unsaturated hydrocarbons are characterized by two or more bonds (C=C for alkenes or C≡C for alkynes) between two carbon atoms. They are not usually found in crude oils, but are produced in cracking processes (converting large molecular hydrocarbons to smaller ones). Unsaturated hydrocarbons can be sub-grouped into alkenes/olefins and alkynes/acetylenes.
Alkenes/olefins are those that contain two carbon bonds with a general molecular formula $CnH2n$.

Alkynes/acetylenes are those that contain three carbon bonds with a general molecular formula $CnH2n-2$.

Aromatic hydrocarbons are characterized by a benzene ring structure. The benzene ring contains six carbons; each carbon in the ring binds with one hydrogen. Depending on the number of rings that an aromatic hydrocarbon molecule contains, they are often further divided into single ring aromatics and polycyclic aromatics (containing two rings or more).

A summary of the different types of hydrocarbons is given in Fig. 1. Having an understanding of the basic hydrocarbon chemistry is useful. It will help with an appreciation of what is meant by oil in water, in particular, when covering topics such as aliphatic, aromatic hydrocarbons, dissolved and dispersed oils, solvent extract clean-up to remove the polar components, etc.

Polyaromatic hydrocarbons (PAHs) comprise a special subclass of the aromatic hydrocarbons. PAHs consist of 2-8 conjugated ring systems. Especially napthalenes occur abundantly amongst the PAHs found in oils. They are a highly important group due to their toxicity to organisms, and comprise the highest environmental impact elicted by oil products. PAHs are ubiquitous in crude and refined oils such as diesel or light fuel oil, but occur in far lower concentrations in synthetic oil products. PAHs are also key in detection of oil using off-line or in situ fluorometric methods.

Petroleum (crude oil) typically contains approximately 30% alkanes, 50% naphthenes (a type of cycloalkane), and 15% aromatics, with the remaining composition comprised of asphaltics. [46]

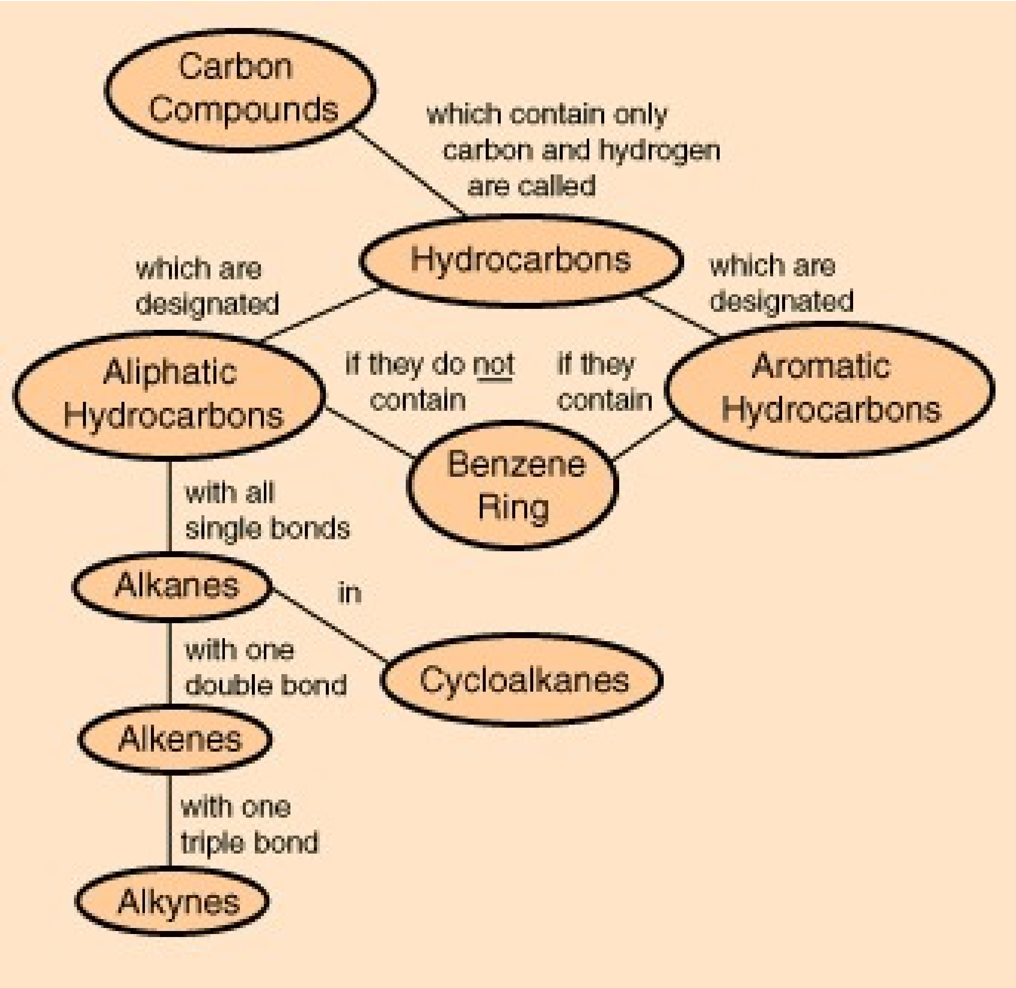


Figure 1 Principal scheme of hydrocarbons [46]

Image credit: IEEE GlobalSpec

1.3 Existing laboratory protocols for the determination of oil in water

The detection of oil, or more specifically concentration of dispersed and dissolved constituents of oil, in water is method-dependent. Some of the existing detection methods are standardized e.g. rely on DIN protocols or those devised by the international oceanographic committee. These protocols always include a stringent quality assurance, i.e. use of calibrants, controls and blanks. These methods can be used as a reference in the implementation of the newer, in situ techniques. By rule, reference methods are more time-consuming and provide lower throughput times (temporal resolution) than in situ field methods, but are essential for the determination of the accuracy (trueness) of in situ monitoring. Three types of reference methods and nine types of field measurements are discussed below.

1.3.1 Reference processes

Infrared Absorption

This method provides the total concentration of oil and begins by extracting a water sample using a solvent. The sample is then purified, dried, and placed into an infrared instrument, which transmits infrared radiation through the sample. By comparing the absorbance and transmittance of this radiation to known standards (calibrants), the concentration can be determined. Infrared absorption may involve the transmission of one or three separate wavelengths.

While single-wavelength testing is capable of measuring only the total concentration ofhydrocarbons within a sample, the three-wavelength method allows the calculation of aromatic and aliphatic compounds.

Despite the fact that both infrared methods are well-established and fairly simple to employ using portable instruments, their lack of compositional detail and frequent use of ozone-depleting Freon solvents in unregulated testing has rendered them less-used.

Gravimetric

Gravimetric methods yield the total concentration of oil and rely on the determination of weight of the target substance. The samples are extracted with a solvent (typically hexane) that then evaporated, leaving only the residual oil, which is dried and weighed. Solid phase extraction (SPE) may also be used as pretreatment.

While gravimetric methods are simple and inexpensive to perform, they lack compositional analysis and can fall victim to volatile compound loss through evaporation. They are generally not suitable in cases where the concentration of oil is low, e.g. in the order of micrograms per litre or less.

Gas chromatography

Perhaps the most traditional chromatographic method for the analysis of hydrocarbons is gas chromatography combined with flame ionization detection (GC-FID). GC-FID has been available since the 1960’s. They are nowadays increasingly being replaced by gas chromatography – mass spectrometry (GC-MS) techniques. The GC protocols are suitable for the quantification of aliphatic hydrocarbons, PAHs and other adequately volatile compounds.

For example, in GC-FID (Fig. 2), the sample is extracted by a solvent as in the two other methods. The sample is dried and purified before injection into a GC instrument. A carrier gas is used to move the sample through a column, while different hydrocarbons leave the column at different times, at which point they are measured, ionized in a hydrogen flame and detected by the flame ionization detector (FID).

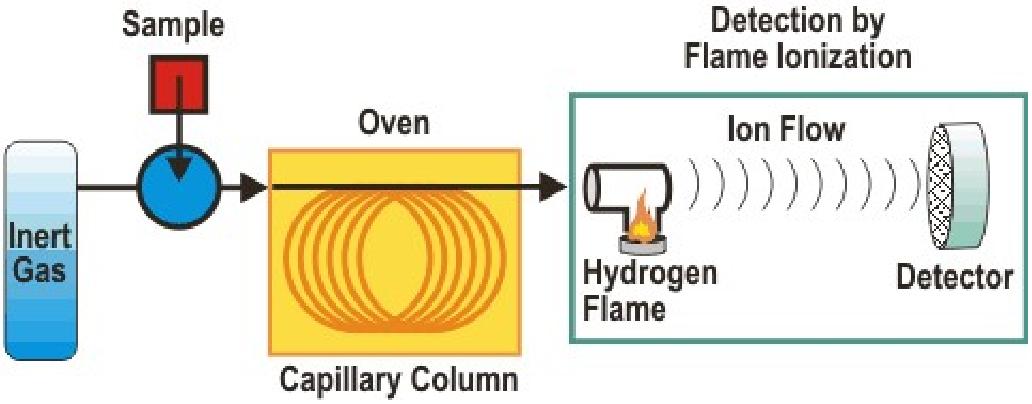


Figure 2 Simplified scheme of GC-FID process [46] Image credit: ETS Laboratories

GC methods are in wide use globally. Their benefit is that they provide detailed information on the quantity of selected molecules in mixtures that other methods cannot deliver. The drawback of the chromatographic approaches, however, is that the instrumentation requires dedicated laboratory space, is relatively expensive and requires skilled operators.

Fluorometry

Fluorometry (FLD) provides the total concentration of dissolved or dispersed oil. It is typically a straight-forward protocol. Water samples are extracted with n-hexane. Dissolved crude oil in the same solved in varying concentrations is used in calibration. The fluorescence (elicted by aromatic hydrocarbons) of the sample extract is determined and thereby the concentration of oil in the original sample is obtained. The method has been developed by the international oceanographic commission (IOC) and has been used in the Helsinki Commission (HELCOM) COMBINE monitoring of the Baltic Sea since the 1970's.

1.3.2 Field measurement processes

While reference methods are effective (and essential) for standard monitoring programs, comparing the results of different measurement campaigns and developing the legislation and guidelines. Laboratory methods can be too slow or complicated for processes, which requires repeated, quick results. For this reason, inexpensive benchtop or online devices are available for taking field measurements.
Benchtop units may be correlated to a specific reference method and typically use one of the following processes for measurement.

Colorimetric measurement using a spectrophotometer. Samples tested by this method must show color, as colorless oil is undetectable using the process.

Fiber optic sensing using a directly-injected sensor. The sensor's polymer coating absorbs hydrocarbons from the sample; the light transmitted through the fiber is measured before and after absorption to determine the hydrocarbon content.

Various means of **infrared testing**, which are similar to the reference method. These processes may or may not use solvents and are particularly useful for measuring aliphatic compounds. Depending upon the specific infrared method used, this testing may or may not release volatile compounds.

Ultraviolet methods are typically used to determine concentration of aromatic compounds, which absorb UV light. UV fluorescence is one of the most common field measurement techniques.

Online instruments should be able to detect and monitor hydrocarbons continuously, in a process stream and may use one of the methods described below

UV fluorescence method, probably most widespread one, is using UV-light to stimulate the fluorescence of oil products, receiver part of the sensor detects intensity of fluorescence, which in turn gives concentration of oil products in water.

Focused ultrasonic acoustics method involve a directly-inserted transducer which detects the acoustic echoes of solid particles and oil droplets. The acoustic signals are used to calculate particle size and oil concentration.

Fiber optic sensing, which is the same process used in benchtop units, where the sensor's polymer coating absorbs hydrocarbons from the sample; the light transmitted through the fiber is measured before and after absorption to determine the hydrocarbon content.

Image analysis method uses video microscopes to capture images of a sample stream. Particles on each image are counted and analyzed according to the sample volume. Particles are typically distinguished by shape, as oil droplets are nearly spherical.

Light scattering method involves passing light through an oily sample. Particles scatter light and reduce the transmitted light; by measuring both quantities of light at different angles, oil particles can be detected and measured.

Photoacoustic method uses pulsed lasers to cause sudden local heating around oil particles. This heating causes high frequency pressure waves, which are measured and correlated to determine oil concentration.

Oceanographic mass spectrometric methods are based on formation and detection of ionized molecules. They have been tested in deployments but are not commercially available yet.

1.4 Principles of UV fluorescence oil detection method

Oils are known to fluoresence, and the oil detection sensor detects the presence of oil by means of excitating and measuring fluorescence. Fluorescence is an optical phenomenon in which a compound absorbs light at one wavelength and emits it at a longer wavelength. When fluorescent compounds are excited, some of the energy is absorbed through the excitation of electrons to higher energy states. Once the light source is removed the excited electrons fall back to their ground state, giving off light in the process. This process is very similar to what makes glow-in-the-dark materials possible, except it takes place in a much shorter time period. Because some energy (i.e. heat) is lost in the absorption-emission process, the wavelength of the emitted light is always longer than the wavelength of the absorbed light. Typically, the absorbed light is in the ultraviolet (UV) range and the emitted light is in the visible range (the visible longer-wavelength light often appears violet or blue). For example, oils typically absorb light between 300 and 400nm, and emit light in the 450 to 650nm range (Fig. 3). [3]

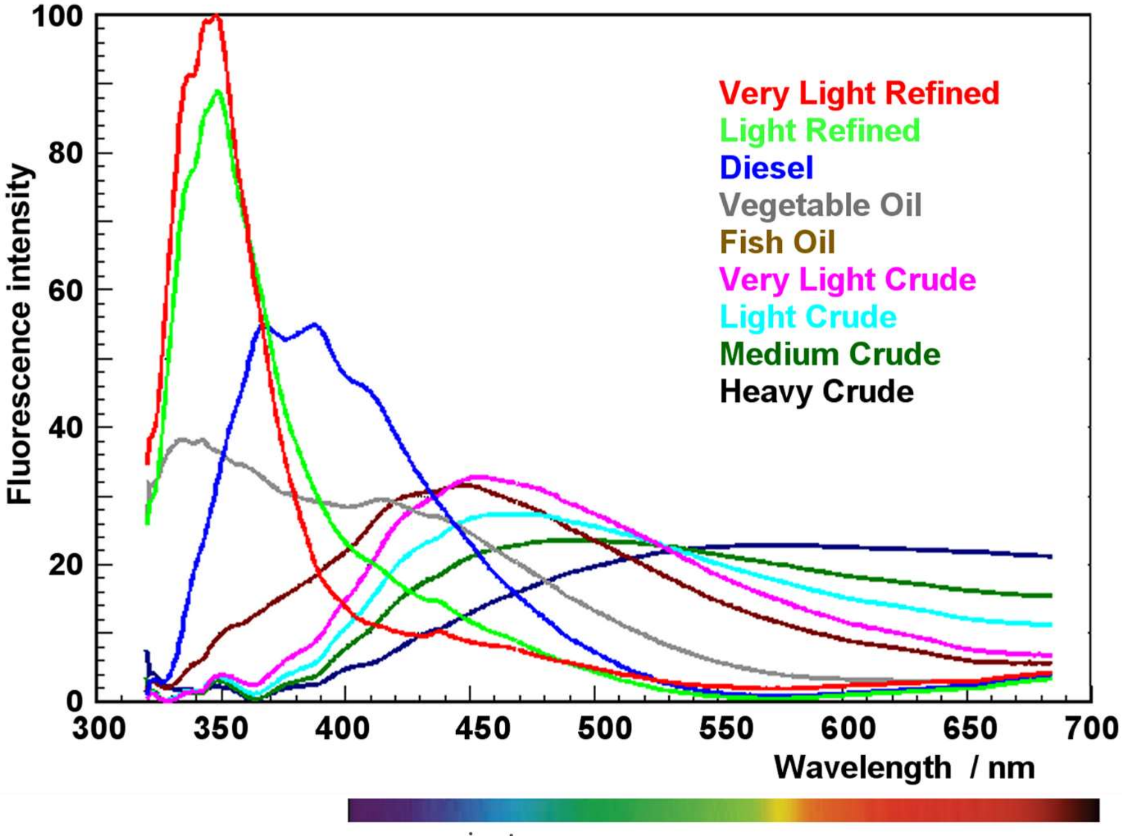


Image credit: SEOS

Figure 3 Hydrocarbons fluorescence depending on wavelength of exposure light signal. Ultraviolet fluorescence is dependent from the spike of fluorescence seen between 300 and 400 nm (part of the UV spectrum). [47]

1.5 Summary of methods

Measurements are always method-dependent. Using different methods will almost certainly result in different values. There have been many reference methods for the analysis of oil in water, which are mainly based on three principles – infrared absorption, gravimetry and gas chromatography. Infrared-based methods have been dominant and popular until recent years, but due to issues associated with the use and availability of the chlorofluorocarbons, they are becoming obsolete. Reference methods are important, since without them the comparison of results is impossible, and the regulatory framework for compliance monitoring cannot be constructed. Yet reference methods are not always user-friendly and practical in the field. As a result, alternative methods that may be inexpensive, easy to use, and can produce results quickly, are needed in particular for routine measurements. There are many techniques and instruments now available for both laboratory bench-top and online monitoring. For laboratory bench-top types, UV fluorescence and HATR instruments are probably most widely used for oil in water measurements. Recently, however, a solventless approach based on membrane filtration and infrared has been developed. Also, a new infrared method that uses a non-traditional wavelength has been made available. For online monitoring, light scattering and UV fluorescence oil sensors and instruments were popular. Together with recent development the Laser Induced Fluorescence, UV fluorescence is nowadays becoming the main technology for online analysis of oil in water.

1.6 Field instrument selection

As discussed in the previous sections, there are many different techniques and instruments to choose from, when it comes to a specific application. For laboratory bench-top instruments, parameters to be considered may include the following:

- Purpose of measurement: e.g. for process optimization and control or for reporting. For process control and optimization, repeatability is perhaps more important while for reporting, in addition to repeatability, accuracy also becomes very important.
- Property and characteristics of produced water: e.g. oil color, presence of chemicals and solid particles. Color of oil is extremely important if one is to use a colorimetric based method. Some production chemicals can be extracted together with oil and can affect UV methods. Solids will have a detrimental effect on the filtration infrared method. For methods involving evaporation, light components can be lost.
- The use of solvents: if a solvent is used, one needs to check the method must be environmentally sound and user friendly. Availability and cost must be considered.
- Calibration procedures: what is involved in the calibration? What calibration check is required and at what frequency?
- Instrument compactness and ease of use: for offshore operations, space is limited and, handheld or portable instruments are more welcome. Most bench-top instruments are easy to use with minimal training, and should not be an issue for a laboratory technician.
- Costs: these include Capital Expenditure (Capex) and Operation Expenditure (Opex). Costs of instrument and measurement (operations) vary significantly. Costs associated with Opex may include the purchase of solvent and its disposal. Opex depends on the number of analyses involved.
- Maintenance and after-sale service: this not only affects the operating costs, it can also have an impact on production.[1]

For **online monitoring**, most of these points apply. However, certain issues specific to online monitor applications may need to be carefully considered when it comes to instrument selection:

- Properties and characteristics: in addition to those mentioned for bench-top methods, online monitoring requires consideration of things such as gas or air bubbles in measured water stream.
- Space available for fitting the instrument: for online monitoring, instruments should be fitted downstream of a turbulent region where oil is well mixed with water. If a by-pass line is to be used, then the length of this line should be minimized. Online monitors come in a variety of configurations. Some even come with a sample pre-conditioning system to generate uniform dispersion. The amount of available space might determine the type of online monitor chosen.
- Previous applications and field test data: although no two applications will be the same, it will be very useful if the instrument suppliers have already found similar applications and can provide test results.
- Others: additional considerations include pressure, temperature, flow rate (minimum and maximum for by-pass line) and pressure rating. [1]

2. Applications of portable UV fluorescence sensors

As mentioned previously fluorescence detection or fluorometry and is by no means new technology in and of itself. The objective of this section to review some of the applications of portable in-situ fluorometers.

The results of a literature search on fluorescence-based portable detectors to measure the real-time concentration of oil are well reported in paper by Lambert [2], some of which are also shortly mentioned in the section below. The focus of this paper is to extract specific information from references about how the instruments were used, including set up and calibration procedures, the oil and dispersant measured, the approximate concentration range of the oil in the water column, and how the real-time data compared to traditional laboratory techniques.

The authors Green et al. [4] reports on a total of three experimental spills conducted at Royal Roads in Victoria, British Columbia, in 1978. The field trials were part of a larger program to look at the fate of chemically dispersed oil. This portion of the field program used Prudhoe Bay crude oil (sometimes called North Slope crude oil in the report) and Corexit 9527 dispersant. It was noted in the report that two systems employing fluorescent spectroscopy were employed, a flow through system and a laboratory system. The instrument was the Turner model 130 unit equipped with a no. 110-811 excitation filter (300–400 nm wavelength).

Gill et al. [5] and Swiss and Gill [6] reported on a test that took place off Halifax, Nova Scotia in September of 1983. The program used Alberta Sweet Mixed Blend crude oil and the dispersants Corexit 9527, 9550 and a prototype product MA700. An extensive sample collection procedure was instituted. Following the trial, the samples were extracted with methylene chloride and hydrocarbon content determined by fluorescence spectroscopy. Calibration was carried out using prepared oil-in-solvent standards. The bench top fluorometer was a Turner model 112 equipped with a Turner 2A (>410 nm) emission filter, 7-60 (320–390 nm) excitation filter and a general-purpose UV lamp. Two Turner model 10-005 flow-through instruments were also used.

The November 1984 program is reported in Brown [7] and Brown et al. [8] while the April of 1985 program is reported in Brown [9]. The program's objective was to evaluate the effectiveness of dispersant in cold water. Sub-surface monitoring was employed for all programs using continuous in situ fluorometers. A summary containing significant information on the instrumentation can be found in the reference Brown et al. [10]. In the 11/84 trials, there were three Turner model 10-005 units equipped with a short wavelength kit (excitation at 254 nm wavelength and emission at 350 nm wavelength). The fourth unit was a Sequoia-Turner model 112, continuous flow cell and a long wavelength kit (excitation at 350 nm wavelength and emission at 450 nm wavelength).

In July of 1985, a field trial was conducted in a freshwater fen lake in north central Alberta [11,12]. The objective was to study the impact of oil and dispersant in a freshwater environment. NormanWells crude oil and Corexit 9550 were used. The reference by Quaife [12], describes a piping system constructed throughout the fen to draw water over to a workstation where flow-through fluorometers (two units) were set up and samples were collected from the units' output for additional analysis. One fluorometer was the Turner model 10-005 and the other a Sequoia-Turner model 112. It was stated that both were equipped with a short wavelength (254 nm excitation and 350 nm emission) kit and standard calibration procedures were employed.

The 1981 Baffin Island, NWT project, commonly referred to as BIOS, was a large scale effort undertaken by a consortium of international participants from both industry and government. The project looked at dispersant issues as part of several oil spill studies. A detailed summary of the studies can be found in Sergy and Blackall [13]. The test program used Lagomedio crude oil that was premixed with the dispersant Corexit 9527. Details regarding the apparatus used to monitor the dispersed oil concentration are found in Green et al. [14,15] and Humphrey et al. [16]. The references state that a total of five fluorometers were used to monitor the dispersed oil concentration. Four were the Turner model 10-005 flow-through type and the fifth was a submersible unit called the Endeco Petrotrack also containing a Turner model 10-005.

In the report by Hiltabrand [17], information was provided on field trials of the Endeco towed fluorometer. The trials took place during March 1978 off the coast of Louisiana in the Gulf of Mexico. Designed as a submersible unit, it contains a Turner fluorometer for continuous monitoring.

SMART protocol is an operational plan developed for the Turner model 10AU fluorometer primarily for use at oil spills-of-opportunity in which dispersants are a potential countermeasure. The primary objective of the plan is to provide a means of monitoring the dispersed plume of oil [18].

Walker and Lunel [19] describe the 1994 North Sea trials in which Forties blend crude oil, a demulsifier solution (50:50 mixture of LA 1834:Surdyne X113) and Slickgone dispersant were used. At the 1994 trials, a total of eight Turner 10AU flow-through fluorometers were deployed to measure the oil-in-water concentration between 0.5 and 5m depth. Another field trial employing continuous flow fluorometers was also conducted in conjunction with the 1994 North Sea trails and reported in Lunel et al. [21]. A medium fuel oil/gas oil mix (50:50) and the dispersant Corexit 9527 were used.

The Sea Empress spill of 1996 (Lunel et al. [22,23]) was a spill-of-opportunity in which much of the knowledge gained during the previous sea trials was applied. The mixture of Forties blend crude oil and heavy fuel oil (HFO) was treated with demulsifier (a 50:50 mixture of Shell LA1834 and Surdyne) and the dispersants Dasic LTSW, Finasol OSR-51, Dasic Slickgone NS, Dispolene 34S, Superdispersant 25, Enersperse 1583 and Corexit 9500.

The 1997 field trial is described in Lewis et al. 24]. Forties blend crude oil, Alaskan North Slope crude oil and IFO-180 were tested using the dispersant Corexit 9500 and Dasic Slickgone NS. A total of six Turner model 10AU fluorometers were used to measure oil-in-water concentrations.

In the papers by Hurford et al. [25,26], he compares the performance during a sea trial of the Turner flow-through fluorometer to a submersible fluorometric sensor unit called the AQUAtracka by Chelsea Environmental Instruments.

Reports by Brandvik et al. [27] and Lewis et al. [28] presents findings from a 1994 North Sea trail employing a Sture blend crude oil and the dispersant Corexit 9500. In this trial, three Turner model 10AU instruments were employed to monitor oil-in-water concentrations.

Paper by Lambert et al. [29] reports on the findings from a laboratory study of the Turner Instrument flow-through models 10AU and 10 fluorometers. It was conducted to review their ability to measure real-time oil-in-water concentrations, to compare the results to other total petroleum hydrocarbon (TPH) procedures and to improve the understanding of the relationship of the fluorescence to the chemical composition of the oils.

In situ fluorometers were deployed during the Deepwater Horizon (DWH) Gulf of Mexico oil spill to track the subsea oil plume. Uncertainties regarding instrument specifications and capabilities necessitated performance testing of sensors exposed to simulated, dispersed oil plumes. Dynamic ranges of the Chelsea Technologies Group AQUAtracka, Turner Designs Cyclops, Satlantic SUNA and WET Labs, Inc. ECO, exposed to fresh and artificially weathered crude oil, were determined. Sensors were standardized against known oil volumes and total petrooleum hydrocarbons and benzene-toluene-ethylbenzene-xylene measurements - both collected during spills, providing oil estimates during wave tank dilution experiments (Conmy et al. [30]).

Tedetti et al [31] evaluated the performances of a submersible UV fluorometer (EnviroFlu-HC, TriOS Optical Sensors) dedicated to the real time measurement of Polycyclic Aromatic Hydrocarbons (PAHs) in the aquatic media. They conducted calibration experiments and in situ measurements in the coastal Mediterranean Sea. They found that the EnviroFlu-HC was not strictly specific to PAHs, even though it exhibited the highest sensitivity for phenanthrene, but could response to tryptophan-like material as well, and in a much less extent, to humic substances. The sensor signal showed great spatial and temporal variations in clean and polluted sites, with likely a high contribution of PAHs in the harbors, and a high contribution of tryptophan-like and humic-like materials in the sewage effluent.

3. Overview of UV fluorescence oil sensors on the market

In this section, technology review of available on market oil in water sensors is given. Fluorometers listed here are compact, submersible, with low power consumption and robust design – suitable for in-situ field measurements.

Table 1 Oil sensors dimensions, weights, operating range and resolution

	Dimentions	Weight	Operating range	Resolution (lower limit of detection)
Cyclops-7™	14.48 x 2.23 cm	142 g	0-2700 ppb (PTSA), >10,000 ppb (1,5 NDDS), >100 ppm (BTEX)	0,2ppb (PTSA), 10ppb (BTEX), 10 ppm (1,5 NDDS)
C3™	23 x 10 cm	1,64 kg	0-2700 ppb (PTSA), >10,000 ppb (1,5 NDDS), >100 ppm (BTEX))	0,2ppb (PTSA), 10ppb (BTEX), 10 ppm (1,5 NDDS)
FP 360 sc		2,8 kg	0-500 or 0-5000 ppb (PAH)	0,1 ppb (PAH)
SeaOWL UV-A™	56,6 x 54,6 mm	340 g	3-80 ppb crude oil	3 ppb crude oil
UV ATF	406 x 89 mm	5,5 kg	0.001 to 10 ug/l (Carbazole/Perylene)	0.001 ug/l Carbazole/Perylene (1% of reading)
UviLux	70 x 149 mm	800 g	0,005-200 µg/L, CDOM 0,002-15 µg/L (PAH)	PAH 0,005 µg/L (Carbazole), CDOM 0,002 µg/L (Perylene)
Seapoint UF		1 kg	50-1500 µg/L	0,05 µg/L (Quinine Sulfate)
enviroFlu-HC	80 x 414 mm	4,5 kg	500 ppb or 5000 ppb	0,3 or 0,5 ppb

3.1 UviLux Fluorometer

The UviLux fluorometer (Fig. 4) from Chelsey Technology Group (UK) is an innovative, sensitive, low cost, in-situ digital UV fluorometer providing many unique features. Variants of the UviLux enable real-time monitoring of the following parameters: Polycyclic Aromatic Hydrocarbon (PAH); Colored Dissolved Organic Matter (CDOM); Tryptophan-like fluorescence, which is a surrogate marker for Biological Oxygen Demand (BOD) and is associated with bacterial contamination in waste, recycled and natural water supplies; and Optical Brighteners used for detecting household wastewater misconnections.

The UviLux uses a deep UV LED light source and a miniature Photomultiplier Detector to provide state-of-the-art measurement sensitivity at the parts-per-trillion level. Fluorometer sensitivity and hence measurement dynamic range is fully user configurable for different applications. Sophisticated electronic signal processing, combined with cowl design principles employed in UV AquaTracka earlier, enables the UviLux to operate successfully also in high levels of ambient light. The high quality optical filtration used in both the excitation and emission optical paths gives excellent turbidity rejection, while internal referencing of the LED light source intensity provides long-term calibration stability.

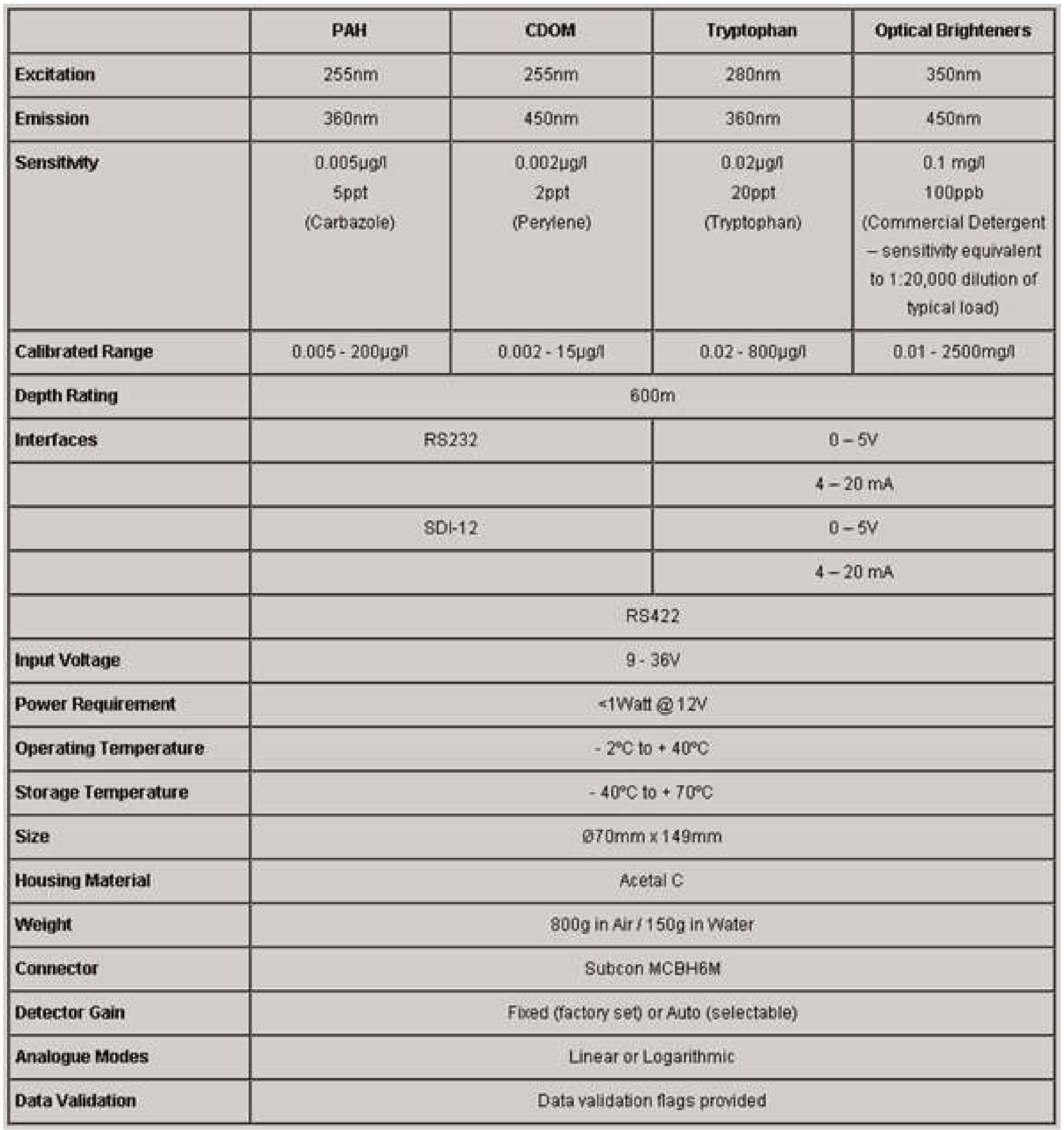
Figure 4 UviLux Fluorometer by Chelsey Technology Group Image credit: Chelsey Technology Group

The UviLux can be used in wide range of oceanographic and fresh water applications. The UviLux has a chemically inert acetal resin housing suitable for deploying independently as well as from submersible vehicles, moored or profiling systems. This robust, compact, lightweight fluorometer has low power consumption, is easy to use and gives accurate and repeatable measurements.

Two signals are obtained from the standard UviLux: a digital RS232 serial output in engineering units and a calibrated analogue voltage between 0.5V to 5V. Single RS422, SDI-12 and 4-20mA outputs are also available as options. This flexibility makes the UviLux ideally suited for integrating into many different systems and platforms.

The Windows based Tplot software supplied with the fluorometer allows the user to both plot and record time stamped data when operating the UviLux directly from a PC and gives control over many instrument parameters, including sampling rate, detector sensitivity and calibration factors. Although small and low cost, the UviLux maintains the performance standards and build quality associated with CTG's range of in-situ fluorometers. [37]

Table 2 Specifications of UviLux Fluorometer [37]



	PAH	CDOM	Tryptophan	Optical Brighteners
Excitation	255nm	255nm	280nm	350nm
Emission	360nm	450nm	360nm	450nm
Sensitivity	0.005µg/l 5ppt (Carbazole)	0.002µg/l 2ppt (Perylene)	0.02µg/l 20ppt (Tryptophan)	0.1 mg/l 100ppb (Commercial Detergent – sensitivity equivalent to 1:20,000 dilution of typical load)
Calibrated Range	0.005 - 200µg/l	0.002 - 15µg/l	0.02 - 800µg/l	0.01 - 2500mg/l
Depth Rating	600m			
Interfaces	RS232		0 – 5V	
			4 – 20 mA	
	SDI-12		0 – 5V	
			4 – 20 mA	
	RS422			
Input Voltage	9 - 36V			
Power Requirement	<1Watt @ 12V			
Operating Temperature	- 2ºC to + 40ºC			
Storage Temperature	- 40ºC to + 70ºC			
Size	Ø70mm x 149mm			
Housing Material	Acetal C			
Weight	800g in Air / 150g in Water			
Connector	Subcon MCBH6M			
Detector Gain	Fixed (factory set) or Auto (selectable)			
Analogue Modes	Linear or Logarithmic			
Data Validation	Data validation flags provided			

3.2 Turner C3™ Submersible Fluorometer

Housing up to three optical sensors within a single system, Turner Designs' C3 Submersible Fluorometer (Fig. 5) has the ability to simultaneously collect data on multiple water quality parameters.

The C3's fast sampling rate, integrated pressure sensor, and large internal memory that stores up to 480,000 data points allow users to collect detailed information that helps characterize an aquatic system.

The C3 is rated for a depth of 600 meters and can operate at temperatures ranging from -2 to 50 degrees Celsius. A temperature sensor is included, and an optional mechanical wiper is available to reduce fouling on the optical elements if the unit is submerged over a long period of time.

The submersible fluorometer can be used in freshwater, coastal, and open ocean applications. Available optical sensors range from the ultraviolet to infrared wavelengths and include:

- Turbidity
- Chlorophyll
- Blue-green algae (Phycocyanin and Phycoerythrin)
- Fluorescein dye
- Rhodamine dye
- CDOM
- Optical brighteners for wastewater treatment
- Crude oil
- Refined fuels

An optional external submersible lithium ion battery allows the C3 to run during extended deployments. The included C-Soft Windows-based software allows for straightforward calibration, data logging setup, file management, and digital or analog data integration. [38]

Figure 5 Turner C3™ Submersible Fluorometer

Image credit: Turner Designs

Table 3 Specifications of C3™ Submersible Fluorometer [38]

Application	Minimum Detection Limit	Dynamic Range
CDOM/FDOM	0.15 ppb**	0-1250 ppb**
	0.5 ppb***	0-5000 ppb***
Chlorophyll in vivo		
Blue Excitation	0.025 µg/L	0-500 µg/L
Red Excitation	0.5 µg/L	>500 µg/L
Fluorescein Dye	0.01 ppb	0-500 ppb
Oil - Crude	0.2 ppb***	0-2700 ppb***
Oil - Fine	10 ppb*	>10,000 ppb*
	10 ppm****	>100 ppm****
Optical Brighteners	0.6 ppb***	0-15,000 ppb***
Phycocyanin (Freshwater Cyanobacteria)	2 ppbPC	0-40,000 ppbPC
Phycoerythrin (Marine Cyanobacteria)	0.15 ppbPE	0-750 ppbPE
PTSA Dye	0.1 ppb***	0-650 ppb***
Rhodamine Dye	0.01 ppb	0-1000 ppb
Tryptophan	3 ppb	>20,000 ppb
Turbidity	0.05 NTU	0-3000 NTU
Weight in Air	1.64 kg; 3.6 lbs	
Length	23 cm; 9.1 in	
Diameter	10 cm; 3.9 in	
Material	Delrin Plastic	
Temperature	-2 to 50 degrees C.	
Depth	0 to 600 meters	
Output	Digital (ASCII); Analog (0 to 5 volt) - optional	
Interface	RS232 Interface	
Minimum Sample Interval	1 Second	
Minimum Power Supply	8 to 30 volts; 5 watts	
Maximum Current Draw at 12 volts		
- operational	200 mA	
- sleep mode	3 mA	

* 1,5 Napthalene Disulfonic Disodium Salt

** Quinine Sulfate

*** PTSA (1,3, 6, 8 - Pyrenetetrasulfonic Acid Tetrasodium Salt)

**** BTEX (Benzene, Toluene, Ethylbenzene, Xylenes)

PC Phycocyanin pigment from Prozyme diluted in Deionized water

PE Phycoerythrin pigment from Prozyme diluted in Deionized water

3.3 Turner Cyclops-7™ Submersible Sensor

The CYCLOPS-7™ line of submersible sensors (Fig. 6) is designed for integration into multi-parameter platforms requiring a high performance, compact sensor at a significantly lower price than traditional submersible sensors. The Turner Designs CYCLOPS-7 Submersible Fluorometer/Turbidimeter is an accurate single channel detector that can be used for many different applications. This instrument can be designed to detect pigment fluorescence, dye fluorescence for dye tracing applications, fluorescence of dissolved organic matter, or be used as a turbidimeter. It is intended to be integrated into a multi-parameter system to obtain its power and to deliver an output voltage to the system data logger, which is proportional to the concentration of the fluorophore, particle or compound of interest. The CYCLOPS-7™ combination of price, performance and size makes the sensor very attractive for oceanographic, freshwater and dye tracing applications. CYCLOPS-7™ was designed specifically for integration into any platform that supplies power and data logging. [39]

Figure 6 Turner Cyclops-7™ Submersible Sensor Turner Designs

Image credit: Turner Designs

Table 4 Specifications of Cyclops-7™ Submersible Oil Sensor [39]

Application	Minimum Detection Limit	Dynamic Range
CDOM/FDOM	0.15 ppb**	0-1250 ppb**
	0.5 ppb***	0-5000 ppb***
Chlorophyll in vivo		
Blue Excitation	0.025 µg/L	0-500 µg/L
Red Excitation	0.5 µg/L	>500 µg/L
Fluorescein Dye	0.01 ppb	0-500 ppb
Oil - Crude	0.2 ppb***	0-2700 ppb***
Oil - Fine	10 ppb*	>10,000 ppb*
	10 ppm****	>100 ppm****
Optical Brighteners	0.6 ppb***	0-15,000 ppb***
Phycocyanin (Freshwater Cyanobacteria)	2 ppbPC	0-40,000 ppbPC
Phycoerythrin (Marine Cyanobacteria)	0.15 ppbPE	0-750 ppbPE
PTSA Dye	0.1 ppb***	0-650 ppb***
Rhodamine Dye	0.01 ppb	0-1000 ppb
Tryptophan	3 ppb	>20,000 ppb
Turbidity	0.05 NTU	0-3000 NTU
Length x Diameter	5.7" x 0.9"; 14.48 x 2.23 cm (SSt or Ti)	
	5.7" x 1.25", 14.48 x 3.18 cm (Delrin)	
Weight	5.0 oz; 142 grams	
Temperature Range	Ambient: 0 to 50 deg C	
	Water Temp: -2 to 50 deg C	
Depth Range	600 meters	
Signal Output	0 - 5 VDC	
Supply Voltage Range	3 - 15 VDC	
Power Requirements	< 300mW typical	

* 1,5 Napthalene Disulfonic Disodium Salt
** Quinine Sulfate
*** PTSA (1,3, 6, 8 - Pyrenetetrasulfonic Acid Tetrasodium Salt)
**** BTEX (Benzene, Toluene, Ethylbenzene, Xylenes)
PC Phycocyanin pigment from Prozyme diluted in Deionized water
PE Phycoerythrin pigment from Prozyme diluted in Deionized water

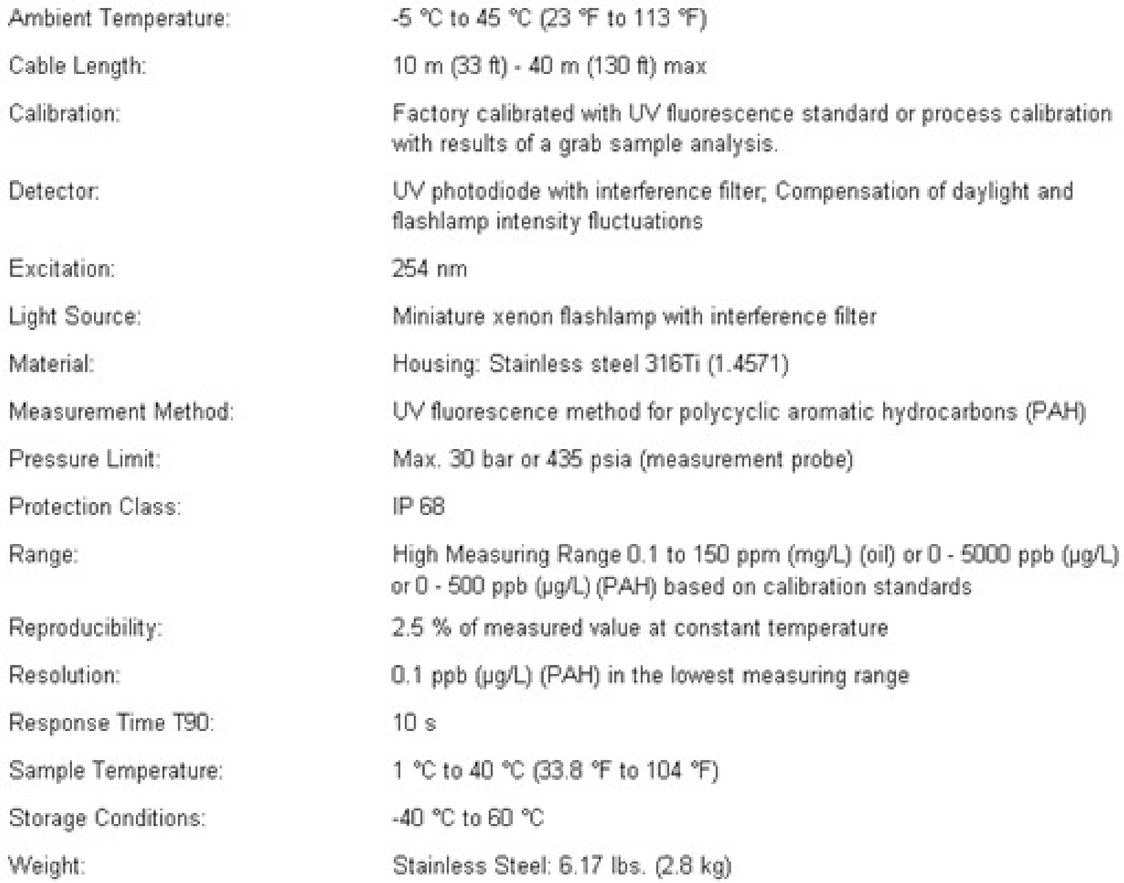
3.4 FP 360 sc Oil-in-Water Sensor (500ppb and 5000ppb)

The FP 360 sc by Hach (Fig. 7) from USA is specifically designed to detect traces of mineral oils in water while providing the necessary value and benefits for a positive return on investment. Sensor monitors surface water, process water and industrial water continuously. It has a submersible probe design. Simply wipe off the sensor's measurement window to clean. Calibrate once every two years. Available in stainless steel or titanium. [40,41]

Figure 7 FP 360 sc Oil-in-Water Sensor (500ppb and 5000ppb)

Image credit: Hach

Table 5 Specifications of FP 360 sc Oil-in-Water Sensor (500ppb and 5000ppb) [40,41]



Ambient Temperature:	-5 °C to 45 °C (23 °F to 113 °F)
Cable Length:	10 m (33 ft) - 40 m (130 ft) max
Calibration:	Factory calibrated with UV fluorescence standard or process calibration with results of a grab sample analysis.
Detector:	UV photodiode with interference filter; Compensation of daylight and flashlamp intensity fluctuations
Excitation:	254 nm
Light Source:	Miniature xenon flashlamp with interference filter
Material:	Housing: Stainless steel 316Ti (1.4571)
Measurement Method:	UV fluorescence method for polycyclic aromatic hydrocarbons (PAH)
Pressure Limit:	Max. 30 bar or 435 psia (measurement probe)
Protection Class:	IP 68
Range:	High Measuring Range 0.1 to 150 ppm (mg/L) (oil) or 0 - 5000 ppb (µg/L) or 0 - 500 ppb (µg/L) (PAH) based on calibration standards
Reproducibility:	2.5 % of measured value at constant temperature
Resolution:	0.1 ppb (µg/L) (PAH) in the lowest measuring range
Response Time T90:	10 s
Sample Temperature:	1 °C to 40 °C (33.8 °F to 104 °F)
Storage Conditions:	-40 °C to 60 °C
Weight:	Stainless Steel: 6.17 lbs. (2.8 kg)

3.5 UV AquaTracka Fluorometer

The UV AquaTracka (Fig. 8) by Chelsea Technologies Group from UK is a submersible fluorometer to monitor the concentration of refined hydrocarbons (360nm) or crude hydrocarbons (440nm) in a wide range of oceanographic applications. In support of this, it has been designed to be deployed from undulating vehicles, moored or profiling systems. This robust, compact, lightweight instrument has built in test (BITE) circuitry which ensures high stability. The instrument is easy to use and gives accurate and repeatable measurements.

The UV AquaTracka's pressure housing is manufactured in titanium for long life. It utilizes a pulsed xenon light source, a miniature PMT as the detector and incorporates a 20-bit ADC under the control of a micro controller. Data output is factory set as logarithmic analogue. The turret mechanical arrangement and main PCB allows for an optional Pt100 temperature probe. This option allows user correction of the fluorescence signal quantum yield variation with temperature. For deck and laboratory applications a flow through cowling is available. The instrument is rated to 6000m and has an optional ambient light baffling cowl for use in surface waters. [42]

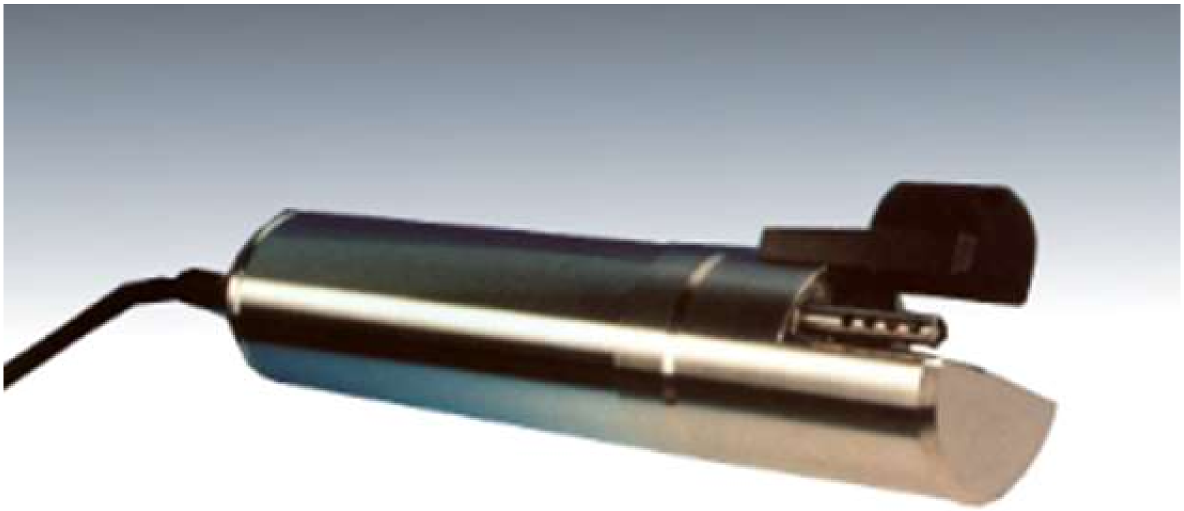
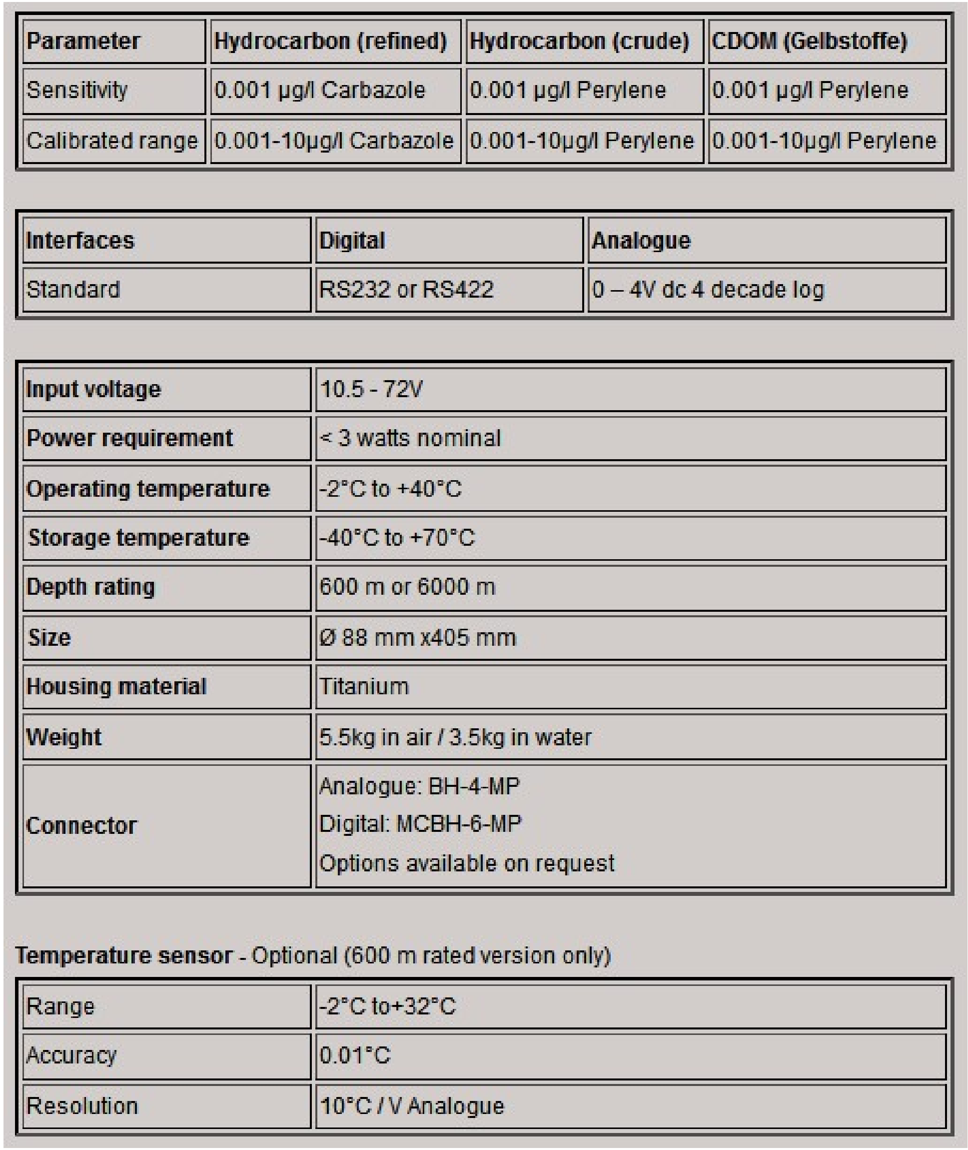


Figure 8 The UV AquaTracka

Image credit: Chelsey Technology Group

Table 6 Specifications of UV AquaTracka Fluorometer [42]



Parameter	**Hydrocarbon (refined)**	**Hydrocarbon (crude)**	**CDOM (Gelbstoffe)**
Sensitivity	0.001 µg/l Carbazole	0.001 µg/l Perylene	0.001 µg/l Perylene
Calibrated range	0.001-10µg/l Carbazole	0.001-10µg/l Perylene	0.001-10µg/l Perylene

Interfaces	**Digital**	**Analogue**
Standard	RS232 or RS422	0 – 4V dc 4 decade log

Input voltage	10.5 - 72V
Power requirement	< 3 watts nominal
Operating temperature	-2°C to +40°C
Storage temperature	-40°C to +70°C
Depth rating	600 m or 6000 m
Size	Ø 88 mm x405 mm
Housing material	Titanium
Weight	5.5kg in air / 3.5kg in water
Connector	Analogue: BH-4-MP Digital: MCBH-6-MP Options available on request

Temperature sensor - Optional (600 m rated version only)

Range	-2°C to+32°C
Accuracy	0.01°C
Resolution	10°C / V Analogue

3.6 Seapoint UV Fluorometer

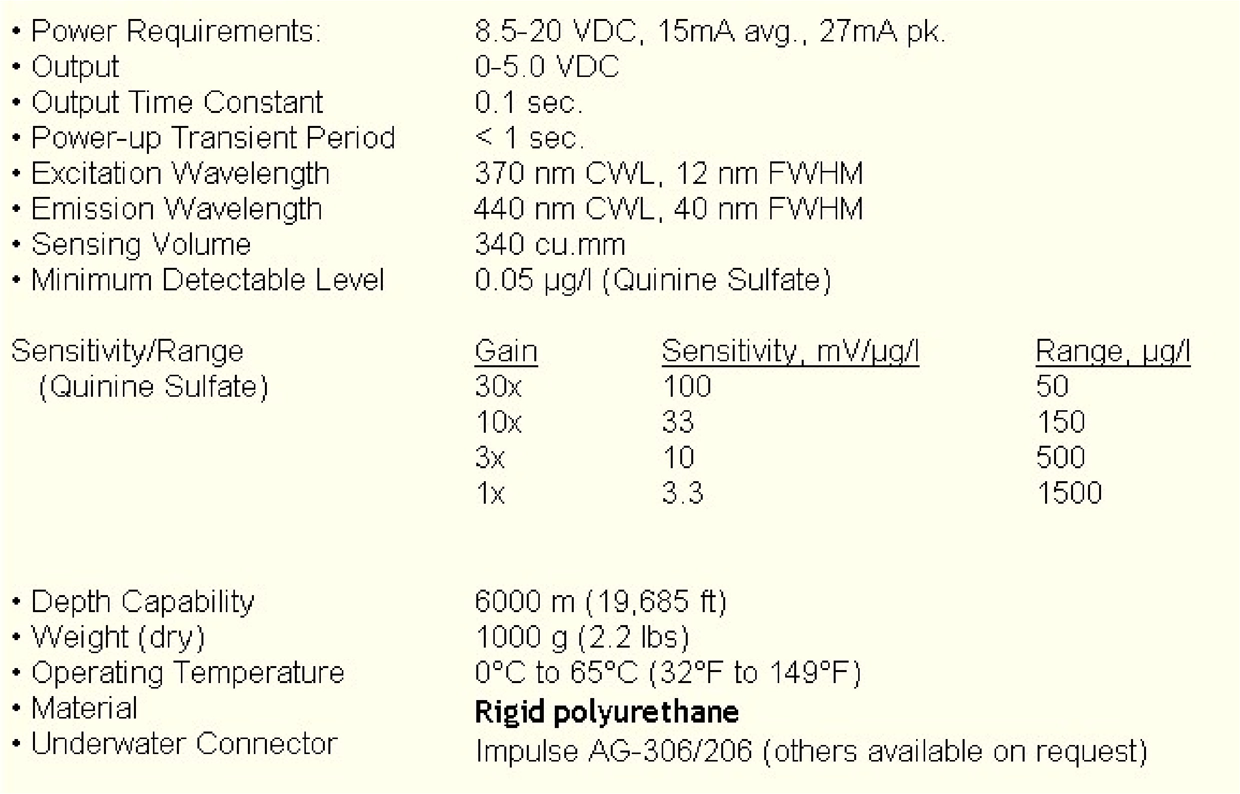
The Seapoint Ultraviolet Fluorometer (SUVF) (Fig. 9) by Seapoint Sensors inc. (USA) is a high-performance, low power instrument for in situ measurement of fluorescent materials including chromophoric dissolved organic matter (CDOM), crude oil, and UV fluorescent dyes. Its small size, very low power consumption, high sensitivity, wide dynamic range, 6000 meter depth capability, and open or pump-through sample volume options provide the power and flexibility to operate in a wide variety of conditions. The SUVF uses modulated ultraviolet LED lamps and optical filter for excitation. The fluorescent light signal passes through a blue emission filter and is detected by a silicon photodiode. The low level signal is then processed using synchronous demodulation circuitry which generates an output voltage proportional to the amount of fluorescent light received. The SUVF may be operated with or without a pump. The sensing volume may be left open to the surrounding water, or, with the use of the supplied cap, can have water pumped through it. Two control lines allow the user to set the range to one of four options. These lines may be hardwired or microprocessor controlled to provide a suitable range and resolution for a given application. The sensor is easily interfaced with data acquisition packages; a 5 ft. cable is supplied. Custom configurations are available on demand.

More technical information available from manufactures website: http://www.seapoint.com/suvf.htm [43]

Figure 9 Seapoint Ultraviolet Fluorometer

Image credit: by Seapoint Sensors inc.

Table 7 Specifications of Seapoint Ultraviolet Flurometer [43]



• Power Requirements:	8.5-20 VDC, 15mA avg., 27mA pk.
• Output	0-5.0 VDC
• Output Time Constant	0.1 sec.
• Power-up Transient Period	< 1 sec.
• Excitation Wavelength	370 nm CWL, 12 nm FWHM
• Emission Wavelength	440 nm CWL, 40 nm FWHM
• Sensing Volume	340 cu.mm
• Minimum Detectable Level	0.05 µg/l (Quinine Sulfate)

Sensitivity/Range (Quinine Sulfate)	Gain	Sensitivity, mV/µg/l	Range, µg/l
	30x	100	50
	10x	33	150
	3x	10	500
	1x	3.3	1500

• Depth Capability	6000 m (19,685 ft)
• Weight (dry)	1000 g (2.2 lbs)
• Operating Temperature	0°C to 65°C (32°F to 149°F)
• Material	**Rigid polyurethane**
• Underwater Connector	Impulse AG-306/206 (others available on request)

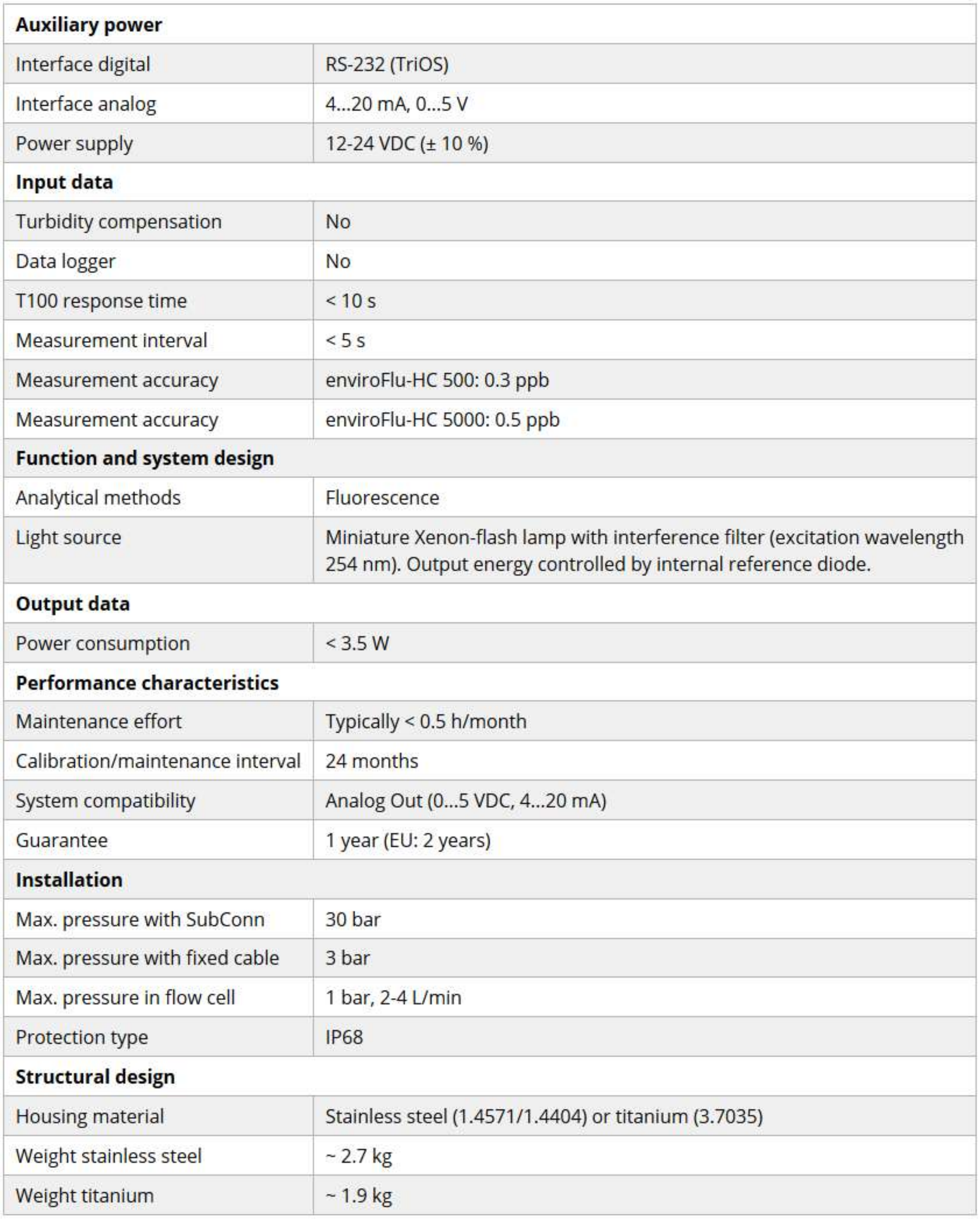
3.7 enviroFlu-HC oil in water sensor

enviroFlu-HC (Fig. 10) by Trios (Germany) is a new generation of high sensitive submersible sensors for oil-in-water measurement. The used UV fluorescence principle for detection is much more sensitive than any other existing detection principle, like infrared scattering, etc. This allows the detection of PAH traces in water, e.g. in drinking water or condensate applications. Typical applications are discharge monitoring of airports and factories, leakage detection and many others. The sensors can be used either in stationary or portable applications. A new innovative nano-coating on the lenses is preventing the optics from fouling and oil-films, making the enviroFlu-HC longterm stable and virtually maintenance free. In addition, the enviroFlu-HC can be used with a compressed air cleaning system. For a chemical-free check on location solid standards, so called SolidCAL's, are available. On request, special application requirements can be met by changing the filter combinations, possible for example is an enviroFlu-BT for determination of BTX in water. [44]

Figure 10 enviroFlu HC oil in water sensor

Image credit: Trios

Table 8 Specifications EnviroFlu-HC [44]



Auxiliary power	
Interface digital	RS-232 (TriOS)
Interface analog	4...20 mA, 0...5 V
Power supply	12-24 VDC (± 10 %)
Input data	
Turbidity compensation	No
Data logger	No
T100 response time	< 10 s
Measurement interval	< 5 s
Measurement accuracy	enviroFlu-HC 500: 0.3 ppb
Measurement accuracy	enviroFlu-HC 5000: 0.5 ppb
Function and system design	
Analytical methods	Fluorescence
Light source	Miniature Xenon-flash lamp with interference filter (excitation wavelength 254 nm). Output energy controlled by internal reference diode.
Output data	
Power consumption	< 3.5 W
Performance characteristics	
Maintenance effort	Typically < 0.5 h/month
Calibration/maintenance interval	24 months
System compatibility	Analog Out (0...5 VDC, 4...20 mA)
Guarantee	1 year (EU: 2 years)
Installation	
Max. pressure with SubConn	30 bar
Max. pressure with fixed cable	3 bar
Max. pressure in flow cell	1 bar, 2-4 L/min
Protection type	IP68
Structural design	
Housing material	Stainless steel (1.4571/1.4404) or titanium (3.7035)
Weight stainless steel	~ 2.7 kg
Weight titanium	~ 1.9 kg

3.8 SeaOWL UV-A™ (Sea Oil-in-Water™ Locator)

SeaOWL UV-A^{TM} (Fig. 11) by Sea-Bird Scientific (USA) measures crude oil-in-water using the UV-A excitation and blue emission wavelengths (370 nm EX/ 460 nm EM), currently used in the ECO CDOM fluorometer. The SeaOWL UV-A^{TM} improves the resolution and range of the ECO with a greater depth of field, optimized electronics and dynamic gain stage modulation. The dynamic gain provides industry leading sensitivity across a large detection range making saturation unlikely in even the most heavily impacted environments. The compact SeaOWL UV-A^{TM} design also includes chlorophyll fluorescence and 700 nm backscattering measurements to discriminate crude oil from phytoplankton and other natural sources of FDOM. [45]

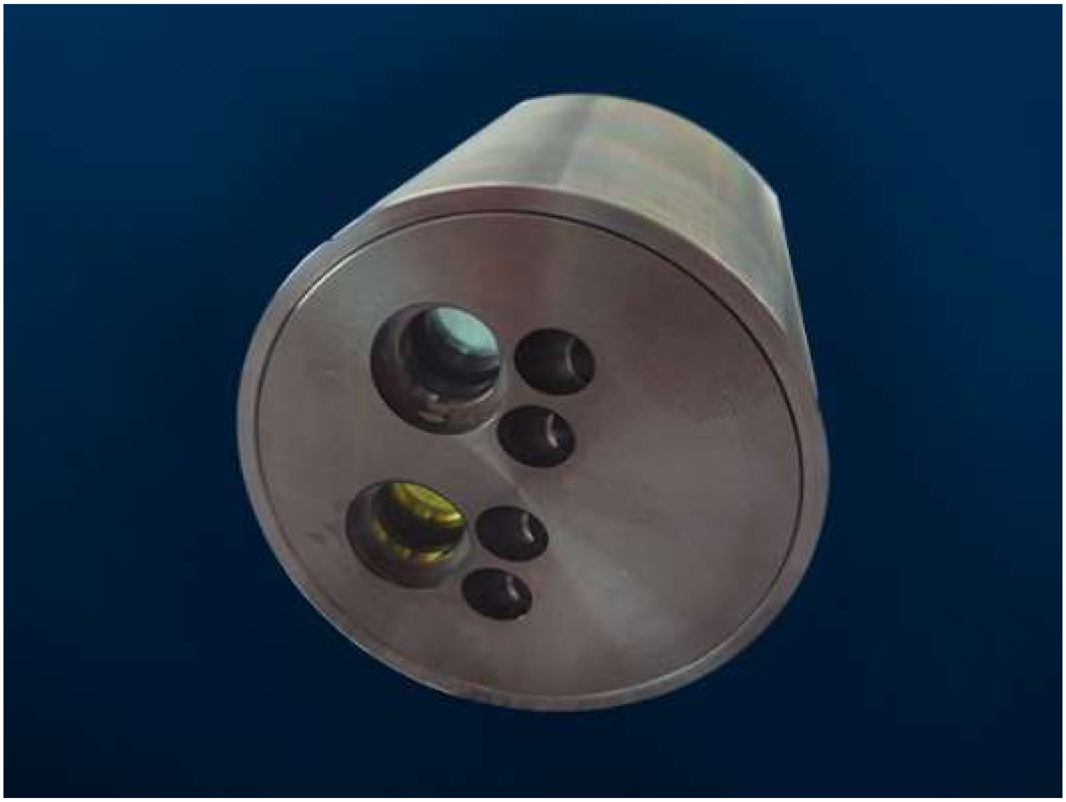
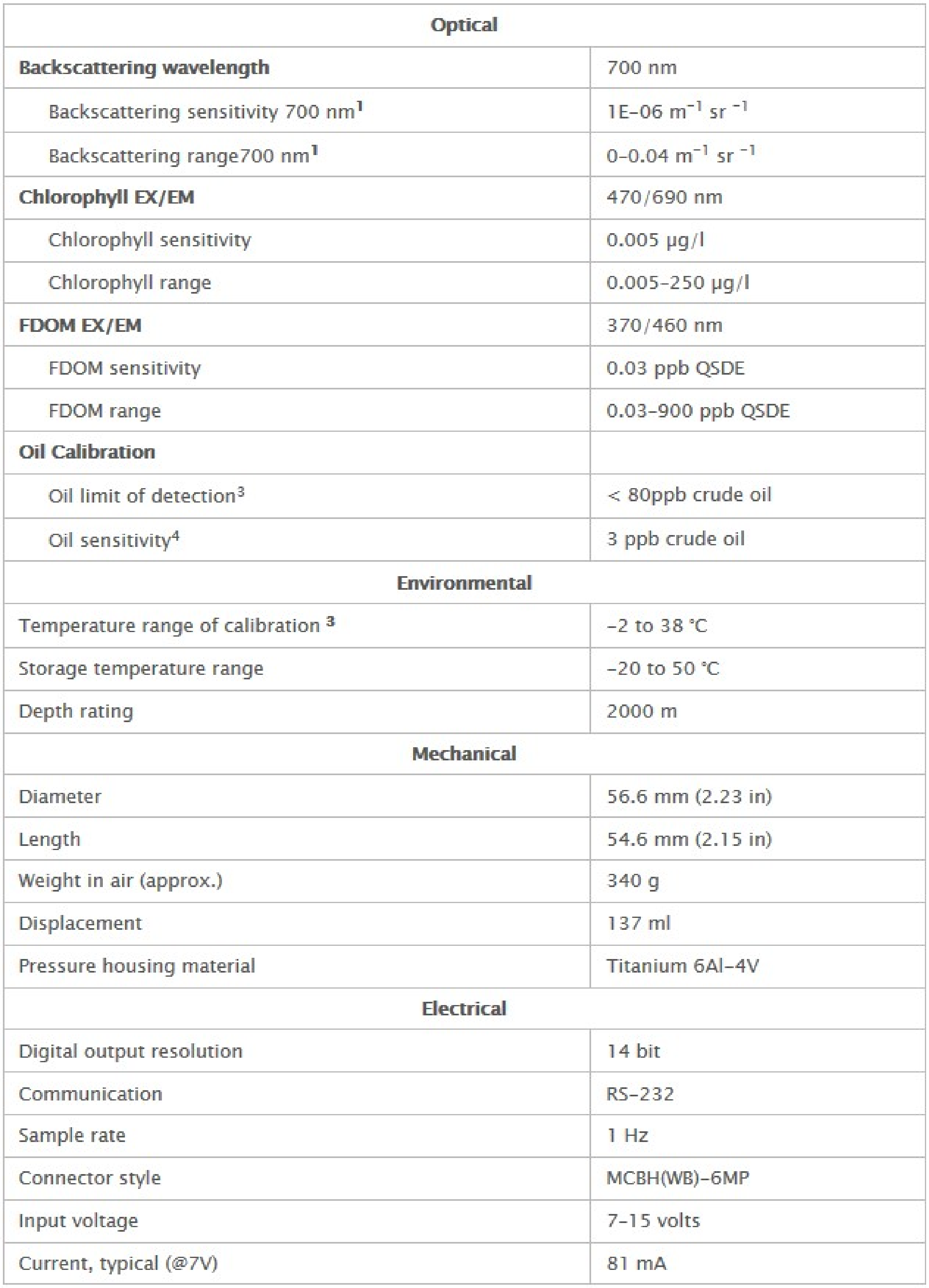


Figure 11 SeaOWL UV-A™ Image credit: Sea-Bird Scientific

Table 9 Specifications of SeaOWL UV-A^{TM} [45]



Optical	
Backscattering wavelength	700 nm
Backscattering sensitivity 700 nm[1]	1E-06 m^{-1} sr^{-1}
Backscattering range700 nm[1]	0-0.04 m^{-1} sr^{-1}
Chlorophyll EX/EM	470/690 nm
Chlorophyll sensitivity	0.005 µg/l
Chlorophyll range	0.005-250 µg/l
FDOM EX/EM	370/460 nm
FDOM sensitivity	0.03 ppb QSDE
FDOM range	0.03-900 ppb QSDE
Oil Calibration	
Oil limit of detection[3]	< 80ppb crude oil
Oil sensitivity[4]	3 ppb crude oil
Environmental	
Temperature range of calibration [3]	-2 to 38 °C
Storage temperature range	-20 to 50 °C
Depth rating	2000 m
Mechanical	
Diameter	56.6 mm (2.23 in)
Length	54.6 mm (2.15 in)
Weight in air (approx.)	340 g
Displacement	137 ml
Pressure housing material	Titanium 6Al-4V
Electrical	
Digital output resolution	14 bit
Communication	RS-232
Sample rate	1 Hz
Connector style	MCBH(WB)-6MP
Input voltage	7-15 volts
Current, typical (@7V)	81 mA

4. Experimental study of oil in water sensor performance - UviLux case study

The UviLux UV fluorometer was chosen for testing, because it is robust, compact and lightweight, has low power consumption, is easy to use and gives accurate and repeatable measurements. It is suitable for deploying independently as well as from submersible vehicles, moored or profiling systems and has special flow-through chamber, which can be integrated into existing FerryBox systems.

The fundamental objectives of this performance study are to:

- verify manufacturer claims on the performance characteristics of the UviLux sensor when tested in a controlled laboratory setting.
- verify performance characteristics of the UviLux sensor when applied in real world applications in a diverse range of coastal environments and on a FerryBox system.

Alliance for Coastal Technologies has conducted quite thorough evaluation of the performance (response range, accuracy, precision and reliability) of the Chelsea UviLux fluorometer; testing it in laboratory, wave tank. Also moored field test and vertical profiling test were conducted on the east coast of USA. Quality assurance/quality control were also made and available [32].

4.1 Laboratory study of the UviLux oil in water sensor

A laboratory study of the Uvilux fluorometer (Fig.13, 14) was conducted mainly to study oil sensor UviLux signal stability and sensitivity to sample oil, as well review its ability to measure real-time oil-in-water concentrations. The sensor was first placed into clean tap water for approximately 68 hours and during second test approximately 68 hours to a container with mixture of water and mineral motor oil. For testing the UviLux sensor was integrated with portable modem/datalogger system and a battery, allowing (Fig.12, 15) autonomous operation with sensor.

Figure 12 The UviLux sensor, integrated with portable modem/datalogger system and a battery, allowing autonomous operations both in field and lab

Figure 13 The UviLux sensor and 5 meter connection cable

Figure 14 Close-up of the UviLux sensor window

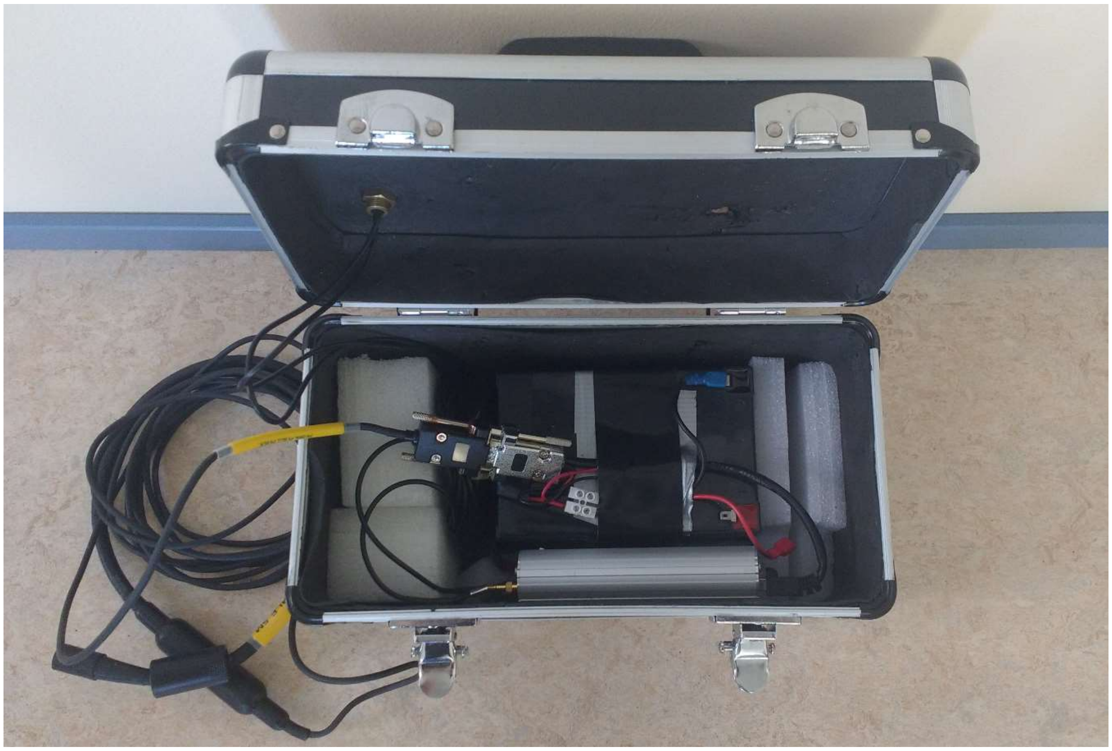


Figure 15 Portable modem/datalogger system with GPS and a battery

4.1.1 Laboratory study of the UviLux sensor in clean water

Sensor was undulated into water in special basin with volume about 5 liters, freely hanging, with water depth about 14 cm and sensor depth 10 cm. The measuring interval was 1 measurement per minute. Sensor shows very good stability during approximately 68 hours of operation with variations inside 0,009 units. At the beginning of the test, the readings are lower and then rise about 0,006 units, and then becomes more or less stable. This small rise can be due the water temperature change, or some kind of fouling.

The negative values can be explained by the small sensor output due the absence of PAH-s. That is because manufacturer used Carbazole as calibration hydrocarbon for this sensor and the following formula was derived from the readings to relate instrument output to Carbazole concentration (signal is reported sensor output):
[Carbazole] = 0,0000129 x signal - 0,0866

Calibration of the fluorometer is generally carried out using a specific oil, thus, the concentration results obtained in the field are relative to the specific oil and the procedure used to calibrate the instrument – as mentioned, in this case Carbazole.

Sensitivity of UviLux seems to be quite good, as very small variations of the measured parameter can be seen on Fig. 16. One important issue is also the sensors noise and possibility to separate it from actually measured parameter values, but this could be done only by comparing different sensors and/or involving measurements with other technologies and reference methods.

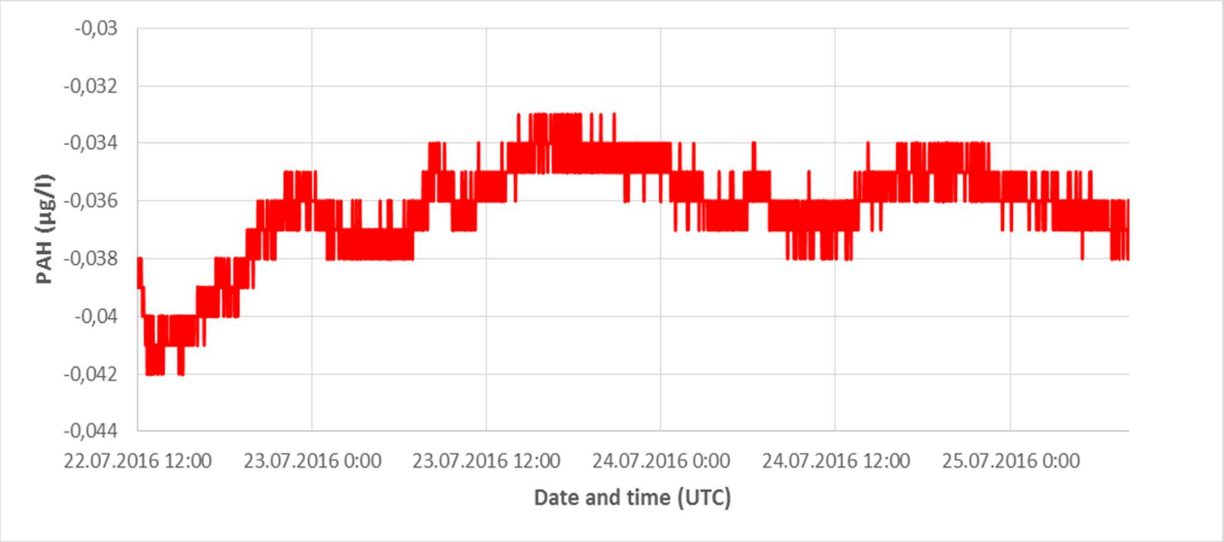


Figure 16 UviLux sensor stability experiment, PAH concentrations (in terms of Carbazole) measured in clean tap water

4.1.2 Laboratory study of the UviLux sensor with motoroil

The mixture consisted of two liters of tap water and 5 ml of unused mineral motor oil “Kamaz”. It was mixed with an electric drill for 10 minutes. Then the UviLux sensor was undulated into water in special basin with volume about 10 liters, freely hanging, with water depth about 15 cm and sensor depth 10 cm and then switched on. The measuring interval was 1 measurement per minute.
At the beginning of the test, the readings peak during the first hour at 1,566 µg/l (Fig. 17), which can be explained by the recent mixing. After that, the readings slowly rise for about 18 hours and then decline steadily until the end of the experiment (Fig.17). This may be due different physical and chemical features of the oil and its degradation and adhesion with the sensor and container walls.

When planning the sensors tests it is important to take into account different response of different oil products in terms of UV fluorescence, which is presented on Fig. 3 and Fig. 18. Motor oil was chosen as it is easy to acquire, but also has to be taken into consideration that UV fluorescence response of the oil is moderate compared to other oil types (Fig. 18). The fluorescence is quite close to that of diesel (light fuel oil) abundant in Baltic Sea oil spills.

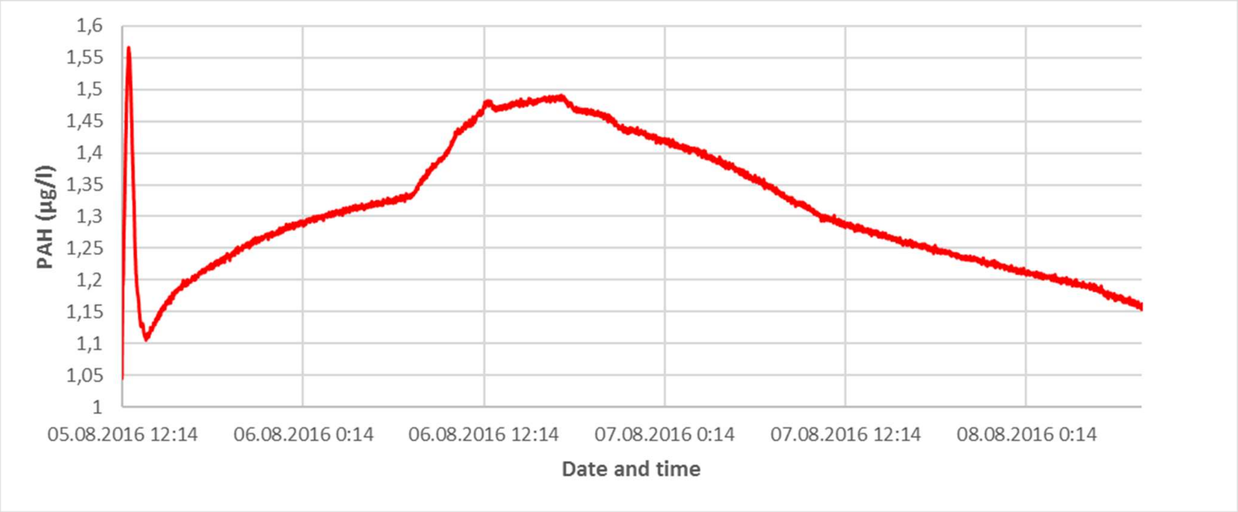


Figure 17 PAH concentrations (in terms of Carbazole) measured with UviLux oil in water sensor during 68 hours period in test basin

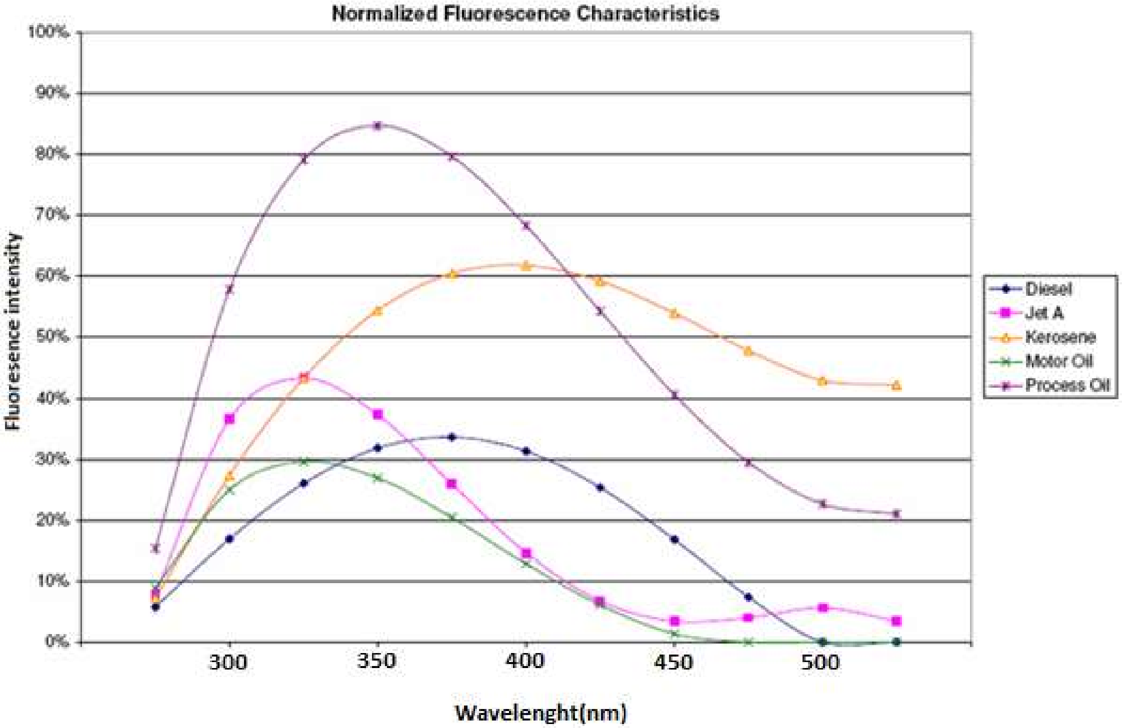


Figure 18 Relative fluorescence of various hydrocarbons, including motor oil [3]

4.2 Field test with the UviLux sensor

A field test was conducted to review Uvilux fluorometers ability to measure real-time oil-in-water concentrations. The UviLux sensor was deployed for a short time in five different harbors around Estonian coast (Fig. 19) (in two harbors to two locations); where due shipping and other industrial operations may have higher concentration of PAH-s in water. The aim was to see if there is differences between the concentrations of PAH-s between those harbors. The Muuga harbor is the biggest cargo harbor in Estonia and nearly 3/4 of cargo loaded includes crude oil and oil products. The harbors on the west coast and islands deal mainly with ferry transport, fishing vessels, dry bulk and other types of cargo.

Measuring depth was 0,5 m. Measurement interval was 1 once per second. The UviLux sensor was integrated with portable modem/datalogger system and a battery, allowing autonomous operation with sensor (Fig.20).

Figure 19 Locations of harbors of Estonian coast where the UviLux sensor was tested

Figure 20 Portable system with UviLux sensor, battery and modem/datalogger deployed in Virtsu harbor

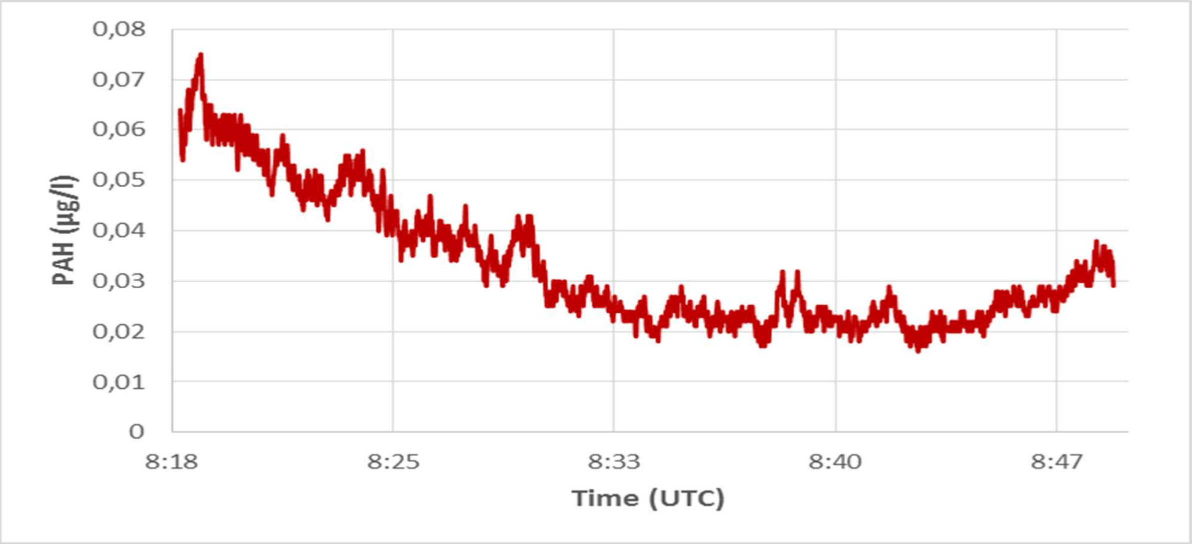


Figure 21 PAH concentrations (in terms of Carbazole) measured with UviLux oil sensor in Virtsu harbor during 31 minutes period in 04.05.2016 (08:18-08:49 UTC)

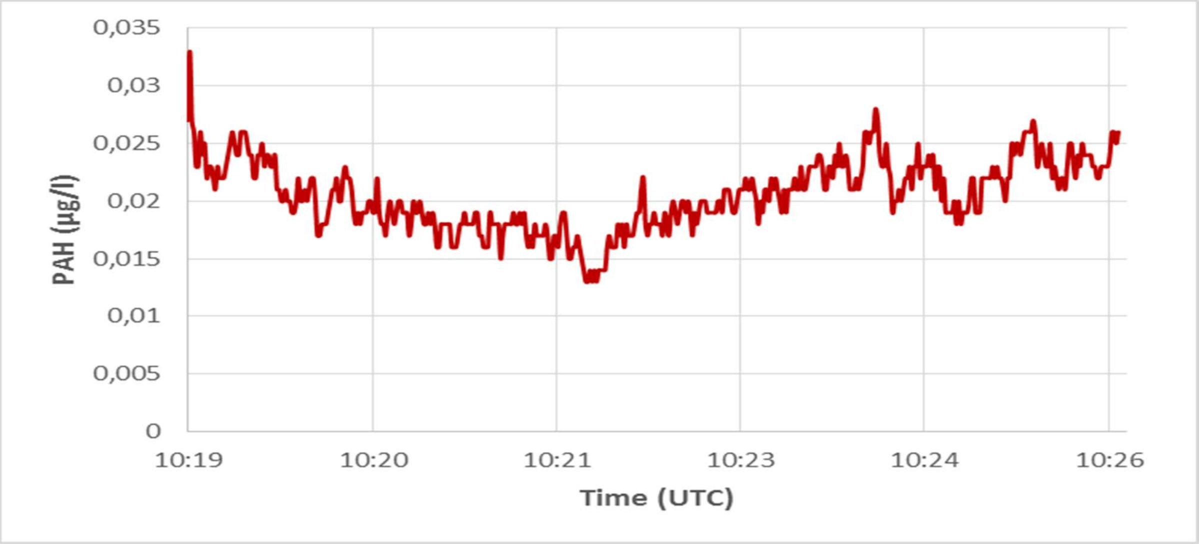


Figure 22 PAH concentrations (in terms of Carbazole) measured with UviLux oil sensor with Virtsu harbor 8 minutes period during second deployment in 04.05.2016 (10:19-10:26 UTC)

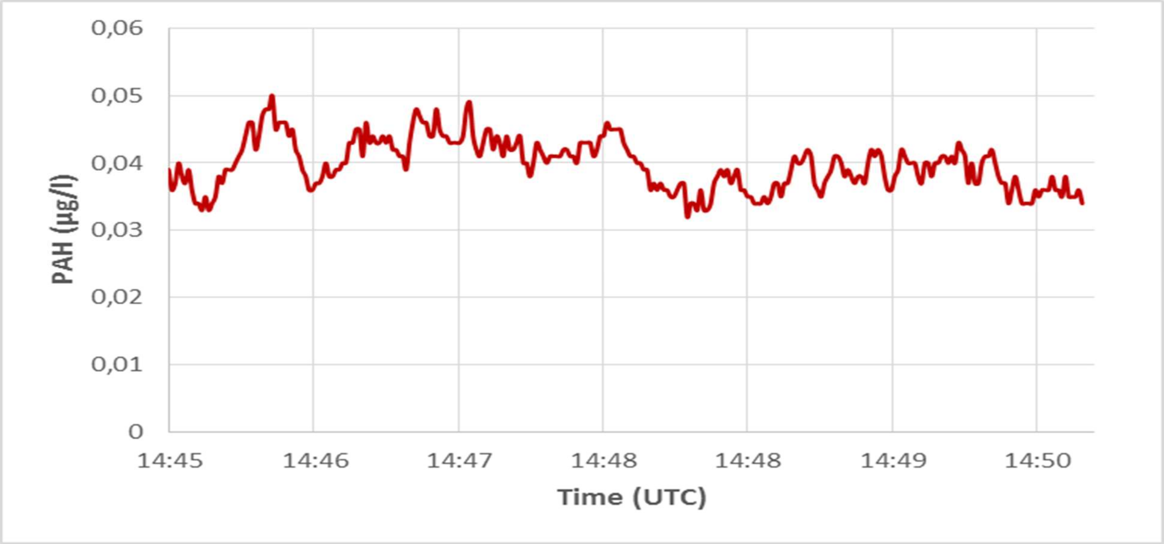


Figure 23 PAH (in terms of Carbazole) concentrations measured with UviLux oil sensor in Triigi harbor during 5 minutes period in 04.05.2016 (14:45-14:50 UTC)

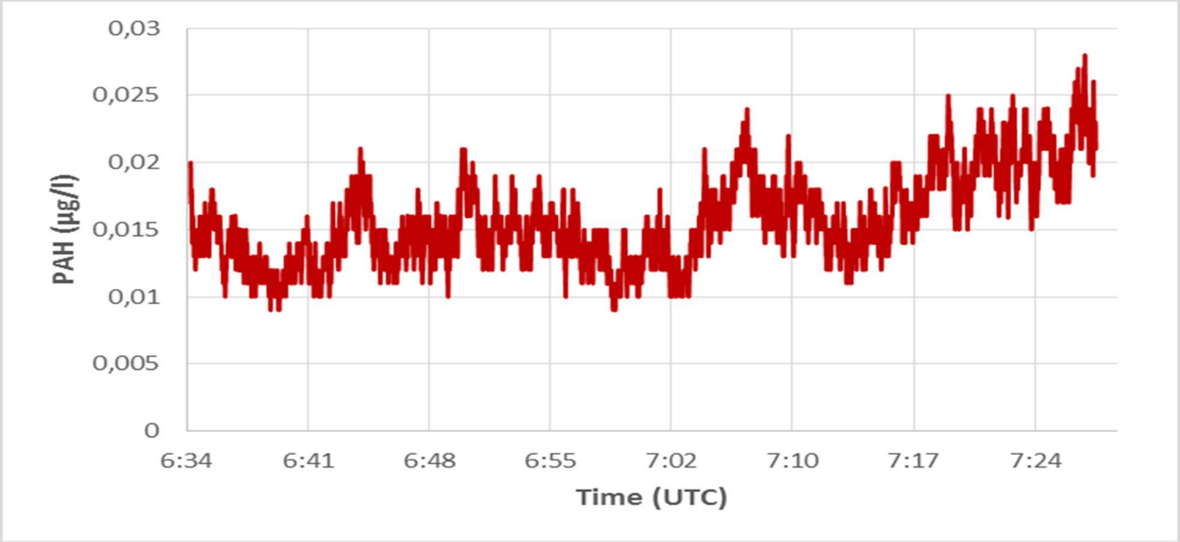


Figure 24 PAH concentrations (in terms of Carbazole) measured with UviLux oil in Lehtma harbor during 54 minutes period in 05.05.2016 (06:34-07:29 UTC)

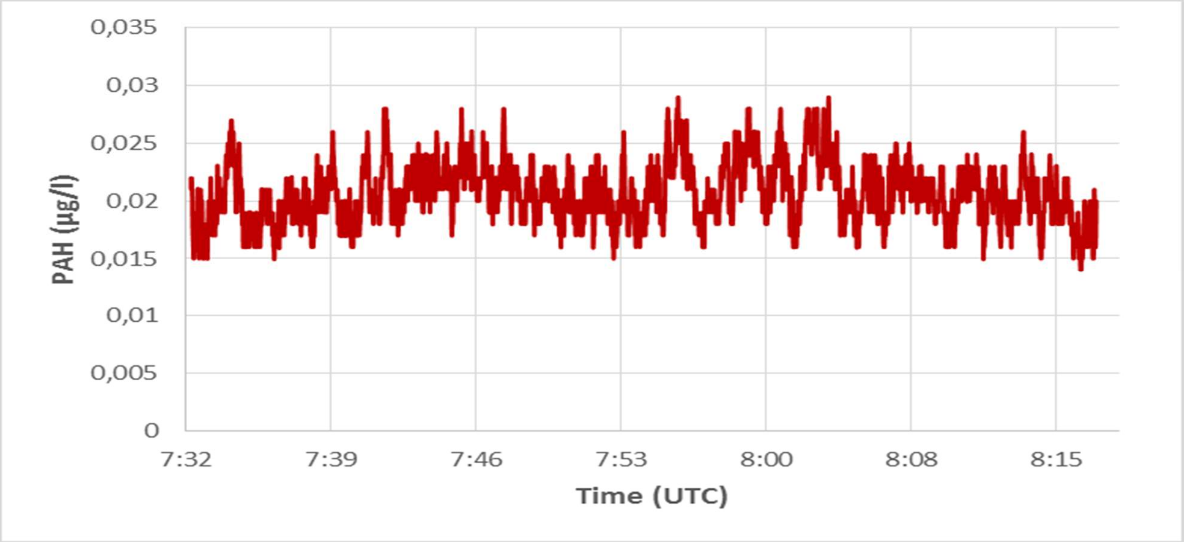


Figure 25 PAH concentrations (in terms of Carbazole) measured with UviLux oil sensor in Lehtma harbor during 45 minutes period during second deployment in 05.05.2016 (07:32-08:18 UTC)

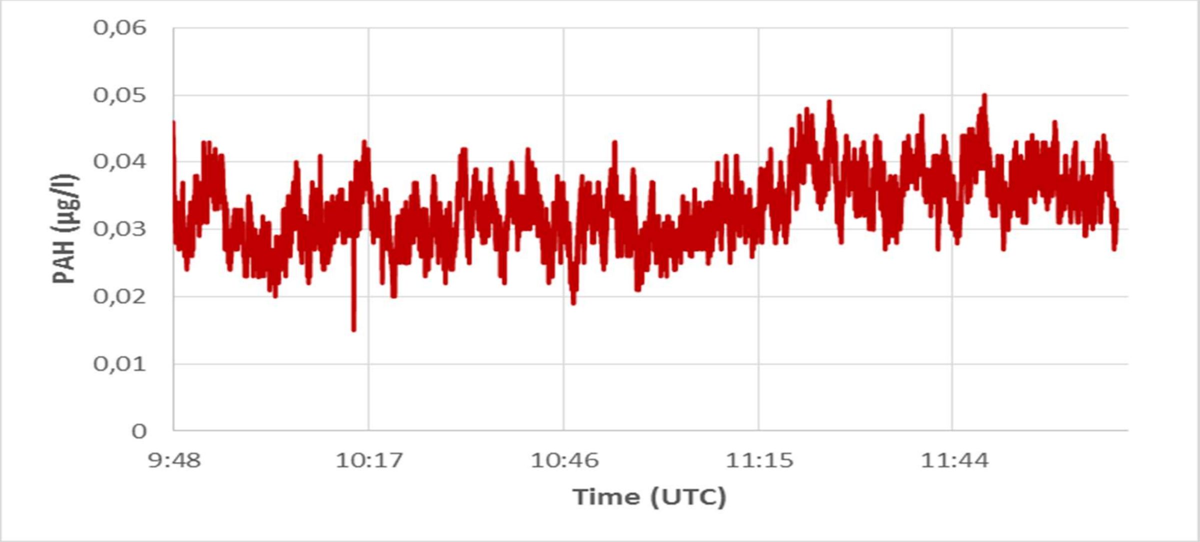


Figure 26 PAH concentrations measured with UviLux oil sensor in Sõru harbor during 140 minutes period in 05.05.2016, (09:48-12:11 UTC)

Figure 27 Portable system with UviLux sensor deployed in Sõru harbor

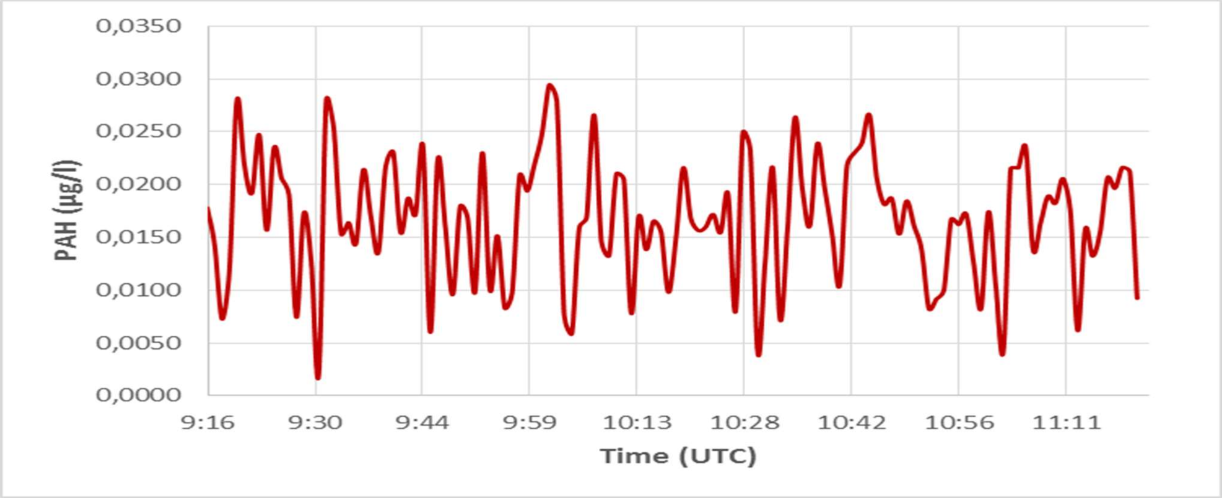


Figure 28 PAH concentrations (in terms of Carbazole) measured with UviLux oil sensor in Muuga harbor during 126 minutes period 09:16-11:23 UTC 02.05.2016. Graph presents data measured with 1-second intervals, averaged over one minute.

Table 10 PAH concentrations (in terms of Carbazole) and weather conditions during measurement campaigns with UviLux

Harbor	Date	Time (UTC)	Air temperature (°C)	Water temperature (°C)	Wind direction	Wind speed (m/s)	PAH min-max (µg/l)	PAH average (µg/l)	Standard deviations of measured values
Muuga	2.05.2016	09:16-11:23	11	10	NE	3,4 -4,0	0,002 - 0,0295	0,0167	0,049796
Virtsu	4.05.2016	08:18-08:49	11	11	NW	2,5-4,3	0,020 - 0,074	0,033	0,01336271
Virtsu 2	4.05.2016	10:19-10:26	12	11	NW	3,5-5,0	0,017 - 0,024	0,021	0,00302901
Triigi	4.05.2016	14:45-14:50	16	10	N	2,8-6	0,037 - 0,043	0,039	0,0037
Lehtma	5.05.2016	06:34-07:29	8	14	NW	1,2-3,8	0,011 - 0,023	0,016	0,003348657
Lehtma2	5.05.2016	07:32-08:18	10	13	NW	2,0-3,4	0,016 - 0,024	0,021	0,002605044
Sõru	5.05.2016	09:48-12:11	14	14	NE	1,6-2,7	0,023 - 0,044	0,033	0,004960122

The aim of the field experiments was to see if there is differences between the concentrations of PAH-s between different harbors. The smallest average concentration of PAH-s were in Lehtma harbor (Fig.24, 25), which is quite small, and open to waves and wind and currents. Triigi and Sõru harbors had the biggest average PAH concentrations (Table 10), that may be because their boat harbors, where the measurement were made are quite isolated from the main waterbody and water exchange there is slow. The first deployment in Virtsu harbor showed also bigger average PAH concentrations and the biggest individual readings, up to 0,074 (µg/l) (Fig. 21), which may be the cause of the small bunkering station near the sampling site.

Regarding data measured in Muuga harbor different approach of data processing was used, the 1-second interval readings were averaged over one minute (Fig. 28).

Overall, the UviLux sensor showed good data quality measuring real-time oil-in-water concentrations and differences between harbors could be seen.

5. Experiment design

Determining the amount of oil dispersed or dissolved in water is always a concern at major oil spills. Many different methodologies exist for measuring oil-in-water concentration. The unique advantages of in-situ portable fluorometers include: instrumentation constructed specifically for field use, ease of operation, low detection limits, and no sample preparation is required.

One major drawback is relating the signals generated by the instrument to the “true” concentration of the oil in the water. Oil is a mixture of hundreds of different chemical compounds yet only a portion of these, specifically some of the aromatic compounds, fluoresce. As well, the relative proportion of aromatic compounds differs between oils and changes as an oil weathers.

Calibration of the fluorometer is generally carried out using a specific oil, thus, the concentration results obtained in the field are relative to the specific oil and the procedure used to calibrate the instrument.

A comparison of the total petroleum hydrocarbon concentration in water using various analytical procedures would provide an insight into the correlation of these methods and gives an opportunity to compare field and laboratory data. In addition, through the examination of the stock oil and the oil dispersed in the water column, a better understanding of the nature of the chemical processes occurring when oil is dispersed into the water column can be achieved. [29]

Experimental design

Keeping in mind, that the oil sensor will be later used on a FerryBox system (Fig. 29), a closed-loop experimental system (Fig. 30) will be set up. In which a pump and tubing will be used to draw water from a vessel, containing water with various concentration of salt (brackish or salt water), through the sample chamber of the fluorometer and then return the water to the original vessel. At noted time intervals, a known amount of oil, an oil and dispersant mixture, or premix, will be added to the vessel. The oil concentration will be allowed to equilibrate throughout the system at which time the fluorometer values will be recorded and a sample of the oily water will be collected.

The stock oils and oily water samples collected from the fluorometer’s discharge line will undergo a detailed chemical analysis to determine the TPH (total petroleum hydrocarbon) using available reference method(s).

The oil and dispersant used in the experiment will be the same used in all of the experiments in project GRACE.

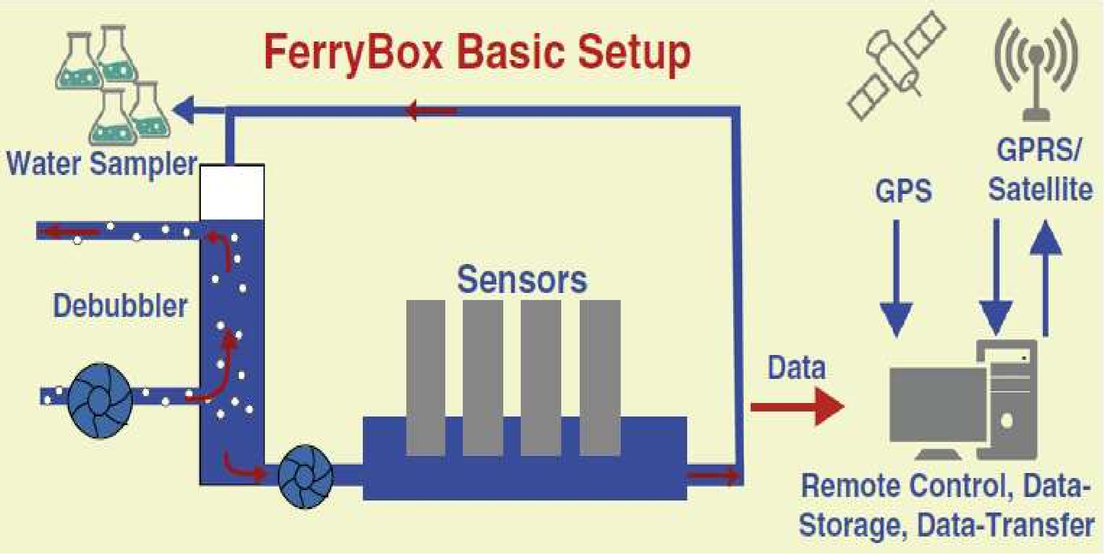


Figure 29 Basic setup of a FerryBox (with optional debubbler) [48]

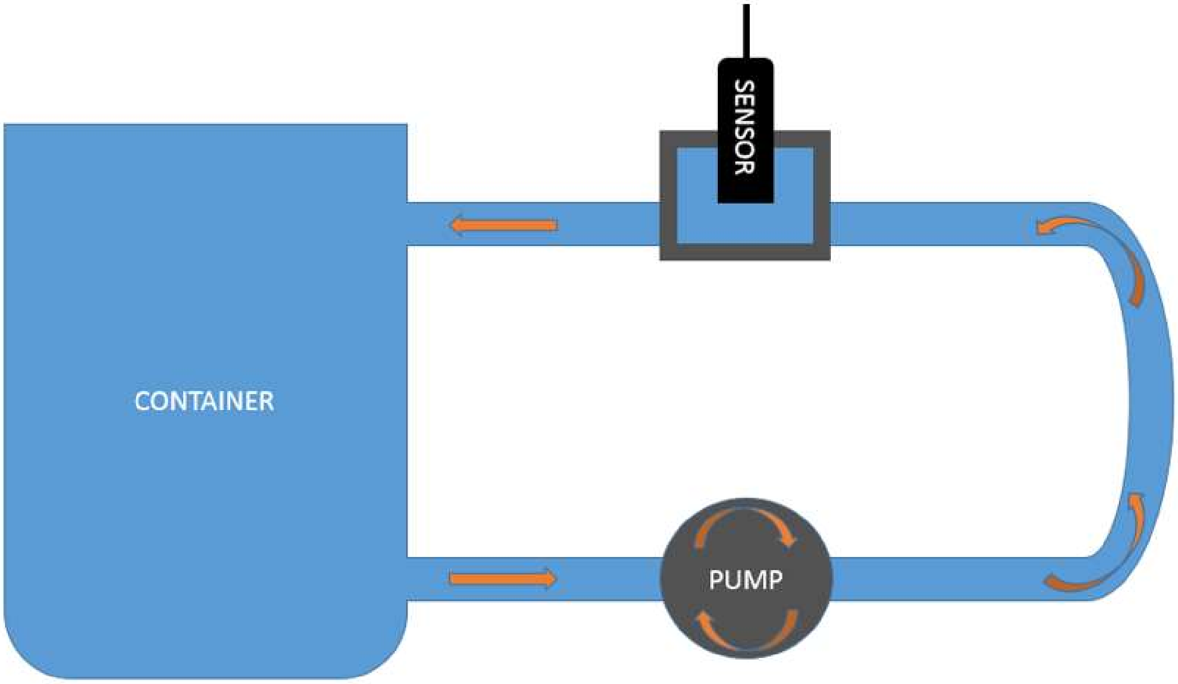


Figure 30 Closed-loop experimental setup

References

[1] M. Yang. Measurement of Oil in Produced Water. Produced Water Environmental Risks and Advances in Mitigation Technologies, 2011, p. 608, pp. 57-88

[2] P. Lambert. A literature review of portable fluorescence-based oil-in-water monitors. Journal of Hazardous Materials , 2003, 102, pp. 39–55

[3] C. R. Chase, L. G. Roberts. Advanced detection technology for early warning – the key to oil spill prevention. International Oil Spill Conference, USA, 2008, p. 16

[4] D. Green, J. Buckley, B. Humphrey, in: Fate of Chemically Dispersed Oil in the Sea. A Report of Two Field Experiments, Environmental Protection Service Report EPS 4-EC-82-5, Environment Canada, 1982, p. 150.

[5] S. Gill, R. Goodman, J. Swiss, Halifax '83 sea trials of oil spill dispersant concentrates, in: Proceedings of the 1985 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1985, pp. 479–482.

[6] J. Swiss, S. Gill, Planning, Development and execution of the 1983 East Coast dispersant trials, in: Proceedings of the Seventh Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1984, pp. 443–453.

[7] H. Brown, Dispersant Effectiveness in Cold Water, Proprietary Report ERCL.RS.85.10, Esso Resources Canada Limited Research Department, Calgary, AB, 1985, p. 45.

[8] H. Brown, R. Goodman, G. Caneari, Dispersant effectiveness in cold water, in: Proceedings of the Eighth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1985, pp. 245–259.

[9] H. Brown, Dispersant Effectiveness in Cold Water 1985 Wave Basin Trials, Proprietary Report ERCL.RS.86.04, Esso Resources Canada Limited Research Department, Calgary, AB, 1986, p. 49.

[10] H. Brown, R. Goodman, G. Caneari, Where has all the oil gone? Dispersed oil detection in a wave basin and at sea, in: Proceedings of the 1987 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1987, pp. 307–312.

[11] H. Brown, R. Goodman, A. Holoboff, C. Peabody, L. Quaife, D. Shaw, Freshwater Oil Spill Research Program Field Trial Final Report, Physical/Chemical, Report ERCL.RS.86.22, Esso Resources Canada Limited Research Department, Calgary, AB, 1986, p. 108.

[12] L. Quaife, Field Report for the Freshwater Oil Spill Research Program Field Trial, Proprietary Report ERCL.RS.86.02, Esso Resources Canada Limited Research Department, Calgary, AB, 1986, p. 103.

[13] G. Sergy, P. Blackall, Design and Conclusions of the Baffin Island Oil Spill Project, Arctic, vol. 40, Suppl. 1, Arctic Institute of North America, University of Calgary, Calgary AB, 1987, pp. 1–10.

[14] D. Green, B. Humphrey, B. Fowler, The use of flow-through fluorometry for tracking dispersed oil, in: Proceedings of the Fifth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1982, pp. 435–444.

[15] D. Green, B. Humphrey, B. Fowler, The use of flow-through fluorometry for tracking dispersed oil, in: Proceedings of the 1983 International Oil Spill Conference, American Petroleum Institute,Washington, DC, 1983, pp. 473–475.

[16] B. Humphrey, D. Green, B. Fowler, D. Hope, P. Boehm, The Fate of Oil in the Water Column Following Experimental Oil Spills in the Arctic Marine Nearshore, Arctic, University of Calgary, Calgary, Canada, J. Arctic Inst. North America 40 (Suppl. 1) (1987) 124–132.

[17] R.R. Hiltabrand, Continuous oil-in-water measurements by fluorometry, in: Oceans'79 Proceedings, The Institute of Electrical and Electronic Engineers (IEEE), Piscataway, NJ, 1979, pp. 566–588.

[18] N. Barnea, R. Laferriere, Smart: scientific monitoring of advanced response technologies, in: Proceedings of the 1999 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1999, pp. 1265–1267.

[19] M.Walker, T. Lunel, Response to oil spills at sea using both demulsifiers and dispersants, in: Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1995, pp. 537–558.

[20] T. Lunel, L. Davis, A. Chen, R. Major, Field test of dispersant application by fire monitor, in: Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1995, pp. 559–602.

[21] T. Lunel, J. Rusin, N. Bailey, C. Halliwell, L. Davies, A successful at sea response to the sea empress spill, in: Proceedings of the Nineteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1996, pp. 1499–1520.

[22] T. Lunel, J. Rusin, N. Bailey, C. Halliwell, L. Davies, The net environmental benefit of a successful dispersant operation at the sea empress incident, in: Proceedings of the 1997 International Oil Spill Conference, American

[23] N. Hurford, I. Buchanan, R.J. Law, P.M. Hudson, Comparison of two fluorometers for measuring oil concentrations in the sea, Oil Chem. Pollut. 5, 1989, pp. 379–389.

[24] A. Lewis, A. Crosbie, L. Davis, T. Lunel, Large scale field experiments into oil weathering at sea and aerial application of dispersant, in: Proceedings of the Twenty-first Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1998, pp. 319–344.

[25] N. Hurford, I. Buchanan, The Use of Flow-Through Techniques to Determine Sub-Surface Concentrations of Oil, LR 552 (OP)M, Warren Spring Laboratory, Stevenage, 1986, p. 25.

[26] N. Hurford, I. Buchanan, R.J. Law, P.M. Hudson, Comparison of Flow-Through and Towed Fluorometers For Measuring Oil Concentrations in the Sea, LR 621 (OP)M, Warren Spring Laboratory, Stevenage, 1987, p. 13.

[27] P. Brandvik, T. Lunel, P. Daling, A. Lewis, Measurements of dispersed oil concentrations by in situ UV fluorescence during the Norwegian experimental oil spill 1994 with Sture blend, in: Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1995, pp. 519–536.

[28] A. Lewis, P. Daling, T. Strom-Kristiansen, A. Nordvik, R. Fiocco, Weathering and chemical dispersion of oil at sea, in: Proceedings of the 1995 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1995, pp. 157–164.

[29] P. Lambert, M. Goldthorp, B. Fieldhouse, Z. Wang, M. Fingas, L. Pearson, E. Collazzi. Field fluorometers as disperssed oil-in-water monitors. Journal of Hazardous Materials, 2003, 102, pp. 57–79

[30] R. N. Conmy, P. G. Coble, J. Farr, A. M. Wood, K. Lee, W. S. Pegau, I. D. Walsh, C. R. Koch, M. I. Abercrombie, M. S. Miles, M. R. Lewis, S. A. Ryan, B. J. Robinson, T. L. King, C. R. Kelble, J. Lacoste. Submersible Optical Sensors Exposed to Chemically Dispersed Crude Oil: Wave Tank Simulations for Improved Oil Spill Monitoring. Environmental Science & Technology, 2014, 48, pp. 1803−1810

[31] M. Tedetti, C. Guigue, M. Goutx. Utilization of a submersible UV fluorometer for monitoring anthropogenic inputs in the Mediterranean coastal waters, Marine Pollution Bulletin, 2010, 60, pp.350-362

[32] T. Johengen, G.J. Smith, H. Purcell, S. Loranger, S. Gilbert, T. Maurer, K. Gundersen, C. Robertson, and M. Tamburri. PERFORMANCE VERIFICATION STATEMENT for the Chelsea UviLux Hydrocarbon and CDOM Fluorometers, Alliance for Coastal Technologies, 2013, p. 57

[33] T. Johengen, G.J. Smith, H. Purcell, S. Loranger, S. Gilbert, T. Maurer, K. Gundersen, C. Robertson, and M. Tamburri. PERFORMANCE VERIFICATION STATEMENT for the Chelsea UV Aquatracka Hydrocarbon Fluorometer, Alliance for Coastal Technologies, 2012, p. 46

[34] V. Malkov, D. Sievert. Oil-in-Water Fluorescence Sensor in Wastewater and Other Industrail applications. PowerPlant Chemistry, 2010, 12(3), p. 11

[35] B. M. Webb. A Personal Watercraft-based System for Costal Ocean Mapping. Mapping the Ocean, 2012, 7(2), pp. 47-68

[36] L. Bristow, M. Cohen, M. Coyle, A. Gravell, C. Kelly, N. King, D. I. Little, R. J. Law, C. F. Moffat, N. Rowlands, D. Runciman. A guide to practices, procedures and methodologies following oil spill contamination incidents. Methods for the Examination of Waters and Associated Materials. Environmental agency, UK, 2004, p. 108

[37] http://www.chelsea.co.uk/allproduct/marine/fluorometers/uvilux-fluorometer

[38] http://www.turnerdesigns.com/products/submersible-fluorometer/c3-submersible-fluorometer

[39] http://www.turnerdesigns.com/products/submersible-fluorometer/cyclops-7-submersible-fluorescence-and-turbidity-sensors

[40] http://www.hach.com/fp-360-sc-oil-in-water-sensor-5-000ppb-stainless-steel-body-10m-32-8-ft-cable/product?id=7640097702

[41] http://www.hach.com/fp-360-sc-oil-in-water-sensor-500ppb-stainless-steel-body-10m-32-8-ft-cable/product?id=7640096696

[42] http://www.chelsea.co.uk/allproduct/marine/fluorometers/uv-aquatracka-fluorometer

[43] http://www.seapoint.com/suvf.htm

[44] http://www.trios.de/en/products/sensors/enviroflu.html

[45] http://wetlabs.com/SeaOWL

[46] http://www.globalspec.com/learnmore/labware_scientific_instruments/environmental_instruments/oil_in_water_monitors

[47] http://www.seos-project.eu/modules/laser-rs/laser-rs-c07-p02.html

[48] W. Petersen. FerryBox Systems (2014): State-of-the-Art in Europe and Future Development, 2014, Journal of Marine Systems 140, pp. 4-12