Sea Surface Scanner (S^3): A Catamaran for High-Resolution Measurements of Biogeochemical Properties of the Sea Surface Microlayer

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ABSTRACT

This paper describes a state-of-the-art research catamaran to investigate processes such as air–sea gas exchange, heat exchange, surface blooms, and photochemistry at the sea surface microlayer (SML) with high-resolution measurements of 0.1-Hz frequency. As the boundary layer between the ocean and the atmosphere, the SML covers 70% of Earth. The remote-controlled *Sea Surface Scanner* is based on a glass disk sampler to automate the sampling of the thin SML, overcoming the disadvantages of techniques such as low volume sampling and ex situ measurement of the SML. A suite of in situ sensors for seven biogeochemical parameters (temperature, pH, dissolved oxygen, salinity, chromophoric dissolved organic matter, chlorophyll-*a*, and photosynthetic efficiency) was implemented to characterize the SML in reference to the mixed bulk water. The *Sea Surface Scanner* has the capability to collect 24 discrete water samples with a volume of 1 L each for further laboratory analysis. Meteorological parameters such as wind speed influence SML properties and are continuously monitored. This paper reports the use of the *Sea Surface Scanner* to identify and study (i) upwelling regions and associated fronts, (ii) rain events, and (iii) the occurrence of surface blooms. The high patchiness of the SML was detected during the observed sea surface phenomena, and high-resolution mapping of the biogeochemical parameters of the oceanic boundary layer to the atmosphere are presented for the first time. The *Sea Surface Scanner* is a new technology to map and understand sea surface processes and, ultimately, to fill the gaps in knowledge about ocean–atmosphere interactions relevant to ocean and climate science.

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1. Introduction

Interactions between the ocean and the atmosphere play a crucial role in many ocean and climate science disciplines, and they have prompted attempts to estimate the exchange rates of climate-relevant gases, heat,

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and particles. However, the sea surface microlayer (SML), the interfacial boundary layer between the ocean and the atmosphere (typically 40–100 μm in thickness), has been widely ignored in the past and current research efforts. Through its unique position at the air–sea interface, the SML plays a central role in a range of global biogeochemical- and climate-related processes (Soloviev and Lukas 2014). The SML's impact on air–sea exchange processes has been known for several decades (Broecker et al. 1978). For example, the reduction of gas transfer velocity in the presence of the SML has been investigated in wind-wave tunnels (Broecker et al. 1978) and, more recently, in the presence of artificial surface films in the North Atlantic (Salter et al. 2011). The SML's role in the emission and deposition of aerosols is even more elusive; however, a recent study indicated a direct link between the SML and the properties of marine aerosols (Wilson et al. 2015). The SML is also known to be a distinct microbial habitat with unique communities (Cunliffe et al. 2011); moreover, under certain conditions, it is recognized to have biofilm-like properties that may influence the CO_2 air–sea exchange (Wurl et al. 2016).

The SML often has remained in a distinct research niche, primarily because it was thought that it did not exist in typical oceanic conditions; furthermore, it is challenging to collect representative SML samples under natural conditions. The first issue has been resolved by a global study (Wurl et al. 2011), indicating that the SML covers the ocean to a significant extent through the ubiquitous presence of surface-active substances in the SML. Wurl et al. (2011) suggested that breaking waves facilitate the reformation of disrupted SML by scavenging surface-active substances on rising air bubble plumes. The second issue, representative sampling, remains challenging because it is time consuming to collect the SML using a hand-operated glass plate (Harvey and Burzell 1972) or a screen sampler (Garrett 1965). Therefore, neither approach resolves the issues related to the dynamic and heterogeneous nature of the SML; that is, the characteristics and concentrations of the materials in the SML may change rapidly during sampling. As outlined in a recent guideline to study the sea surface (Cunliffe and Wurl 2014), sample collection has to be conducted at an appropriate distance ($>200\text{ m}$) from the vessel to avoid contaminating and disturbing the integrity of the SML. Catamarans with rotating glass drums (Carlson et al. 1988; Harvey 1966) or disks (Shinki et al. 2012) allow for the collection of larger volumes and for the use of flow-through sensors (Carlson et al. 1988). Earlier catamarans (Carlson et al. 1988; Harvey 1966) were towed because of technical limitations, but disintegration of the SML may have

occurred due to the wake of the boat. However, more recently, technical advances have allowed for the implementation of radio controls (Frew et al. 2004) and automatic global positioning system (GPS) navigation (Caccia et al. 2005). The few catamarans for SML research described in the literature are vehicles for specialized tasks; for example, they are designed for organic trace analysis (Wurl and Obbard 2005) and wave characterization (Frew et al. 2004). Caccia et al. (2005) developed the Sea Surface Autonomous Modular Unit (SESAMO) catamaran with a state-of-the-art navigation system, but they encountered limitations in sampling the SML with good integrity due to a perpendicularly oriented glass drum. Shinki et al. (2012) described for the first time the use of rotating glass disks instead of glass cylinders that are oriented either perpendicular (Caccia et al. 2005; Harvey 1966) or parallel to the travel direction (Carlson et al. 1988; Wurl and Obbard 2005). Because of the catamaran's own movement, glass discs have the advantage of significantly minimizing the disturbance of the sea surface in comparison to drums, which have a larger surface in contact with the sea surface. To date, the catamarans that have been described in the literature have their own advantages and disadvantages (Wurl and Obbard 2004) depending on their specific purpose or technical possibilities at the time of construction. In the past, limited technology in remote control systems, power supplies, and electronics with sufficient memory capacities has restricted the knowledge for high-resolution in situ measurements at the sea surface.

This study aimed to design, construct, and test a versatile catamaran with state-of-the-art sensor technology to measure biogeochemical properties in situ at the sea surface with high resolution. This paper describes the design and technical features of the catamaran, and its ability to detect sea surface phenomena, such as fronts, upwelling, surface blooms, and wet deposition. It discusses the high-resolution measurements of temperature, fluorescence dissolved organic matter (FDOM), pH, and chlorophyll-*a* (Chl-*a*), as well as photosynthetic parameters.

2. Materials and methods

a. The Sea Surface Scanner catamaran

In this present study, the catamaran *Sea Surface Scanner* (S^3) is based on a commercial sailing catamaran (*New Cat 15*, Erplast, France) with a length of 4.5 m and a width of 2.2 m (Fig. 1). For propulsion, the S^3 uses an electric outboard engine (Travel 1003, Torqueedo, Germany) with a power of 2.22 kW and an integrated lithium-ion (Li-ion) battery of up to 920 Wh. The battery capacity allows for an operation of up to 7 h, depending

FIG. 1. (a) Research catamaran S^3 at sea. (b) Rotating glass discs to collect the sea surface microlayer (SML). (c) Flow-through system.

on the sea state and the prevailing currents. The pilot navigates the S^3 via a radio controller (MX-16, Graupner, Germany) equipped with reliable 2.4-GHz transmission technology and bidirectional communication between the transmitter and the receiver. An accessory throttle (TO-1918-00, Torqueedo, Germany) for the outboard engine was modified with a servo for speed control. An ultrahigh-torque servo (i00600 Torxis Servo, GearWurx, United States) moves the outboard engine via a steering rod for navigation. The radio control system is equipped with a GPS module (33600 GPS, Graupner, Germany) so that the pilot receives the current position, speed, and travel direction of the catamaran on the radio transmitter display. An additional GPS logger (GT-730FL-S, Canmore, Taiwan) on the catamaran saves the current position every 10 s.

A set of six rotating glass discs (diameter: 60 cm; thickness: 0.8 cm) is mounted between the hulls near the bows to collect the SML. The height of the frame holding the discs is adjustable so that the depth of immersion of the discs can be changed. Typically, the discs are immersed to a depth of about 15 cm. To identify periods of collection the SML with poor integrity—for example, by splashing of waves on the glass discs—two action camcorders record sampling on the glass discs.

An electric motor (MBT82M, Leroy-Somer, Germany) with a gear box (SG 1032, Leroy-Somer, Germany) rotates the glass discs via a belt within a range of 6–10 rpm. The speed of rotation is adjusted with an rpm controller (10–50 Vdc, 40 A) that is remotely controlled by a servo via the radio control. The discs are separated by a gap of 5 cm, which is large in comparison to the collected SML (thickness of $<100 \mu\text{m}$). Shinki et al. (2012) used an optical technique measuring light attenuation of dyed films on glass discs, and they did

not detect interferences by the configuration of the glass discs. Water found in the SML adheres to the discs through the process of surface tension on the ascending side, and it is scraped off by a set of wipers mounted on the descending side between the discs. The wipers are made of polycarbonate, and their tilted position allows the SML water to flow by gravity into a low-volume collection vessel, from which it is directly pumped through the sensors (see section 2b) or a radio-controlled water sampler. A rotation speed of 7 rpm collects the SML with a rate of 20 L h^{-1} and a thickness of about $50\text{--}80 \mu\text{m}$ (Shinki et al. 2012), which is generally consistent with the experimentally determined SML thicknesses of $50 \pm 10 \mu\text{m}$, using pH microelectrodes (Zhang et al. 2003). Simultaneously to the SML sampling, the S^3 continuously collects the underlying water (UW) from a depth of 1 m, as a reference to the SML measurements (Fig. 2). The tubing for the collection of UW is fixed within a rigid pipe to ensure a collection depth of 1 m.

The water collector (model 6710, Teledyne Isco, Inc., United States) contains twenty-four 1-L polypropylene bottles and a controller with advanced programming capabilities. The insulated interior of the water collector provides sufficient space for cooling packs to maintain the collected water at $<10^\circ\text{C}$ for several hours depending on the ambient air temperature. A switch module (SXM, Graupner, Germany) was used to trigger the water collector using the radio control. Upon triggering, the distributor arm with the attached discharge tube moves to the next bottle, and the integrated peristaltic pump (P3 in Fig. 2) runs to fill the bottle. Via a radio-controlled pinch valve (V1 in Fig. 2), the pilot selects whether a bottle is to be filled with the SML or the UW. With this configuration, the pilot has full control of the sampling time and

FIG. 2. Schematic view of the flow-through system with pumps (P1–P3), valves (V1), and sensor technology to measure salinity (Sal), pH, oxygen (Oxy), FDOM, Chl-*a*, and photosynthetic parameters (Photo).

the type of sample (SML or UW), for example while navigating through slicks, fronts, and surface blooms.

b. Sensor technology

Sensors are installed either in boxes or on the mast of the S^3 (Fig. 1). The flow-through system with the sensor technology is shown in Fig. 2. Two peristaltic pumps (P1 and P2 in Fig. 2; model CP83, Gemke Technik GmbH, Germany) transfer water from the SML and the UW (1-m depth) into two separate flow-through systems made of polypropylene tubing (internal diameter of 5 mm) with an adjustable flow rate of up to 1.2 L min^{-1} . Specifications of sensors for in situ measurements of pH, salinity, oxygen, temperature, quantum efficiency, and FDOM are listed in Table 1. The flow cells for pH, conductivity, and oxygen were handmade from plumbing T pieces and watertight cable glands for insertion of the electrodes (Fig. 1c). The flow cells for the FDOM sensor and the fluorimeter are available from the manufacturers. To ensure that the measurements are not contaminated, the tubing of the flow-through system is regularly rinsed with freshwater prior to and after operation, and it is rinsed with a cleaning solution for about 10 min or exchanged if necessary. Regarding the cleaning solution, the flow-through system is compatible for technical ethanol to sterilize the flow-through system and 10% hydrochloric acid to remove deposits of organic matter.

Two different instruments were chosen for the pH measurements, depending on the operational needs (Table 1).

The multimeter MU6100H (VWR, Germany) can simultaneously measure two of the three parameters (pH, salinity, and oxygen), but it has an internal memory for 5000 datasets; this means that it is possible to obtain $>13 \text{ h}$ of data recording with a 10-s interval. The alternative device, PCD650 (EuTech Instruments, Singapore), can measure all three parameters simultaneously, but it is limited by an internal memory, which means that it is possible to obtain only $<1.5 \text{ h}$ of data recording with a 10-s interval. The S^3 is usually operated for 3–6 h; thus, the MU6100H allows for complete recording of data. The meters are calibrated 1–2 h prior to deployment in the expected range of measurement.

The FDOM sensor (microFlu-CDOM, TriOS, Germany) has an ultraviolet light-emitting diode (UV-LED) as its light source with an excitation wavelength of 370 nm. Signals are detected at an emission wavelength of 460 nm with full width at half maximum (FWHM) of 100 nm. The outputs of the two sensors (0–5 Vdc) are logged in a two-channel datalogger (Track-IT, Monarch Instruments, Amherst, New Hampshire). Two digital voltmeter modules were incorporated into the circuit displaying real-time data to allow for better quality control and blank assessment. The sensors were calibrated by TriOS without the need for recalibration, and the settings of factory calibration were stored internally.

The active fluorimeter PhytoFlash (Turner Designs, Sunnyvale, California) was used to monitor Chl-*a* and the quantum efficiency of the phytoplankton community in the

TABLE 1. Manufacturers and specifications of the onboard sensors.

Parameter	Manufacturer	Model	Range, unit, and resolution	Sensitivity	Accuracy	Sample ^a
pH	VWR	MU 6100 H	−2.000 to 19.999		±0.005	SML and UW
Salinity ^b	VWR	MU 6100 H	0.0–70.0		±0.2%	SML and UW
Oxygen, concentration	VWR	MU 6100 H	0–20.00 or 20.0–90.0 mg L ^{−1}		±0.5%	SML and UW
Oxygen, saturation	VWR	MU 6100 H	0%–200.0% or 0%–600%		±0.5%	SML and UW
Temperature or ^c	VWR	MU 6100 H	−5.0° to 105.0°C		±0.1°C	SML and UW
pH	EuTech Instruments	PCD650	−2.000 to 20.000		±0.002	SML and UW
Salinity ^b	EuTech Instruments	PCD650	0.0–80.0		±1%	SML and UW
Oxygen, concentration	EuTech Instruments	PCD650	0–90.00 mg L ^{−1}		±0.2 mg L ^{−1}	SML and UW
Oxygen, saturation	EuTech Instruments	PCD650	0%–600%		±0.2%	SML and UW
Temperature	EuTech Instruments	PCD650	−10.0°C to 110.0°C		±0.5°C	SML and UW
FDOM	TriOS	MicroFlu	0.0–20.0 or 0.0–200.0 $\mu\text{g L}^{-1}$	0.2 $\mu\text{g L}^{-1}$		SML and UW
HPT	Dostmann Electronic GmbH	P795	−200.000° to 200.000°C		±0.015°C	2 and 15 cm
Chlorophyll- <i>a</i>	Turner Designs	Phytoflash	0–150.00 $\mu\text{g L}^{-1}$	0.15 $\mu\text{g L}^{-1}$		SML or UW
Photosynthetic yield as ratio Fv/Fm	Turner Designs	Phytoflash	0.000–1.000			SML or UW
Air temperature	Davis Instruments	Vantage Pro2	−40.0°C to 65.0°C		±0.3°C	Atmosphere
Humidity	Davis Instruments	Vantage Pro2	0%–100%		±2%	Atmosphere
Wind speed 1	Davis Instruments	Vantage Pro2	0.5–89 m s ^{−1}		±1 m s ^{−1} or ± 5% ^c	Atmosphere
Wind speed 2	PCE Instruments	PCE-KWG2	0.8–40 m s ^{−1}		±0.5 m s ^{−1} or ± 5% ^d	Atmosphere
Wind direction	Davis Instruments	Vantage Pro2	0°–360°		±3°	Atmosphere
Rain rate	Davis Instruments	Vantage Pro2	0–100 mm h ^{−1}		±4%	Atmosphere
UV radiation dose (280–360 nm)	Davis Instruments	Vantage Pro2	0.1–19.9 MEDs or 20–199 MEDs		±5%	Atmosphere
UV radiation index (280–360 nm)	Davis Instruments	Vantage Pro2	0.0–16.0 index		±5%	Atmosphere
Solar radiation (400–1100 nm)	Davis Instruments	Vantage Pro2	0–1800 W m ^{−2}		±5%	Atmosphere
PAR	Apogee Instruments	MQ-220	0–3000 $\mu\text{mol m}^{-2} \text{s}^{-1}$		±5%	Atmosphere
GPS	Canmore	GT-730FL-S	Latitude and longitude (°)		3 m	

^a SML refers to a operationally defined thickness ranging from 60 to 100 μm . UW refers to a depth of 1 m.

^b Derived from the measurement of conductivity.

^c Depending on operational needs (see text).

^d Whichever is greater.

UW. The PhytoFlash detection system utilizes three low-intensity LEDs to monitor minimum fluorescence (Fo). After saturating the cells with light in the sample chamber

using six high-intensity LEDs, it measures maximum fluorescence (Fm). The variable fluorescence (Fv) is Fm–Fo. The quantum efficiency or yield (Fv/Fm) is a

FIG. 3. Map of stations where the S^3 sampling for the SML and the underlying seawater (UW) was conducted in the Baltic Sea and the North Sea. The map was done using Ocean Data view (Schlitzer 2017).

parameter that describes how well the phytoplankton can assimilate light for photosynthesis. These photosynthetic parameters can be used as baseline data, as they provide an early indication of changes in the primary production of phytoplankton. The sensor is calibrated with reference to a benchtop fluorimeter (see section 2c) according to the supplier's recommended procedure. A solid secondary standard (Turner Designs, Sunnyvale, California) is used to check the stability of the fluorimeter.

High-precision temperatures (HPT) at depths of approximately 2 and 15 cm were recorded with a two-channel temperature logger P-795 (Dostmann Electronic, Germany). Temperature sensors were mounted between the hulls.

The meteorological and radiation sensors (Table 1) were mounted onto the mast at a height of 3 m above the sea surface. Wind speed and associated wave fields are the most crucial driving forces for sea surface processes (Hardy 1982). As wind fields are distorted by larger vessels, two anemometers were installed on S^3 and used to compare and collect fail-safe data (Table 1). In fact, wind speed referenced to 10 m above the sea surface (U_{10}) according to Kleemann and Meli (1993) from S^3 was significant higher than U_{10} from R/V *Meteor* (Mann–Whitney test, p value < 0.0001). In addition, unattenuated radiation can, potentially, have a direct effect on the biochemical properties of the sea surface. Therefore, ultraviolet radiation (UV; 280–360 nm), solar radiation (400–1100 nm), and photosynthetically active radiation (PAR; 410–655 nm) were

monitored. PAR is an essential parameter for estimating primary production, the most important source of surface-active substances to the sea surface that form the SML; it can be monitored using the Vertically Generalized Production Model (VGPM) (Behrenfeld and Falkowski 1997).

c. Field operation

With a team of three, preparation of S^3 prior deployment takes typically 2 h and includes calibrating and configuring of sensors (if required), connecting of supplies, preparing sample bottles, and going through a final check list. With an experienced team, deployment and recovery takes about 20 min. A small boat is required for deployment and recovery to release or attach S^3 's lifting straps from or to the crane hook. A pilot operates S^3 from the main deck up to a distance of 1500 m from the ship. A second person logs the operation and sampling of discrete water samples, and stays in contact with the bridge via radio communication.

In this study, the S^3 was operated during cruises on the R/V *Meteor* in the Baltic Sea (cruise M117, August 2015) and the R/V *Senckenberg* in the North Sea (June 2016). The sampling locations are shown in Fig. 3. The stations were selected according to the observed sea surface phenomena; they and the sampling details are listed in Table 2. Upwelling was observed offshore of the island of land (Sweden) with a temperature gradient of 6°C from station UP3 to station TF0284, based on the shipboard flow-through

measurement. The S^3 was operated for approximately 4 h at each station, navigating from either a small boat or the main deck of the research vessel.

d. Chemical and biological analyses

The concentrations of the surfactants, Chl-*a*, and cell abundances were measured in the discrete SML and UW samples collected by the S^3 . The surfactants were analyzed using phase-sensitive alternating current voltammetry (Metrohm VA 747, Switzerland) with a hanging mercury drop electrode (HDME), as noted by Čosović and Vojvodić (1998).

The Chl-*a* concentrations were measured after extraction in 90% acetone (24 h at 4°C) using an acidification fluorescence technique (Lorenzen 1967). The fluorometer (Jenway 6285; Bibby Scientific Ltd., United Kingdom) was calibrated prior to the analysis using pure Chl-*a* that was extracted from spinach (Sigma Aldrich, Germany). Typically, 500 mL of UW were filtered in triplicate under vacuum onto glass microfiber filters (grade GF/F, Whatman, United Kingdom), and stored at -80°C until analysis. The bacterial cell count was determined using flow cytometry according to Rahlff et al. (2017), and the autotrophic cell count was determined using the procedure reported by Marie et al. (2000).

e. Data management

All the sensors listed in Table 1 record data with a preset interval, typically every 10 s based on their respective internal clock. Full-resolution data products for a typical deployment of 5 h contain 2000 data points. For ease of construction and robustness in operation, the sensor's internal memory with time stamps was used instead of onboard data acquisition. For this reason, all the sensors were synchronized to the coordinated universal time (UTC) based on the time provided by a master computer. The master time was transferred to each sensor through a USB connection and the sensor's software. The master computer time was set according to network time protocol (NTP). After recovery of the catamaran, the data were downloaded and saved to the master computer.

The sensors log data in their internal memory using the ASCII format, but the structure of the format varies among the sensors. An Excel macro is used to apply sensor-specific conversions and to merge data into a single database. The Excel macro consists of a graphical user interface to select data files and other sensor-specific settings, such as the recording interval, the calibration factors, and the range of acceptable values. Values outside of the defined range are replaced by not a number (NaN), which can occur if air bubbles flow through the system, interfering with the measurements.

TABLE 2. Data given as average and standard deviation from wind speed, photosynthetic ratio Fv/Fm, longitude and latitude, and discrete samples (measured a posteriori in the laboratory) in different stations. EF is unitless.

Date	Station	Event	Wind speed (m s^{-1})	Fv/Fm	Lon ($^{\circ}\text{E}$)	Lat ($^{\circ}\text{N}$)	Surfactants ($\mu\text{g Teq L}^{-1}$)			Chl <i>a</i> ($\mu\text{g L}^{-1}$)	
							SML	UW	EF	UW	UW
2 Aug 2015	Up3	Upwelling	2.4 ± 0.7	0.41 ± 0.1	16.65225	56.28476	341 ± 28 ($n = 6$)	337 ± 29 ($n = 6$)	1.0 ± 0.1	6.1 ± 0.1	
6 Aug 2015	TF0284	Nonupwelling	2.0 ± 0.4	0.20 ± 0.1	18.23134	58.58360	393 ± 70 ($n = 9$)	422 ± 68 ($n = 9$)	0.9 ± 0.2	1.9 ± 1.6	
3 Aug 2015	UP2	Influenced by upwelling	2.8 ± 0.8	0.38 ± 0.1	16.71038	56.28399	376 ± 70 ($n = 7$)	344 ± 57 ($n = 7$)	1.1 ± 0.2	8.4 ± 2.5	
3 Aug 2015	UP2-F	Front	3.3 ± 0.6	0.29 ± 0.1	16.70521	56.28660	314 ± 25 ($n = 3$)	350 ± 85 ($n = 3$)	0.9 ± 0.2	—	
11 Aug 2015	TF0286	Cyanobacteria bloom	—	0.25 ± 0.1	19.88330	58.00229	567 ± 127 ($n = 10$)	486 ± 50 ($n = 10$)	1.2 ± 0.4	24.1 ± 6.6	
16 Jun 2016	JB160616BR	Before rain	2.9 ± 1.8	—	8.074867	53.73709	606 ± 634 ($n = 3$)	303 ± 189 ($n = 3$)	3.3 ± 4.6	9.2 ± 2.8	
16 Jun 2016	JB160616AR	After rain	3.2 ± 1.0	—	8.074735	53.72110	421 ± 233 ($n = 3$)	126 ± 33 ($n = 3$)	3.9 ± 3.3	11.0 ± 3.1	

The macro aligns all the data according to the time stamps, and, in a final step, it merges all the datasets into a single database. The final database is inspected by the user using descriptive statistics, the outlier Grubb test, and graphical aids. Detected outliers are confirmed by scientific reasoning and replaced by NaN. Any suspicious values, not detected as outliers but subjective and not explainable in a scientific sense ($\sim 3\%$ of complete dataset), are flagged as part of the project's quality assurance step. The qualifying flag descriptions are used to describe the SeaDataNet coordinated by the British Oceanographic Data Centre (BODC). Quality flags are used to describe the data value. Data from this study have been submitted to PANGAEA (Mustaffa et al. 2016, 2017).

f. Statistical analysis

Statistical analysis of the dataset was performed using R (R Development Core Team 2008) and Graphpad Prism, version 5.1. Null hypothesis testing was considered to be significant when $p < 0.05$. Normal distribution of the data was tested using Shapiro–Wilk and Anderson–Darling tests. The hypotheses were tested using nonparametric tests, as stated. Unless otherwise indicated, the results are presented as means plus/minus one standard deviation. The enrichment factors (EF) were calculated as a ratio—that is, the concentrations in the SML sample referred to the concentrations in the corresponding UW sample.

3. Results and discussion

This paper presents the sampling performance of the S^3 and observations of different sea surface phenomena using high-resolution measurements. The operations of the S^3 were successfully completed up to a sea state of 5 (Beaufort scale), which corresponds to a wind speed of 10 m s^{-1} . Therefore, the S^3 allows observations of the sea surface under typical oceanic conditions, as the averaged wind speed over the ocean was reported to be 6.6 m s^{-1} (Archer and Jacobson 2005).

a. Sampling and system performance

In this present study, the EFs of FDOM monitored by the S^3 ($\text{EF} = 1.2 \pm 0.4$; $n = 4886$) were similar to those reported by Frew et al. (2002) ($\text{EF} = 1.4 \pm 0.6$, $n = 4$) and Wurl et al. (2009) ($\text{EF} = 1.6 \pm 0.6$, $n = 10$). However, the high-resolution measurements of the S^3 show variabilities in the enrichment (the EF ranges for all events are listed in Table 2: 0.2–3.0; Fig. 4). Variabilities in the enrichment of FDOM may occur with the presence of white caps, inducing rising bubble plumes and photochemical degradation (further discussed in section 3b). Therefore,

FIG. 4. Box-and-whisker plot of FDOM enrichment factors (EFs) for different stations in the Baltic Sea and the North Sea (denoted on the x axis). Boxes show the median and the 25th and the 75th percentiles; whiskers are the 10th and the 90th percentiles.

the S^3 provides unique datasets to understand the short-term processes of enrichments at the sea surface (Fig. 5).

In addition, the EF of surfactants from the discrete samples collected by the S^3 ranged from 0.6 to 8.6 (1.4 ± 1.6 , $n = 41$; Table 2). The observed EF is consistent with a large dataset (Wurl et al. 2011) collected manually using the glass plate technique (2.2 ± 1.1 , $n = 274$). This proves that the collection by glass discs mounted on the S^3 is comparable to the established glass plate technique (Cunliffe and Wurl 2014).

Furthermore, the ability of the S^3 to provide microbiological data—for example, bacterial and autofluorescent cell counts measured by flow cytometry—was tested. Sampling obtained using the established glass plate technique (Harvey and Burzell 1972) was compared with triplicate samples obtained from the North Sea (21 April 2016) using the S^3 . No significant differences ($n = 3$, Mann–Whitney test) between the two sampling techniques were detected for the EFs of picoplankton ($p = 0.66$), nanoplankton ($p = 1.0$), and bacterial ($p = 0.20$) cell abundances. This indicates that the S^3 allows for comparable sampling of cell counts. Cleaning prior to and after operations (pumping technical ethanol for 10 min through the flow system for sterilization) and frequent replacement of tubing prevents carryover of the cells between the S^3 runs; hence, this ensures consistent sampling that is comparable to the glass plate technique. For future studies, the S^3 is advantageous due to its high-volume sampling capability (up to 20 L h^{-1}), which is required for detailed microbial community analysis. Whether or not the S^3 can replace the glass plate sampling technique for collecting samples for microbial community analysis still remains to be determined.

FIG. 5. Color points for the FDOM EFs during (a) upwelling and (b) nonupwelling.

In addition, this study discovered the potential of the S^3 to collect neustonic zooplankton, such as surface-living copepods. Selective collection of pontellid copepods, either from the SML (five of six total observations) or from the UW (a single observation), was observed. Interestingly, copepods were never collected in paired samples; this means that they were either collected from the SML or the UW (Table S1). This proves that the S^3 is capable of investigating ecological features of the sea surface, including the migration of surface-living organisms.

b. Upwelling region

To investigate the influence of upwelling on the sea surface properties, three stations were selected: station UP3 was located within an upwelling region in the Baltic Sea; station UP2 was situated farther offshore, but it remained under the influence of upwelling; and station TF0284 was located in a typical nonupwelling region in the central Baltic Sea (Fig. 3). During the upwelling event (station UP3; Fig. 3; Table 2), the S^3 recorded a temperature of $12.2^\circ \pm 0.2^\circ\text{C}$ and $12.0^\circ \pm 0.2^\circ\text{C}$ at a depth of <2 and 15 cm, respectively (Fig. 6a; Table 3). The corresponding nonupwelling stations (UP2 and TF0284; Fig. 3; Table 2) were characterized by a temperature increase of $2^\circ\text{--}5^\circ\text{C}$ in both layers (Figs. 6c, 7a; Table 3). The S^3 recorded significantly higher concentrations of FDOM in the SML at the upwelling station UP3 ($24.7 \pm 0.3 \mu\text{g L}^{-1}$; Fig. 6b) in comparison to station UP2 ($22.4 \pm 0.6 \mu\text{g L}^{-1}$; Fig. 6d) (Mann–Whitney test, $p < 0.0001$). However, the latter continued to be influenced by the

upwelling through seaward-flowing water masses (Kämpf and Chapman 2016; Loucaides et al. 2012); the lowest concentrations were found at the nonupwelling station TF284 ($16.8 \pm 0.8 \mu\text{g L}^{-1}$; Fig. 7b), located 146 n mi (1 n mi = 1.852 km) northeast of the upwelling region. The S^3 was able to distinguish between the significantly higher enrichment of FDOM in the upwelling station UP3 (around 1.5 ± 0.1 , $n = 734$, Table 3) and the FDOM in the nonupwelling station TF284 (around 1.1 ± 0.1 , $n = 634$, Table 3) (Mann–Whitney test, $p < 0.0001$). Such differences in the enrichments are probably undetectable using manual sampling through low numbers of data points; therefore, they would have low statistical confidence.

During the development of the S^3 , the importance of the in situ measurement of the physiological status of the phytoplankton community was recognized as a key source of organic matter to the SML. For example, in the region influenced by the upwelling (stations UP2 and UP3; Fig. 3) the surfactants were found to have an $\text{EF} \geq 1$; in contrast, in the central Baltic Sea, the EF was <1 (Table 2). The photosynthetic ratio Fv/Fm as proxy for the physiological status of the autotrophic organisms and $\text{Chl-}a$ (Moore et al. 2006) was higher in the upwelling station UP3 ($\text{Fv/Fm} = 0.4 \pm 0.1$ and $\text{Chl-}a = 6 \mu\text{g L}^{-1}$) than in the nonupwelling station TF0284 ($\text{Fv/Fm} = 0.2 \pm 0.1$ and $\text{Chl-}a = 2 \mu\text{g L}^{-1}$), indicating a healthier population in the nutrient-rich upwelled waters. The poor physiological status of the phytoplankton communities at station TF0284 possibly resulted in the release of additional surfactants to the UW (Žutić et al. 1981), and low wind

TABLE 3. Data given as average and standard deviation from the in situ sensor measured on board S^3 . EF is unitless.

Station	FDOM ($\mu\text{g L}^{-1}$)			Temperature ($^{\circ}\text{C}$)		Salinity		pH		O ₂ saturation (%)	
	SML	UW	EF	2 cm	15 cm	SML	UW	SML	UW	SML	UW
UP3	24.7 $\pm$ 0.3	16.5 $\pm$ 0.7	1.5 $\pm$ 0.1	12.2 $\pm$ 0.2	12.0 $\pm$ 0.2	7.2 $\pm$ 0.3	—	8.01 $\pm$ 0.01	—	99.6 $\pm$ 33.0	—
TF0284	16.8 $\pm$ 0.8	15.9 $\pm$ 0.9	1.1 $\pm$ 0.1	17.1 $\pm$ 0.2	17.1 $\pm$ 0.2	6.4 $\pm$ 0.1	—	8.31 $\pm$ 0.01	8.48 $\pm$ 0.01	101.1 $\pm$ 1.4	107.9 $\pm$ 1.3
UP2	22.4 $\pm$ 0.6	15.3 $\pm$ 1.1	1.4 $\pm$ 0.2	15.9 $\pm$ 0.3	15.8 $\pm$ 0.3	—	—	—	—	—	—
UP2 (front)	23.2 $\pm$ 0.5	16.9 $\pm$ 0.7	1.4 $\pm$ 0.1	13.3 $\pm$ 1.6	13.1 $\pm$ 1.2	—	—	—	—	—	—
TF0286	15.9 $\pm$ 4.5	14.4 $\pm$ 0.7	1.1 $\pm$ 0.3	19.0 $\pm$ 0.2	18.9 $\pm$ 0.3	7.0 $\pm$ 0.1	6.7 $\pm$ 0.0	8.50 $\pm$ 0.01	8.43 $\pm$ 0.00	100.3 $\pm$ 0.3	111.0 $\pm$ 0.7
JB160616BR (before rain)	9.2 $\pm$ 3.2	20.1 $\pm$ 0.7	0.5 $\pm$ 0.2	15.5 $\pm$ 0.0	15.6 $\pm$ 0.0	—	35.2 $\pm$ 0.1	—	8.08 $\pm$ 0.01	—	—
JB160616AR (after rain)	21.2 $\pm$ 8.1	19.9 $\pm$ 0.3	1.1 $\pm$ 0.4	15.5 $\pm$ 0.1	15.6 $\pm$ 0.1	—	35.3 $\pm$ 0.2	—	8.11 $\pm$ 0.00	—	—

speeds without the presence of white caps prevented the upward transport by the bubbles (Zhou et al. 1998; Wurl et al. 2011), resulting in lower enrichments. For example, averaged wind speeds at stations UP2 ($U_{10} = 3.6 \text{ m s}^{-1}$) and UP3 ($U_{10} = 2.8 \text{ m s}^{-1}$) were above the threshold of $U_{10} = 2.5 \text{ m s}^{-1}$ for the first appearance of breaking waves (Hwang and Sletten 2008). In contrast, the averaged wind speed at station TF0284 ($U_{10} = 2.3 \text{ m s}^{-1}$) indicates no breaking waves, possibly contributing to the lower enrichments of surfactants (Table 2) and FDOM (Table 3). This shows that the S^3 is capable of monitoring not only the accumulation of organic matter but also the phytoplankton communities, as a source, and wind, as a transport mechanism.

FRONTS

During the S^3 deployments in the Baltic Sea (summer 2015), a front was observed at station UP2 (Figs. 3, 1S; Table 2) separating the colder and warmer water masses of the upwelling system. Within the front, the temperature for the 2- and 15-cm depths averaged 13.2°C ($\pm 1.2^{\circ}\text{C}$) and increased to 15.9°C ($\pm 0.3^{\circ}\text{C}$) outside the front. In both cases, the temperature difference between the measuring depths of 2 and 15 cm was insignificant (Table 3). The high-resolution measurement of temperature (Fig. 7a) clearly shows when the S^3 was navigating in and out of the front. These observations are supported by the ship's position on the front, indicated by a mean temperature difference between the starboard and port sensors of 2.5°C (data not shown).

The FDOM concentrations were significantly higher within the front than outside the front (Wilcoxon rank sum test, p value < 0.001), and the increase in the FDOM concentrations within the front could be clearly observed through the high-resolution measurements (Fig. 7b). Even though the differences in the FDOM concentrations (Table 3) were statistically significant, both in the SML and UW, the FDOM concentrations within and outside the front were relatively small. This can be explained by the fact that the FDOM represents dissolved constituents diffusing between the frontal boundary layer. Nevertheless, the differences were detected by the S^3 , as shown through repeatedly navigating the S^3 inside and outside of the front, and by monitoring the FDOM signal and the temperature (Figs. 7a, b). Fronts are convergence zones in which organic matter accumulates at the sea surface (Pelegri et al. 2005), as indicated by the increased FDOM concentrations. Exudation by phytoplankton blooms is another source of organic matter (Eberlein et al. 1985; Riebesell 1993; Schlichting 1971). The photosynthetic ratio Fv/Fm within the front (0.29 ± 0.1) was lower than the ratio outside the front (0.38 ± 0.1); this indicates a more stressed community, and stress potentially triggers exudation (Maršálek and Rojčková 1996). The S^3 was able to identify both the

FIG. 6. Temporal variability of delta high precision temperature (HPT) (HPT 2 cm – HPT 15 cm) and FDOM UW (blue line) and FDOM SML (black line) at the upwelling station UP3 (2 Aug 2015) and nonupwelling station TF284 (8 Aug 2015).

convergence and biological activity as potential sources for the accumulation of organic matter within the SML in fronts.

c. Wet deposition

During a heavy rain event (station JB160616; maximum rain rate = 271 mm h^{-1} ; Table 2), S^3 detected a significant temperature drop of 0.5°C close to the sea

surface during the rain event (Fig. 7c) but not in the deeper layer at 15 cm. In laboratory studies, Zappa et al. (2007) demonstrated that turbulence caused by raindrops diminished within a few centimeters below the sea surface. They found average dissipation rates of $1 \times 10^{-3} \text{ W kg}^{-1}$ at 2 cm below the surface and $1 \times 10^{-4} \text{ W kg}^{-1}$ at a depth of 15 cm. This fact might explain what was observed in this present study and by

FIG. 7. Temporal variability of (a),(c) HPT in 2 (black line) and 15 cm (blue line) and (b),(d) FDOM in SML (black line) and UW (blue line) at station UP2 influenced by (a),(b) an upwelling front (8 Mar 2015) and (c),(d) at station JB160616 (16 Jun 2016) during a rain event. Shaded areas in (a) and (b) show when the S^3 sampled the fronts. Brackets in (c) show two rain events.

Asher et al. (2014), namely, that cooling of the surface layer by rain occurs only a few centimeters below the sea surface. Such observations are important, as turbulence caused by raindrops affects the air–sea exchange of climate-relevant gases (Ho 2004; Komori et al. 2008).

The FDOM was depleted in the SML before the rain event ($EF = 0.5 \pm 0.2$), but the FDOM concentrations in the SML increased twofold during the rain event (Fig. 7d; Table 3), causing a significant increase in its enrichment to $EF = 1.1 \pm 0.4$. Even so, the ubiquitous presence of FDOM in rainwater samples (Kieber et al. 2006) and the increase of organic matter in the SML during rain events (Wurl and Obbard 2005; Lim et al. 2007) are known. Figure 8 shows that the spatiotemporal heterogeneity of EF FDOM changed with still water (e.g., between inflowing and outflowing tide) and not with the rain events. In contrast to the immediate temperature effect (Fig. 7c), the contour map confirms the slow increase of the enrichment (also shown in Fig. 7d). On the other hand, UW concentrations before ($20.1 \pm 0.7 \mu\text{g L}^{-1}$) and after the rain ($19.9 \pm 0.3 \mu\text{g L}^{-1}$) events were similar, indicating that the increase in the SML concentrations and enrichment was most likely primarily caused by the rain. A combined effect of nonlocal rain and tidal currents can explain our observation that changes of EF FDOM did not align with the cooling of the sea surface. Kuznetsova and Lee (2002) reported no statistical difference in the amino acid concentration before and after high tide, probably due to single observations before and after high tide. The high-resolution measurement by the S^3 allowed the enrichment of FDOM to be plotted into contour maps (Fig. 8). With the contour maps, the S^3 has the ability to investigate the patchiness of the SML for the first time, as suggested by Falkowska and Latala (1995) and Frew et al. (2002). Observations of patchiness are likely to provide new insights into the biochemical processes occurring at the sea surface.

In the present study, although the FDOM enrichment increased during the rain event, the enrichment of Chl-*a* (from EF 3.3 to 1.4) decreased. In the case of Chl-*a*, the associated cells might be retained in the UW because a dissipation rate of $1 \times 10^{-3} \text{ W kg}^{-1}$, caused by raindrops at 2-cm depth (Zappa et al. 2007), could limit their upward transport back to the sea surface. In contrast, the dissipation may be sufficient for upward transport of dissolved molecules, such as FDOM or surfactants (Denman and Gargett 1983).

It is likely that rain events cause a drop in the SML salinity (Hasse 2005). However, because of the technical failure of the sensor used in this study, no salinity data are available for the SML (Table 3), so it is not possible to report the actual decrease of salinity during rain events.

d. Cyanobacteria bloom

During deployments of the S^3 in the Baltic Sea (summer 2015), intensive cyanobacterial blooms of *Pseudoanabaena* and *Aphanizomenon* (M. Nausch 2017, personal communication) with a high abundance of floating colonies were observed at station TF0286 (Fig. 3; Table 2). Such blooms occur frequently during the summer in the Baltic Sea (Bianchi et al. 2000; Lehtimäki et al. 1997), creating highly productive patches with a physical/chemical microenvironment that is significantly different from that of the UW (Ploug 2008). In this present study, the S^3 was used to approach the streaks of floating blooms, and a gradual increase was observed in the FDOM concentration in the SML, from $9 \mu\text{g L}^{-1}$ (no bloom) to $20 \mu\text{g L}^{-1}$ (intensive bloom), whereas the FDOM concentration in the UW remained constant at $15 \mu\text{g L}^{-1}$ (Fig. 9). This caused the excess concentration of FDOM to increase from $-7 \mu\text{g L}^{-1}$ (e.g., depletion in the SML) to $6 \mu\text{g L}^{-1}$ (e.g., enrichment in the SML). Navigating in and out of the streaks resulted in sudden changes in the excess concentrations of FDOM (e.g., it increased when approaching the streaks and it decreased when leaving the streaks). The observed variability was probably caused by the presence of patchy surface scum (Ploug 2008).

In this present study, the highest concentrations of surfactants and Chl-*a* were observed within the area of the bloom (Table 2) analyzed from the discrete samples collected by the S^3 . The enrichment of surfactants in the SML was relatively low, with an $EF = 1.2 \pm 0.4$, which was due to high concentrations in the UW. The higher variability of the Chl-*a* concentrations was probably caused by the patchiness of the bloom. Sieburth and Conover (1965) related excretion of carbohydrates by *Trichodesmium* sp. to higher surfactant concentrations in slicks associated with surface blooms in the Sargasso Sea. Capone et al. (1998) reported that surface accumulations of *Trichodesmium erythraeum* in the Arabian Sea were most prominent in the morning, but they decreased to 1 m at midday. Vertical migration is also a common feature of different Baltic Sea-inhabiting cyanobacteria, such as *Anabaena* and *Aphanizomenon* (Hajdu et al. 2007). In the present study, the surface bloom was approached at 1000 UTC [i.e., at 1200 local time (LT)]; therefore, the observations of relatively low enrichments for the FDOM and surfactants are probably due to the sinking colonies, as observed by Capone et al. (1998) and Hajdu et al. (2007). Nevertheless, in this present study, the surface bloom was clearly detectable by the S^3 .

4. Conclusions

This paper describes the state-of-the-art research catamaran S^3 used for high-resolution measurements of

FIG. 8. Contour map of the EF of FDOM (recording interval of 10 s) at station JB160616 during the rain event. Black brackets show two rain events. Blue and red rectangles show the start and end points, respectively of S^3 deployment. Blue arrow shows the direction on the S^3 sailing, following the tidal currents.

biogeochemical parameters in the SML, the uppermost oceanic boundary layer. The S^3 was field approved during expeditions in the North Sea and the Baltic Sea up to a wind speed of 10 m s^{-1} (e.g., under typical coastal and oceanic conditions). Through the capabilities of

measurements with high temporal (few seconds) and spatial ($<1 \text{ m}$) resolution, the S^3 is the first vehicle to map the sea surface directly using biogeochemical parameters. In addition, high-volume discrete samples can be collected for further laboratory analysis.

FIG. 9. Temporal variability of FDOM concentrations during a cyanobacteria bloom at station TF0286 (11 Aug 2015).

It was possible to use the S^3 to observe processes at the sea surface, including upwelling, fronts, rain episodes, and surface plankton blooms. The onboard laboratory with the high-resolution in situ assessment allowed for the detection of small but significant changes during the occurrence of the events, including drops in the surface temperature during rain events or increases in the FDOM concentrations for fronts and surface blooms.

The S^3 remains under further development, including current implementation of an autopilot system and additional sensors, in order to fulfill the additional requirements of future studies. Future application includes the assessment of interactions between the ocean and the atmosphere, marine aerosol production, and the SML as a unique ecosystem.

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