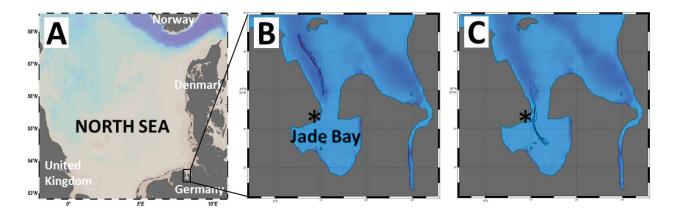
The MILAN Campaign

Studying the Sea Surface Microlayer

Adapted From "The Milan Campaign: Studying Diel Light Effects on the Air-Sea Interface," by Christian Stolle (Leibniz Institute for Baltic Sea Research; Carl-von-Ossietzky University Oldenburg), Mariana Ribas-Ribas. Thomas H. Badewien, Jonathan Barnes, Lucy J. Carpenter, Rosie Chance, Lars Riis Damgaard, Ana María Durán Quesada, Anja Engel, Sanja Frka, Luisa Galgani, Blaženka Gašparović, Michaela Gerriets, Nur Ili Hamizah Mustaffa, Hartmut Herrmann, Liisa Kallajoki, Ryan Pereira, Franziska Radach, Niels Peter Revsbech, Philippa Rickard, Adam Saint, Matthew Salter, Maren Striebel, Nadja Triesch, Guenther Uher, Robert C. Upstill-Goddard, Manuela van Pinxteren, Birthe Zäncker, Paul Zieger, and Oliver Wurl. Published online in BAMS, January 2020. For the full, citable article, see DOI:10.1175 /BAMS-D-17-0329.1.

The sea surface microlayer (SML) occupies the uppermost tens to hundreds of micrometers of the ocean surface. Consequently, it is in direct contact with the atmosphere and covers around 70% of Earth's surface. Compared to the underlying bulk water, the SML has distinct biological and physicochemical properties, which is important given that all ocean-atmosphere exchanges cross it. An improved understanding of the SML is thus essential for studying air-sea exchanges important in global biogeochemical cycles, climate regulation, and air quality. As the climate changes, so too will the SML.

Due to logistical constraints, most of our knowledge about SML derives from daytime observations. Thus, there has been an urgent need to study the diel variability in the coupling between meteorological forcing, SML properties, and air–sea exchange. To learn more, the Sea Surface Microlayer at Night (MILAN) experiment was conducted from 3 to 13 April 2017 in the Wadden Sea region of the southeastern North Sea. This international effort involved scientists from marine (micro)biology, biogeochemistry, marine chemistry, atmospheric chemistry and physics, and physical oceanography. The study combined diverse approaches in the field and in the laboratory to



study not only the diel properties of the SML but also their effects on the air–sea exchange of climate-relevant gases and aerosols.

We aimed to learn, for example, if solar radiation causes diel changes in microbial composition and the food web in the SML, and what the effects are of diel patterns on biochemically active SML substances. In turn, we looked for influences of diel variability on CO_2 fluxes across the SML and how organic matter in sea spray aerosol depends on the diel transformations in the SML.

The Wadden Sea is one of the world's largest areas of intertidal flats (~10⁴ km²), and is divided into several tidal basins. MILAN was planned for early to mid-April because phytoplankton dynamics in the Wadden Sea are strongly regulated by nutrients and solar radiation, which give rise to spring blooms. The MILAN field site was in Jade Bay, one of the Wadden Sea's largest basins, which is influenced by semidiurnal tides with a tidal range of up to 3.8 m. A large water volume ($4 \times 10^8 \text{ m}^3$) flows in and out of Jade Bay during each rising and falling tide. However, direct freshwater discharge is relatively small: the usual salinity range is 29–32 practical salinity units (psu).

During MILAN we performed several field experiments involving the SML in Jade Bay, including two full (over 25-h) diel cycles: cycle 01 on 4–5 April 2017 and cycle 03 on 8–9 April 2017. During each cycle, the radio-controlled catamaran Sea Surface Scanner (S³) and at least one research vessel (R/Vs)—*Senckenberg*, *Otzum*, or *Zephyr*—followed a passively drifting CO₂ buoy. Meteorological conditions and water current speed and direction throughout the entire water column were recorded continuously from the research vessels, supported by observations from land-based Study area (a) in the coastal North Sea using Ocean Data View, showing the drifting courses following tidal currents for the two diel cycles: (b) cycle 01 and (c) cycle 03. Asterisk locates the land-based weather station and the aerosol sampler.

weather stations. Water column physical properties were profiled every hour using sensors for conductivity, temperature, and density. The S³ is equipped with diverse sensors to measure physicochemical properties (e.g., conductivity, temperature, salinity, fluorescent dissolved organic matter) of the SML (<1 mm) and from 1-m water depth, referred to here as underlying water (ULW). Measurements at 1.2–2.0-m water depth came from a CTD (conductivity/ temperature/depth) package.

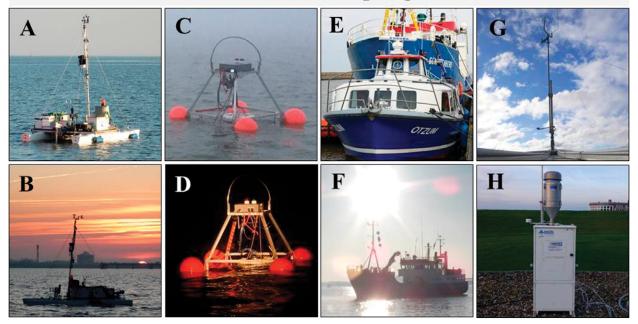
The S^3 additionally collected large water samples (20 L) from the SML and the ULW for subsequent analyses in the laboratory.

Properties of the microlayer

The SML experiences instantaneous meteorological forcing by, for example, solar radiation, wind, and precipitation. Solar radiation directly influences the thermal and saline boundary layer with variable thicknesses on the order of 1,000 μ m and 200 μ m, respectively. Evaporation and precipitation strongly influence the thermal and saline properties of the SML. Furthermore, recent measurements show that large enrichment of organic material in the SML reduces evaporation from the sea surface. The SML also experiences higher exposure to UV radiation than does the underlying water column. Attenuation by optically active components and water itself reduces light exponentially with increasing depth. Whereas light levels in the SML always exceed 98% of surface irradiance, in coastal environments with large amounts of suspended and dissolved organic matter only around 10% of surface UV-B irradiance may reach 0.2–5-m depth.

Wind-induced formation of small capillary waves and microscale breaking causes SML disruption. Wave breaking entrains air into

Field-/ Land-based Sampling Platforms



the water column, forming air bubbles that rise upward to the SML, where they eventually burst. This process concentrates material within the SML and causes rapid reformation of the microlayer. However, for a certain fraction of the material, bubble bursting is also an important route from the underlying bulk water via the SML into the atmosphere. Sea spray aerosols arising from bubble bursting may act as cloud condensation nuclei, supporting the growth of low-level clouds that impact ocean surface temperatures and radiation fluxes and, consequently, Earth's energy budget.

The SML controls air-sea gas exchange by acting as a diffusive boundary layer. According to classical gas exchange theory, the SML resembles a stagnant layer under low winds, when diffusion is the driving force for air-sea gas exchange. In the natural environment this theoretical stagnant layer does not hold true as microscale breaking and buoyancy fluxes occur. Parameterizations for gas transfer velocities solely based on wind speed cannot fully account for in situ observations. For example, CO₂ fluxes derived from wind-speed-based parameterizations typically have around twofold uncertainty due to surface-active organic material, bubbles, fetch, rain, chemical enhancement, and other variables that affect the air-sea exchange of climate-relevant gases.

Coverview of sampling platforms used during the MILAN campaign: (a),(b) the radio-controlled catamaran S³ to sample the SML and ULW; (c),(d) a free-drifting buoy to measure air–sea exchange of CO₂; and (e),(f) three R/Vs to sample the water column. Land-based instruments were installed (g) to record meteorological data at the Institute for Chemistry and Biology of the Marine Environment building and (h) to sample ambient aerosols.

Surface active substances (SAS), or surfactants, in the SML are of mostly biological origin. In coastal waters there may be additional surfactant contributions from terrestrial sources. Surfactants accumulate in the SML via diffusion at low wind speeds or bubble scavenging at moderate to high wind speeds, and have been shown to be present at wind speeds up to 13 m s⁻¹. Laboratory and field experiments have shown surfactants to suppress air-sea gas exchange by up to 50%, and that neglecting this effect can greatly overestimate air-sea gas exchange rates. In addition, photochemical reactions involving SML organics have the potential to modify surfactant concentrations and compositions and can produce trace gases directly. For certain atmospheric gases, most notably ground-level ozone (an air pollutant), chemical reactions taking place at the air-sea interface act as a sink for these gases.

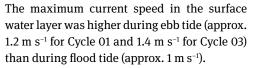
The SML can include complex microbial communities embedded in a gel-matrix described as a "biofilm-like" habitat—for example, large floating cyanobacteria blooms. While the SML is a challenging habitat for organisms, especially due to maximal exposure to solar radiation, it nevertheless has an inherently wide microbial diversity that is often distinct from the underlying water.

The metabolic activity of organisms, especially microorganisms, determines the production, degradation, and modification of organic material in the surface ocean. The underlying processes of primary production and respiration also directly influence the concentration and air–sea fluxes of, for example, CO₂. Primary production by phytoplankton is generally light dependent, but excessive radiation levels may cause inhibition of photosynthesis.

Measurement highlights

Transitions between low and high pressure atmospheric systems were prevalent during MILAN, influencing the intensity of near-surface winds. Throughout the MILAN campaign, low clouds covered between 50% and 70% of the study region. Cover by low clouds was less extensive during cycle 01 than during cycle 03, where increasing cloudiness caused a rapid decrease in surface radiation after noon.

The strong tidal currents of Jade Bay must be taken into account when considering the meteorological forcing of sea surface properties. Temperature– salinity (T–S) diagram of the SML during cycle 03. Day and night measurements for SML and ULW are shown in red and blue, respectively. *

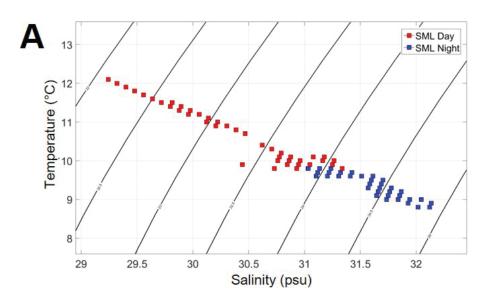


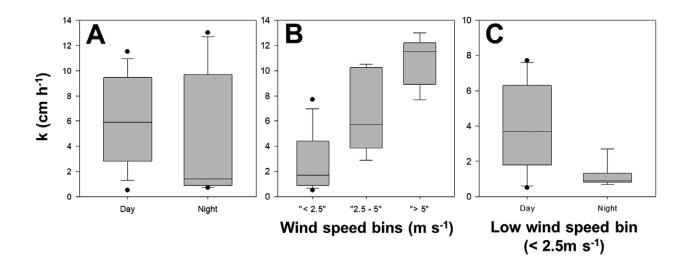
Diel temperature differences generally followed the influence of solar radiation. Land– sea breezes at our coastal study site might have caused additional day/night variation of air temperature. Ongoing analyses of the relation among wind speed and direction, solar radiation, and air temperature will reveal the main drivers of diel temperature changes during MILAN.

The large amounts of suspended material in the water in Jade Bay may partly account for a strong variability observed in, for example, the biomass and abundance of organisms. Tidal currents generally influence water column properties such as salinity and temperature. During both cycles we followed a free-drifting buoy; hourly CTD measurements confirmed that we were able to follow the same water mass. The CTD data showed that salinity and temperature were clearly different at night between SML and ULW within the uppermost 1 m of the water column, suggesting that SML represents a distinct water layer. SML material and organisms are often recruited from the ULW, and this transport might be a function of tidal current velocities. Preliminary analysis did not reveal any relationships between current velocities and the enrichment of material and organisms in the SML. Nevertheless, addressing potential tidal effects is an important focus of ongoing analysis.

Our initial results point to a radiation de-

pendence of several SML processes. Some of these support previous observations and conclusions, such as increasing lipid degradation in the SML during the night, which most likely reflects diel changes in the relative importance of phytoplankton production and bacterial degradation. Some of our findings-for example, a dose-dependent enrichment of the phytoplankton group cryptophytes in the SML-will help to refine our knowledge of the specific species inhabiting the SML. Other results were seemingly contradictory. For example, while experiments with a





solar simulator clearly implied daytime surfactant production, surfactant concentrations in the field were actually highest at night, which has not been reported before. Such contrasts highlight a need to understand the microbiological and photochemical turnover of surfactants. Other results imply that bacterial enrichment of the SML is not negatively affected by solar radiation, and the strongest bacterial depletion was at night.

Earlier studies in the equatorial Pacific concluded that diel heating cycles can sometimes affect gas transfer velocities of CO_2 more than wind speed. In Jade Bay during spring, oscillating insolation was not as pronounced as in the equatorial Pacific, and turbulent mixing was probably the dominant process driving gas exchange. There was no day–night difference between high and medium wind observations of gas transfer velocities, but our initial data suggest that day and night CO_2 fluxes might differ if wind speed is low (<2.5 m s⁻¹).

Prior observations and experiments from the daytime SML undoubtedly produced greatly valuable information. An overall conclusion of MILAN, however, is that future progress in understanding will require additional information on day–night contrasts. MILAN has shown that combining expertise from diverse disciplines as well as from field and laboratory experiments is the most appropriate approach to achieve this. We are convinced that strengthening the links between disciplines is an important step to deepen the first insights presented here and to further unravel the complexity of air–sea interaction, particularly across the SML. We are convinced that strengthening the links between disciplines is an important step to deepen the first insights presented here and to further unravel the complexity of air-sea interaction

.

Based on measurements from drifting buoy instruments, box-and-whisker plots show the gas transfer velocities of CO_2 (k; cm h⁻¹) for (a) day and night, where no significant difference is found. But separating wind observations into (b) different speed bins helps show one of the important findings of MILAN—the significant day–night difference in (c) at low wind speed.

The coastal zone is very important for biogeochemical cycles, especially considering the strong anthropogenic forcing in coastal habitats. Coastal oceans are additionally important for air-sea gas exchange and the formation of new aerosol particles. Nevertheless, while in coastal regions like Jade Bay, high numbers of suspended particles greatly inhibit downward light penetration, in more oligotrophic systems with lower suspended particle concentrations the contrasting effects of radiation on the biogeochemical properties of the SML and ULW will likely be quite different. Future studies should therefore target a broad range of oceanic regions and seasons (e.g., summer phytoplankton blooms), and we hope that MILAN will stimulate further diel studies of air-sea interface processes. In light of the global importance of matter and energy exchange across the SML, the focus of these studies should be on improving our understanding of the longand short-term effects of climate change. We predict that in a future ocean, changes in wind regimes, radiation intensities, and precipitation rates will greatly modify SML properties, leading to subsequent altered feedbacks affecting many aspects of air–sea interaction. 🖡

APRIL 2020 BAMS | 303 Brought to you by FLORIDA ATLANTIC UNIVERSITY | Unauthenticated | Downloaded 07/07/21 07:04 PM UTC

BAMS: What motivated MILAN?

Mariana Ribas-Ribas (Carl-von-Ossietzky University Oldenburg):

Although scientists seem to know a lot, there are still some super-basic things that we knew nothing about, like what happens in the sea surface ocean during the night, which is half of a year.

Ana M. Durán-Quesada (University of

Costa Rica): Big research efforts are dedicated to land surface layers, but the most extensive surface layer in the planet is understudied. It defines energy and matter exchange fundamental for weather system development in shorter time scales and fundamental for defining the CO₂ exchange and for climate forcing in general. Efforts related to CO₂ exchange, such as blue carbon initiatives, can greatly benefit from a better understanding of the ocean surface microlayer.

Niels Peter Revsbech (Aarhus

University): It is difficult to sufficiently appreciate the importance of the sea–water interface for processes and transport of dissolved or gaseous species. In our laboratory we have studied microscale processes associated with interfaces for the last 40 years, developing microscale electrochemical sensors for that purpose. We are highly interested in how transformations of species such as O_2 and CO_2 affect transport to the atmosphere and thus our climate.

BAMS: How did these basic questions become a scientific project?

MRR: Christian and I organized a discussion session at the SOLAS (Surface–Ocean–Land–Atmosphere Studies) Open Science conference in Kiel in 2015. One attendee pointed out that one of the unknowns was "NIGHT." So we followed up on this one word until it became MILAN.

Christian Stolle: It is so exciting to see how that one single post, by Dave Carlson, initiated this campaign. Ever since my Ph.D., air–sea interface processes were within my focus. I was very excited to study the temporal variability during diel cycles, because having better estimates about this variability finally allows a better assessment of "true" changes.

BAMS: What was the biggest challenge you encountered while doing this work?

MRR: We had problems securing funding, as it was not fitting in most of the "normal" calls. But at the end it turned out that we did it without additional funding, with everyone bringing what they could from their ongoing projects.

CS: MILAN was special in several ways: joining the needs and approaches of many disciplines into one campaign, being land-based and in the field, involving the whole Institute for Chemistry and Biology of the Marine Environment to support on many technical and logistical issues, relying on good weather conditions, and bringing together the international team all with their own funding.

NPR: As an example, even when approaching the sea-air interface from below, sensors cause turbulence in stirred water and thereby change the thickness of the diffusive boundary layer.

ADQ: Data integration. We have generated an amazing dataset that can be used to work around different applications, and it is difficult sometimes to decide what would be first.

MRR: We also had some difficulties setting up everything in our home institute before the campaign started. ICBM is relatively small, and all of sudden we had 20 more people working full time.

BAMS: How did you meet so many challenges taking MILAN from a one-word idea to an international experiment?

ADQ: The way the experiment was planned certainly made things a lot easier, as the objectives were set clearly from the start. The most rewarding experience for me is how a very complex problem can be assessed with the support of scientists with a wide variety of expertise, and moreover, the way we are learning from each other during the process. Also, the way that open scientific discussion with colleagues can enable the development of efficient solutions to problems.

MRR: With the help of all technical and administrative staff, we somehow manage to overcome all problems! Good people can work together if they really want to. From the planning, through the sampling and work and the manuscript preparation, the MILAN team has been amazing to work with.

CS: Everything worked out, which still gives me a very strong feeling of gratitude and satisfaction!

BAMS: With so many problems to solve up front, what surprises were left for you to uncover?

MRR: The gas transfer velocities during low wind speed were amazingly different between day and night. If we take into consideration the high frequency of low wind speed over the ocean, and that night is half of the year, we are surely making a mistake on all our calculations on global airsea transfers. Due to technical problems, we unfortunately only have one day-night cycle to observe this fact, so more observations are needed.

BAMS: What's the takeaway lesson?

ADQ: Realize the complexity of the surface microlayer system. The study of such a system opens opportunities for multidisciplinary research.