Martin Gade, Heinrich Hühnerfuss, Gerald Korenowski

Marine Surface Films

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Chemical Characteristics, Influence on Air-Sea Interactions and Remote Sensing

With 126 Figures, 4 in colour

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Preface

Marine surface films are encountered at many places of the world's oceans, particularly in marginal seas and coastal regions. Their impact on basic processes at the air-water interface is well known since ancient times and has been a matter of scientific research ever since. There has been, however, a lack of a comprehensive compendium that provides the state-of-the-art knowledge on the chemical nature of marine surface films, with particular emphasis on their influence on air-sea interaction processes.

Since the 1960s natural surface films ("sea slicks"), that tend to exhibit thicknesses of one molecule only, have been in the focus of interdisciplinary research that required input by various disciplines such as oceanography, meteorology, physics and chemistry. Albeit the thickness of such monomolecular surface films is small compared to that of mineral oil films their wave damping capability and, thus, their influence on air-sea interactions is comparable. Consequently, they are still often mixed up with mineral oil films ("oil spills"), particularly in the frame of remote sensing applications. It is the aim of the present book to provide a scientific basis that allows avoiding such misinterpretation in the future.

This book is organized in four scientific chapters that are preceded by a general section. The latter provides a historical survey of more than two thousand years of marine surface film research. A biography of Carlo Marangoni, who formed a basis for the modern sea slick research, is followed by a tribute to Erik John Bock who contributed to this book, but died before its publication. The first scientific chapter provides information on the chemical characteristics of both sea slicks and oil spills, thereby putting more emphasis on monomolecular surface films. Chapter 2 and 3 summarize theoretical and experimental work on air-sea exchange processes in the presence of surface films, and on numerical modelling with emphasis on remote sensing of marine surface films. Finally, Chapter 4 describes remote sensing applications that benefit from a deeper knowledge of the results from the previous chapters.

The editors sincerely hope that the present contributed book will conserve existing knowledge and help to avoid misinterpretations of data, or even misplanning of experiments in the future.

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General Section

Oil on troubled waters – a historical survey

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1 Early observations and applications

Damping of water waves by “oil films” has already been appreciated since ancient times, however, knowledge regarding the causes of this effect has progressed only very slowly since the first attempted explanations in classical times. The first to describe this phenomenon was Aristotle in his *Problemata Physica*:

Why is it that the sea, which is heavier than fresh water, is more transparent? Is it because of its fattier composition? Now oil poured on the surface of water makes it more transparent, and the sea, having fat in it, is naturally more transparent.

Furthermore, Plutarch in his *Moralia: Quaestiones Naturales* ascribed to Aristotle (probably from lost parts of that author’s *Problemata*):

Is it, as Aristotle says, that the wind, slipping over the smoothness so caused, makes no impression and raises no swell? ...... They say that when (sponge) divers take oil into their mouths and blow it out in the depths they get illumination and see through the water. Surely it is impossible to adduce slipping of the wind as the cause there.

In addition to these astonishingly correct explanations Plutarch offered alternative but relatively obscure interpretations.

Another practical application of organic surface films added to the sea surface was reported by Pliny the Elder (77 A.D.) describing the seamen’s practice of calming water waves in a storm by pouring oil onto the sea, in order to prevent shipwrecking. A similar utilisation of oil was reported by Bede (Baeda Venerabilis ≡ The Venerable Bede) who spent most of his life at the monastery Jarrow where he wrote the first comprehensive history book on British history *Historia Ecclesiastica Brittanorum.* He gives an account of one of Aidan´s miracles, as told to him by Cynemund, a priest of Jarrow. A priest named Utta, making a long sea journey, was instructed to pour oil on the sea in the event of a storm:

.... and the wind will immediately drop, giving you a pleasant, calm voyage.....He .... poured some of it over the sea, which immediately ceased its raging as Aidan had foretold (cited in the translation after Scott 1979).

Further early reports on wave damping by oil can be found in manuscripts by St. Germanus, Theophilact Simocrate, St. Nicholas, Erasmus Roterdamus, H. Canisius, S. Maiolus, M. Martin, V. Donati, T. Pennant, and L. Poinsinet de Sivry. The exact references are summarised in the bibliography by Scott (1979), presumably the most comprehensive one with regard to this subject.

From a scientific point of view, Benjamin Franklin was the first to perform experiments with "oils" on natural waters. On June 20th, 1757, a convoy of ships set sail northwards from New York, bound for Louisburg, a French fortress near the eastern tip of Cape Breton Island, northeast of Nova Scotia (Giles 1969). The convoy consisted of transports carrying British troops, their escorting frigates, and some vessels carrying civilian passengers. One of these passengers happened to be watching the accompanying fleet when something unusual in the appearance of the sea around a vessel attracted his attention. This passenger was Benjamin Franklin, who had been appointed by the American House of Assembly in Philadelphia as their agent to petition George II against the action of the Proprietors of Pennsylvania. After a frustrating wait of nearly three months in New York until permission was given for the fleet to sail, he set out with about 40 others, passengers included, in one of three packet boats, which for protection sailed in convoy with the fleet and steered for England. The incident, which captured his attention, led to the first scientific recognition of the importance of surface films on water. Some years later he described it, and its sequel, in these words (Franklin 1774):

In 1757, being at sea in a fleet of 96 sail bound against Louisburg, I observed the wakes of two of the ships to be remarkably smooth, while the others were ruffled by the wind, which blew fresh. Being puzzled with the differing appearance, I at last pointed it out to our captain, and asked him the meaning of it? "The cooks", says he, "have, I suppose, been just emptying their greasy water through the scuppers, which has greased the sides of those ships a little"; and this answer he gave me with an air of some little contempt as to a person ignorant of what everybody else knew. In my own mind I at first slighted his solution, tho' I was not able to think of another. But recollecting what I had formerly read in Pliny, I resolved to make some experiment of the effect of oil on water, when I should have opportunity......

At length being at Clapham where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropt a little of it on the water. I saw it spread itself with surprising swiftness upon the surface..... I then went to the windward side, where (the *waves) began to form; and there the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass* (1 acre = 43 560 sq. feet = 63 x 63 m^2).

After this, I contrived to take with me, whenever I went into the country, a little oil in the upper hollow joint of my bamboo cane, with which I might repeat the experiment as opportunity to succeed...... In these experiments, one circumstance struck me with particular surprize. This was the sudden, wide and forcible spreading of a drop of oil on the face of the water, which I do not know that anybody has hitherto considered. If a drop of oil is put on a polished marble table, or on a looking-glass that lies horizontally; the drop remains in its place, spreading very little. But when put on water it spreads instantly many feet around, becoming so thin as to produce the prismatic colours, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance. It seems as if a mutual repulsion between its particles took place as soon as it touched the water, and a repulsion so strong as to act on other bodies swimming on the surface, as straws, leaves, chips, etc., forcing them to recede every way from the drop, as from a center, leaving a large clear space. The quantity of its force and the distance at which it will operate, I have not yet ascertained, but I think it a curious enquiry, and I wish to understand whence it arises.....

Benjamin Franklin's experiments with a "teaspoonful of oil" on Clapham pond in 1773 inspired many investigators to consider sea surface phenomena or to conduct experiments with oil films. This early work was reviewed by Scott (1979), Giles (1969), Giles and Forrester (1970), and Tanford (1989). Franklin's studies with experimental slicks can be regarded as the beginning of surface film chemistry. His speculations on the wave damping influence of oil induced him to perform the first qualitative experiment with artificial sea slicks at Portsmouth (England) in October of 1773. Although the sea was calmed and very few "white caps" appeared in the oil-covered area, the swell continued through the oiled area to Franklin's great disappointment.

2 Early laboratory experiments and theories

In addition to early experiments on the open sea, basic studies were performed in the laboratory, in order to gain basic insight into the wave damping mechanism induced by surface-active oil film materials ("slicks"). The first to carry out systematic wave tank investigations appears to have been Achard in the year 1778 who used a trough 4.3 m long, 1.2 m wide, and 1.2 m deep, in which standing waves were generated by a hand-cranked rotating-cylinder assembly (Achard 1778). The effect of the waves on a model ship, 15 cm long, was observed, and the action of an oil film in suppressing the breaking of waves over the ship was demonstrated. The effect of oil was, however, not remarkable, and the greater wave-suppressing action of air-filled glass spheres tethered to the model ship led the author to the conclusion that the effect of both oil and floating solid bodies was a result of the mass they added to the surface.

Otto (1798) gave perhaps the earliest comprehensive account of the classical and medieval authors, and in his descriptions of uses he draws heavily on Franklin and Lelyveld (see Scott 1979). In explaining the effect he favours the hypothesis that the oil discourages the natural affinity of water for air, and prevents the force of the wind from being transmitted to the water. He does not, however, reject the hypothesis of Achard that floating solid bodies may have a similar, and more permanent, calming effect. Kries (1799) described his reasons for scepticisms regarding all of the mechanisms so far proposed for explaining the action of oil on waves: Achard’s work with a model system is criticised as unrealistic; Otto`s belief in the chemical effect, waves being generated by the affinity between water and air, was thought to be unlikely compared with the mechanical effect of the fluctuating force of the wind, and Müller’s suggestion (see Scott 1979) that the viscous skin on the surface hinders wave breaking, although felt to be plausible, was seen to require more experiments to determine whether the oil layer is sufficiently strong for this effect. Principally concerned with explaining the damping of large amplitude waves observed by Franklin at an oil/water interface, Robinet (1807) suggested that an oil film can only exert a marked effect on waves whose amplitude is less than the film thickness. Since all waves must start from small amplitudes, however, he considered that the effect on storm waves is credible. By the way of contrast, Weber and Weber (1825) conjectured that an oil layer does not adhere to the water, and thus absorbs the horizontal component of the wind stress. Van Beek (1842) concurred with Franklin and Aristotle that the effect of oil is in the prevention of small waves which would allow the wind to grip the breakers. He attempted to explain this damping action, his argument being based on some effect of the oil on horizontal components of the wind velocity.

The basis for our present models describing wave damping by monomolecular surface films was formed by a paper published by Marangoni in 1872:

Spargendo dell’olio sul mare si sostituische alla superficie elastica dell’aqua la superficie non elastica dell’olio; sicche il vento smuoverá localmente le particelle dell’olio senza che il movimento venga a communicarsi per una grande estensione, e di qui il cessare dell’increspamento della superficie coll’effusione dell’olio.

Marangoni described investigations which showed that motions of bodies at the surface of a liquid may be opposed by elastic forces associated with a surface layer. The conclusion of Plateau that such effects are due to an increased viscosity of the surface layer was shown to be inadequate. The importance of the surface elasticity (or more precise visco-elasticity in modern terms) in the damping of wind waves was pointed out (*Abbonacciamento delle onde, pp 268-270*) and the explanation of the effect that the change of elasticity associated with the oil is sufficient to prevent excitation of waves by the wind, is essentially that still held today. However, it should be noted that Marangoni´s conclusions are rather confused from a modern point of view, the water being found to be *elastic* and the oil surface *not elastic*. On the other hand, Marangoni´s views inspired many models related to the influence of surface-active chemical compounds on the motion of fluids (*Marangoni effect, Marangoni damping*), including models in the field of Applied and Technical Chemistry. It may also be of interest to the readers that several observations of daily life are closely associated with the Marangoni effect. For example, if wine is poured into a wine glass, and then moderately shaken around such that the wine is moving along the outer parts of the glass, one can observe the wine creeping up the walls. This upward movement is driven by surface tension gradients (Marangoni effect) caused by different intense evaporation of ethanol at the lower and upper parts of the walls.

A more precise interpretation of water wave damping through the elastic nature of a spread oil film was given by Reynolds (1880). The full text is as follows:

The paper contained a short account of an investigation from which it appeared that the effect of oil on the surface of water to prevent wind-waves and destroy waves already existing, was owing to surface-tension of the water over which the oil spread varying inversely as the thickness of the oil, thus introducing tangential stiffness into the oil-sheet, which prevented the oil taking up the tangential motion of the water beneath. Several other phenomena were also mentioned. The author hopes shortly to publish a full account of the investigation.

This full account apparently never appeared, except for a few lines given in Reynolds 1884 (see Scott 1979).

Lord Rayleigh carried out very detailed laboratory experiments, which showed the damping of wind-excited *ripples* by a drop of oil. The phenomenon was explained in terms of the resistance to wave motion associated with the differences in surface tension, which arise during the periodic extensions and contractions of the surface. Related experiments on the properties of soap films and the spreading of organic materials were also described. The very comprehensive work was published in three papers (Rayleigh 1890a, 1890b, 1890c).

The first to perform wave-damping measurements in a kind of *Langmuir trough*, i.e., under different compression status of the monolayer, was Agnes Pockels (1891). Ironically, she described for the first time an apparatus that was later also used by Langmuir and named after him (according to a publication in 1917). Pockels performed relatively delicate experiments on the contamination of water surfaces by organic materials. A shallow trough divided by a movable barrier was used to vary the area of a water surface and thus the compression status of the monolayer, and marked variations of the damping of ripples were found. A rapid increase in damping with increasing surface concentration was found.

The earliest available hydrodynamic theory of water wave damping by elastic surface films was published by Lamb (1895). He refers to Reynolds (1880) and the experiments by Aitken (see Scott 1979, Giles and Forrester 1970), but prior publication of the detailed theory is not indicated. All but the outline of the theory was omitted from later editions of this book, and it is likely that Lamb assumed that damping was greatest with an inextensible film, and that intermediate elasticities, therefore, had less effect (cited after Scott 1979). This conclusion was shown by Dorrestein (1951) to be incorrect. The paper by Levich (1940) was the first to present in detail the linearised hydrodynamics of waves on a water surface with surface dilational elasticity. The only cases considered in detail concern insoluble films, and represent the clean and incompressible-film-covered surface. A detailed treatment of the hydrodynamic theory of surface waves, including the effect of an elastic surface film, was published by Levich in 1962. In addition, the damping caused by dissolved surface-active material was considered. Further laboratory experiments performed until 1978 were briefly reviewed by Scott (1979).

3 Utilisation for basic studies of air-sea interactions

Giles (1969) reviewed the literature published after Franklin's experiments and found 17 authors discussing wave damping by oil prior to 1951. But apart from some experiments on wave quelling by John Shields in the harbours of Peterhead and Aberdeen (Scotland) in 1882, 70 years passed again, before surface films again became of interest as a tool for the practical modification of air-sea interaction processes, when Mansfield and several other authors started large-scale investigations on the retardation of evaporation by monomolecular surface films (La Mer 1962). Basically, long-chain saturated alkanols and carboxylic acids are able to reduce the rate of evaporation of water from lakes and reservoirs in hot, arid regions where the amount of water lost by evaporation may exceed the amount regularly used. In other terms, evaporation may lower the level of a reservoir by as much as ten feet annually. In order to reduce this evaporation by using only a monolayer of surface-active compounds, has not only the advantage that quite small amounts are required, but also that the oxygen necessary to support life can still diffuse into the water, and stagnation of the lake is thereby avoided (Davies and Rideal 1963). The reason that enough oxygen penetrates a quiescent surface covered with a monolayer lies in the high diffusional resistance R_L encountered in the aqueous solution subjacent to the surface: compared with this resistance, the monolayer has a small effect. If, however, a thick film layer such as a crude oil spill were used to retard evaporation, its enormous resistance would become dominant in retarding the entry of oxygen. Under natural conditions the exchange both of water and oxygen between a reservoir and the air is aided by the wind. However, in the presence of , e.g., hexadecanol monolayers the exchange rates may be influenced. While the evaporation retardation may thus attain values of about 90 %, the oxygen content may be reduced to 80 % of saturation only (Davies and Rideal, 1963). This has little effect on living organisms. The experiments carried out in the 50ties and 60ties of the last century supplied sufficient evidence that these assumptions are realistic. However, it turned out that continuous application of surface films on reservoirs was ineffective, if winds were blowing with ≥ 5 ms^{-1}. On the other hand, many insights gained during evaporation retardation experiments carried out at reservoirs supplied deepened insights into ocean/air exchange processes as well.

In recent years, experimental sea slicks are being utilised for basic studies of air-sea interaction processes including wind wave generation (Hühnerfuss and Garrett 1981, Hühnerfuss et al. 1981a, 1981b, 1983, 1987, Alpers and Hühnerfuss 1989, Barger et al. 1970, Mallinger and Mickelson 1973), wind-induced drift response of the ocean surface (Lange and Hühnerfuss 1978), and gas exchange (Brockmann et al. 1982) as well as for the investigation of the modification of remote sensing signals by biogenic and anthropogenic surface-active chemicals on the ocean surface (Hühnerfuss et al. 1994, 1996, Gade et al. 1998a, 1998b).

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Carlo Marangoni and the Laboratory of Physics at the High School "Liceo Classico Dante" in Firenze (Italy).

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Since 1869 until 1910, during 41 years, Carlo Marangoni continuously held the Chair of Physics at the High School *Liceo Classico Dante* at Florence. In the course of his long permanence, Marangoni to a large extent developed the ancient laboratory of Physics of the "Liceo".

At Pavia, where he was born in 1840, Carlo Marangoni studied Physics including all courses until the University Degree in Physics (*Laurea di fisica*), which he obtained after defending a thesis on the phenomena occurring in liquids due to the action of surface tension, under the advice of Professor G. Cantoni (1). In 1868, Marangoni moved to Florence and joined the *Specola*, a section of the *Istituto di Studi Superiori* (2). Here, he focused his attention upon meteorological research subjects. In this field, a very short note is particularly worth mentioning, published in *Nuovo Cimento* in the year 1868 at page 318, entitled *The thermometer of Mr. Marchi, with maximum and minimum values*. Later on, Marangoni equipped the Laboratory of Physics of the *Liceo* with this kind of instrument, which he judged especially accurate.

Furthermore, Marangoni always showed particular attention and devotion to Acoustics, a typical science of the Nineteenth Century. The rich collection of acoustic instruments, present in the High School, testimonies the above-mentioned devotion. Moreover, an article (3) about physiologic acoustics, executed in the Laboratory of Physics of the *Istituto Tecnico* at Firenze, was published in collaboration with Emilio Villari.

In 1869, Marangoni started his teaching activity at the *Liceo Classico Dante* (4), accompanied by research activities, as documented by numerous and important articles in *Nuovo Cimento* (5,6) and in *Rendiconti dell'Accademia dei Lincei*. In Ref. 5, Carlo Marangoni and Pietro Stefanelli, teachers in the *Regio Liceo Classico Dante* and in the *Scuola Tecnica Dante* at Firenze, respectively, wrote that they used a good "Sine Galvanometer" that was present in the Laboratory. This galvanometer, showing a label "made by Officina Galileo", is up to now in a good functioning state and it represents one among the earliest products of the Officina Galileo.

Fig. 1. Carlo Marangoni, year 1909

In Ref. 6, the fore-mentioned authors described the transport phenomena occurring in liquids due to surface tension gradients. During his active life, Carlo Maragoni also devoted his time to the preparation of laboratory experiments, to devising new instruments and he participated in thorough and state-of-the-art discussions on the principal developments of scientific research at the end of the Nineteenth Century, as documented by his collaboration with the journal *Rivista Scientifico-Industriale* edited by Mr. Vimercati.

The continuous work of Marangoni, during more than 40 years, is reflected by the instrumentation of the Laboratory of Physics, which attained a high qualitative and quantitative level under his direction. Such an important achievement was, in addition to the prestigious quality of Marangoni as a teacher and as a scientist, also due to the widely held intention of the contemporary governments for remedying the large scientific lag of the country. Actually, during the second part of the Nineteenth Century, a great part of the scientific research was conducted in the laboratories of the high school institutes. Moreover, numerous teachers had available comparable (if not better) laboratories as compared with university laboratories and performed an appreciable and, as much as possible, advanced experimental activity.

Note. The present short biography of Marangoni is available on the Website of the *Liceo Classico Dante*. The text has been edited and translated into English by Giuseppe Loglio. Figure 1 is cropped out from the image of a group of professors and students, celebrating the final High School Degree, in the year 1909. The original photograph belongs to a private collection (Dr. Valleri). A photographic reproduction of the original photograph is deposited in the archive of *Liceo Classico Dante* (by a courtesy of the Rector of the High School and of Prof. Maria Teresa Aristodemo Renzi).

References

1. G. Cantoni (1818-1897), was the successor of Giuseppe Belli on the Chair of Physics of the University of Pavia, which formerly was the Chair of Alessandro Volta
2. The "Istituto di Studi Superiori" changed its name into "Universita' degli Studi di Firenze" at the beginning of the Twentieth Century.
3. "Ricerche sul limite della percezione dei suoni in riguardo alla loro durata"; del prof. Emilio Villari e del dottor C. Marangoni; Nuovo Cimento serie 2, vol I, pp. 382-397, 1869.
4. Liceo Classico Dante is still operative in the original building, Via Francesco Puccinotti n. 55, 50129 Firenze (Italy), Tel.: +39-055-490268, Web-site : http://www.liceoclassicodante.fi.it
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Tribute to Erik John Bock

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The oceanographic and remote sensing communities recently lost a valued colleague. Dr. Erik John Bock, of the University of Heidelberg, Germany. Erik died unexpectedly near his home in Obrigheim, Germany on June 25, 2001, of injuries suffered in a bicycle accident. He was 39 years old.

Erik was born in Buffalo, New York on November 2, 1961 and grew up in Cheektowaga and Boston, New York. An avid Boy Scout and early achiever, he attained the rank of Eagle Scout and was Salutatorian of his Orchard Park High School Class of 1980. Erik went on to study chemistry at the Renssalaer Polytechnic Institute in Troy, New York, earning a B.S. in chemistry (*magna cum laude*) in 1984, an M.S. in Chemistry in 1986, and then his Ph.D. in Chemistry in 1987. Following three years as Research Assistant Professor at Renssalaer, Erik joined the Woods Hole Oceanographic Institution as Assistant Scientist in 1990, becoming an Associate Scientist in 1994. In 1998, he moved to the University of Heidelberg as Guest Scientist to work with B. Jähne in the new Aeolotron wind-wave facility.

Erik's research focused on the interfacial properties of the ocean surface, and, in particular, how the chemistry of the air-sea interface affects the dynamics of short waves, nearsurface flows and interfacial fluxes of heat, mass and momentum. During his short career, he contributed to over 30 scientific publications in this area. His doctoral research, carried out under the tutelage of well-known colloid and surface chemist, Sydney Ross, concerned the propagating characteristics of surface waves in the presence of adsorbed films. That work was eventually published as a series of seminal papers on capillary ripples, and his theoretical treatment of ripple propagation and a corrected dispersion relation for surface waves in the presence of a surface dilational modulus (with J. Adin Mann, Jr.) still stand as the definitive word on the subject.

Erik considered himself first and foremost a surface chemist, although the timely relevance of his work to ocean wave dynamics and to remote sensing questions pushed him strongly in the direction of ocean physics.

He became a leading expert in designing and deploying instruments to measure small-scale ocean waves, which play an important role in many air-sea exchange processes. Increasing interest in the high frequency tail of the ocean wave spectrum and the role of small-scale waves in the scattering of microwave radar led him to develop novel optical slope gauges that provided ripple frequency spectra and later, full three-dimensional frequency-wavenumber spectra of ripples. These instruments played a central role in numerous field campaigns to study radar imaging of the sea surface and the role of surface roughness in boundary layer processes. In collaboration with colleagues at Woods Hole, Heidelberg, and the University of Rhode Island, Erik explored the relationship between the mean square slope of small-scale waves and air-sea gas transfer velocity, work that subsequently led to estimation of global gas transfer velocity fields using satellite altimeters. In the laboratory, he continued his interest in interfacial phenomena, including the influence of surface films on near-surface vortical flows, the subject of a contribution with S. McKenna in this volume.

Erik was mentor and teacher to several postdoctoral investigators, graduate students and undergraduates, who benefited from his clear explanations of physical phenomena and his competent engineering advice. Erik made a huge contribution to the field of ocean physics by providing detailed spatiotemporal spectra of small-scale ocean waves. His colleagues and the community-at-large will sorely miss his keen insight and jovial presence.

Erik J. Bock. Picture taken during the Gasex 2001 expedition in February, 2001.