Dissolved oxygen supersaturation and its impact on bubble formation in the southern Baltic Sea coastal waters

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ABSTRACT

The dissolved oxygen supersaturation in the surface waters was investigated as a factor influencing bubble formation in the southern Baltic Sea coastal waters in Warszów, Lubiatowo and Hel from 1995 to 2007. To quantify the changes of oxygen supersaturation, data were collected along transects using integrated dissolved oxygen and water temperature sensors, either mounted on a remotely operated platform or deployed manually.

Data revealed that an excess of solar energy in the nutrient-rich Baltic Sea coastal waters caused an immediate warming of sea bed and bottom water, which induced gaseous supersaturation and enhanced biological production of oxygen by phytoplankton. Both processes increased the degree of dissolved oxygen saturation, which became highly supersaturated, especially during the spring and summer time. Such conditions are favourable for enhanced formation of bubbles in the water, which enhanced the release of gases (mostly oxygen) into the air. Gaseous evasion is, in particular, enhanced in the presence of breaking waves and whitecaps that are typically formed over coastal ridges and at the shore line. Laboratory experiments indicated that, with the increasing degree of dissolved oxygen supersaturation, both the number of bubbles produced in the water and their sizes increase.

Key words | bubble formation, coastal waters, dissolved chemistry, gases, oxygen

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INTRODUCTION

The amount of gases which can be dissolved in the water depends directly on water temperature (Ward *et al.* 2004). Other factors, e.g. water salinity and atmospheric pressure, are less significant. In general, gas solubility in the water increases with decreasing temperature and salinity. A decrease in atmospheric pressure lowers the partial pressure of gaseous compounds; thus their equilibrated amounts at the water–air interface decrease (Simpson 1984).

Oxygen in sea water is primarily a product of direct photosynthesis, a process underlying phytoplankton primary production. In the Baltic Sea, primary production begins in spring, peaks in summer and declines in autumn (see Łysiak-Pastuszak & Trzosińska 1995). The highest amounts of oxygen are released during large algal blooms (see Pliński 1995). Spring blooms are enhanced by the increasing availability of sunlight energy which, in addition, is more efficiently transferred via the troposphere which is clearer than in autumn and winter. This particular effect is caused both by a reduced cloudiness over the cold surface waters and reduced anthropogenic aerosol loads, a situation typical of spring conditions (Krüger *et al.* 2004). Under such circumstances, both the high nutrient contents and the high concentrations of gases dissolved in cold water during winter become available to the photosynthesising phytoplankton, which is conducive to the formation of immense algal blooms in the Baltic.

doi: 10.2166/nh.2008.021

Oxygen can also be transferred into the water column from the air, which may take place under conditions of oxygen depletion, usually prevalent during winter (see Łysiak-Pastuszak & Trzosińska 1995; Kruczalak & Marks 1998).

The dissolved oxygen concentration is usually expressed in ml/dm^3, reflecting the volume of dissolved oxygen concentration in the water, for a given water temperature, salinity and atmospheric pressure. On the other hand, oxygen saturation is often expressed as a percentage, directly reflecting the ratio of the amount of oxygen dissolved in the water to that which would equilibrate with its atmospheric content under conditions mentioned above. This means that saturation values exceeding 100% indicate a state of supersaturation with regard to the oxygen dissolved in water. Such conditions usually prevail during plankton blooms, as reported by a number of authors (Garbalewski & Marks 1985; Cyberska & Lauer 1990; Kruczalak & Marks 1998; Łysiak-Pastuszak & Trzosińska 1995). Oxygen supersaturation can also evolve under water warming conditions during the spring (see Blanchard & Woodcock 1957).

Southern Baltic water oxygen concentrations averaged over 1989–1993 indicate an increase in the number of days with oxygen-supersaturated surface waters to the present value of more than 250 d/yr (Łysiak-Pastuszak & Trzosińska 1995). This trend probably reflects climate changes resulting in an increased number of warm days, combined with increasing loads of nutrients released to the Baltic Sea ecosystem. In general, oxygen supersaturation in the surface waters prevails for about 70% of d/yr and dominates during spring and summer (Łysiak-Pastuszak & Trzosińska 1995).

Bubble formation in the surface sea water affects the exchange of air and water constituents; in particular, it controls the transfer of all gaseous compounds across the air–sea interface (Liss 1983; Woolf 1997). Specifically, wave breaking into a gas-supersaturated water results in enhanced production of small bubbles in the water, thus affecting the water-to-air gas transfer and related aerosol production by the bursting bubbles (Stramska *et al.* 1990). Such conditions are conducive to the production of a significant number of small bubbles (probably mostly of oxygen), which remain in the water longer than the bubbles produced in saturated water. In addition, such small bubbles are more effective in scavenging suspended particulates from the water column, including bacteria and viruses, which may become airborne after the bubble with its cargo reaches the water surface and bursts (Blanchard & Syzdek 1970; Marks *et al.* 2001).

Bubbles which are present in the water column also have to be regarded as a major contributor to the water–air interfacial area which controls the air–sea mass exchange and plays a significant role in the dissipation of wave energy (Woolf 1997).

METHODS AND MEASUREMENTS

The iodometric reaction of Winkler (1888) has been traditionally used for a precise measurement of dissolved oxygen content in the water and as a reference for other oxygen measuring techniques. However, the method requires collection of water samples and a time-consuming titration; thus it is not suitable for continuous or rapid measurements. Another, and much faster, method involves the use of galvanic oxygen-sensitive membrane electrodes. The measuring device consists of two metal electrodes remaining in contact with a supporting electrolyte, separated from the test solution by a selective membrane (Wilber 1983). The greater the oxygen partial pressure outside the device, the more oxygen diffuses through the membrane.

Data presented in this study were collected by CX-315 and CO-315 microcomputer-controlled oxygen membrane electrodes manufactured by Elmetron. Prior to each set of measurements, the probes were equilibrated for about 10–15 min to the actual water temperature. Most of the data were recorded by dataloggers operating at a 1–5 s frequency. In all cases, the oxygen sensors were submerged about 10 cm below the water surface and exposed to a steady movement of water resulting from movement of the platform with a speed of c. 0.2 m/s. Each set of data consisted of oxygen and temperature readings. All the values measured were corrected for the atmospheric pressure and water salinity. The accuracy of the oxygen meters used was checked and compared with the results of the traditional Winkler titration. The difference between the values obtained with the two methods was $< 1\%$.

Measurements of dissolved oxygen saturation and water temperature were taken in 1995–2006 along southern

Baltic coastal transects in Hel, Lubiatowo and Świnoujście-Warszów (Figure 1). The transects started at the water's edge and extended into the offshore waters to cross the breaking waves. Most of the transects were sampled with a 1 m long portable "radio-operated ship-vehicle" (Marks & Suwalski 2006). That platform, beside oxygen and temperature sensors, was equipped with a watertight box (protecting the electronic parts) and a water vacuum pump, allowing frequent sampling of the surface water.

The Świnoujście-Warszów datasets were collected from short transects which allowed direct measurements and readings. Such data were traced at 5 m intervals, perpendicular to the shoreline. In 2006 and 2007, experiments were conducted to investigate thermal processes at the sea floor, which may influence oxygen supersaturation. In these cases, data were collected by means of a pole (see Figure 2) equipped with a set of thermocouples (AZ, type K, model 8852) of 0.1°C resolution. A sea-floor pair of thermocouples was fixed onto the pole and grounded (one probe at the seabed and the other 10 mm above the sediment). The near-surface thermocouple pair floated at c. 1 mm and 10 mm below the water surface. These measurements aimed at tracing in a precise way the temperature at and above the sea bed–water interface as well as at and below the sea water surface. However, due to limited length of thermocouple cables the collection of data was possible only within the most shallow 20 m long (c. 50 cm deep) transects.

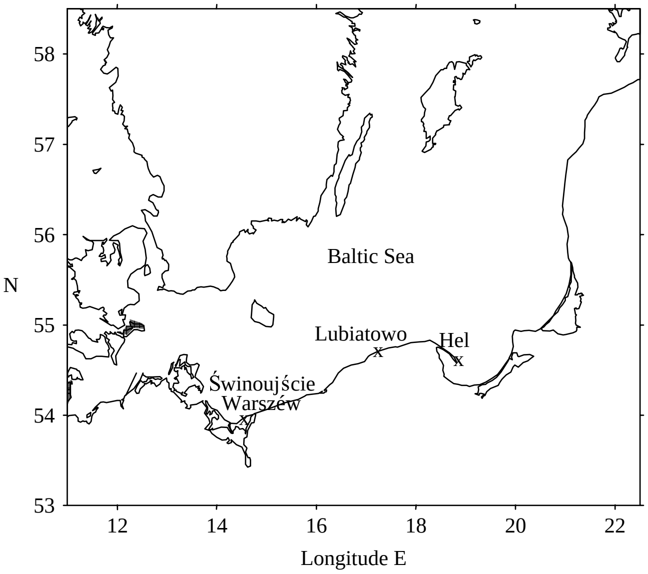

Figure 1 | Location of measurements in the southern Baltic Sea coast.

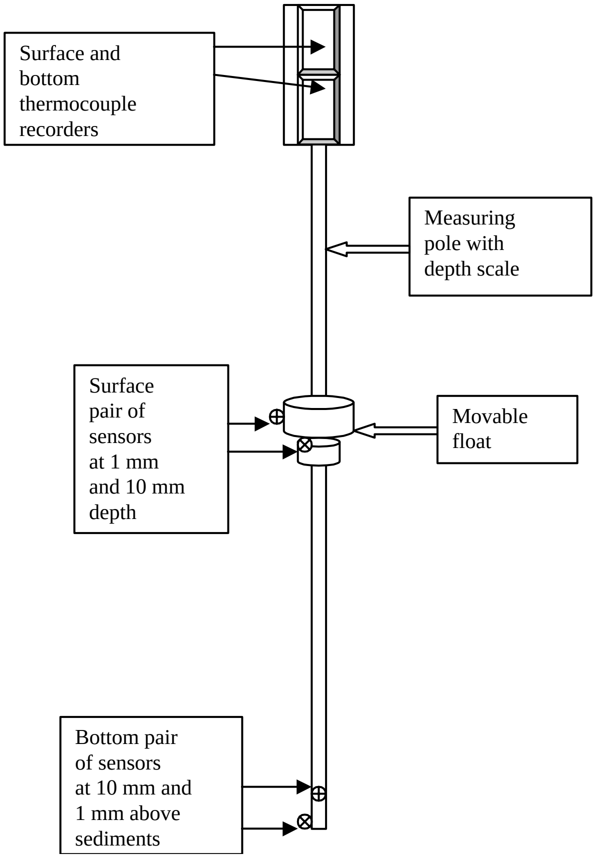

Figure 2 | Schematic representation of thermocouple measuring pole used to trace the surface and bottom water temperature in coastal waters, up to 1 m depth.

Meteorological variables during the measurements were recorded with an OMEGA WMS-14 or a portable OREGON Weather Station. The parameters recorded included wind speed and direction, air temperature and humidity, atmospheric pressure and precipitation. In addition, wave height, the presence of breaking waves and the distances between wave breakers were recorded with a camera or logged based on visual observations. Altogether, measurements were taken from a total of 72 coastal transects, including 8 sampled during autumn–winter.

To study bubble formation in gas-supersaturated water separate measurements were performed using the sea water collected from the Gulf of Gdańsk in March and April 1997. Five litre water samples were transported to the laboratory and temperature-equilibrated at c. 20°C. During the thermal stabilisation, oxygen and other supersaturated gases evaded continuously from the water and formed bubbles; thus, oxygen saturation increased at first due to warming and slowly decreased thereafter, indicating thermal stabilisation at room temperature. Once the water was thermally stabilised, its oxygen saturation was measured and a small volume of water was removed by submerging, to about 3 cm below the water surface, two microscope slides forming a "sandwich" able to collect c. 416 μm thick water layer. This technique made it possible to count the bubbles and to measure their sizes under the microscope in the laboratory.

COASTAL MEASUREMENTS

To illustrate a typical coastal water distribution of dissolved oxygen supersaturation for the open southern Baltic Sea, a set of data recorded in Lubiatowo on 11 September 1995 are shown in Figure 3. Measurements from the shoreline to 300 m offshore showed that, within 300 m to 100 m offshore, a high but very stable dissolved oxygen supersaturation (120–123%) was developed. However, oxygen saturation rapidly increased to 132% close to the shoreline, within the adjacent 30 m. The highest oxygen supersaturation was recorded about 75 m off-shore, indicating that the biological oxygen production is at its highest within a belt of rather shallow water along the shoreline. Four maximum saturation readings (132, 128, 126 and 124%) were recorded 75, 50, 20 and 5 m off-shore, respectively. As one approached the water line, particularly within the breaking wave areas, the oxygen supersaturation values recorded were observed to decrease to the four minima (126.2, 122.9, 122.7 and 122.5%) recorded 60, 40 and 10 m off-shore and at the water's edge, respectively (Figure 3). The results indicate that the highest enhancement of dissolved oxygen production takes place in shallow waters, along the coast, within a c. 100 m wide offshore band. If breaking waves are present within that band, narrowed-down sub-bands of elevated and suppressed dissolved oxygen supersaturation are formed, corresponding to the non-breaking and breaking wave areas, respectively.

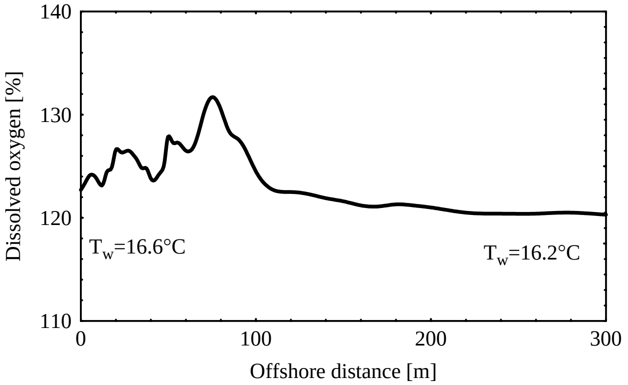

Figure 3 | Coastal measurements of dissolved oxygen saturation in the surface water measured from the waterline to 300 m off-shore distance, data recorded in Lubiatowo on 11 September 1995.

To illustrate another phenomenon observed in the coastal waters and associated with oxygen supersaturation, data recorded on 7 July 1997 and 19 July 1997 in Hel are presented in Figure 4. Measurements along the two transects were taken under similar conditions of c. 5 m/s off-shore winds, therefore in the absence of breaking waves. On both occasions, the ea water in the vicinity of the shore-line showed a low oxygen content and the supersaturation increasing offshore.

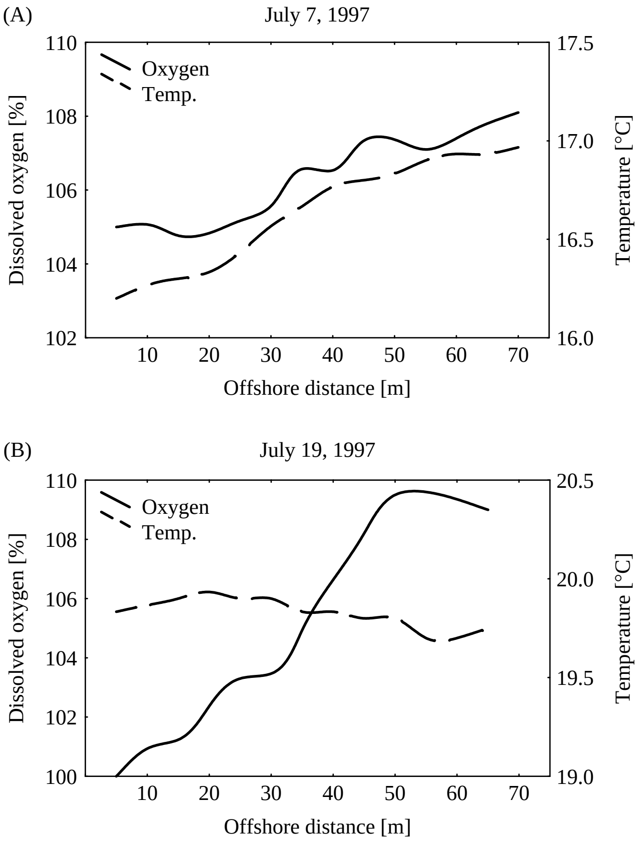

Figure 4 | Off-shore oxygen rise recorded in the coastal water in Hel on 7 July 1997 (A) and on 19 July 1997 (B).

In the case of upwelled colder (16.2–17.0°C), probably deeper water, oxygen saturation increased by as little as about 3% (cf. panel A in Figure 4), while a more pronounced increase in saturation (by 10%) was observed in warmer (19.6–19.7°C), probably mostly surface water (Figure 4B). In both cases, the increase in oxygen saturation along a 60 m long stretch is indicative of enhanced phytoplankton activity which, in the nutrient-rich coastal waters, depends upon direct availability of solar energy and is more effective in warmer water.

To illustrate the effects of solar energy with respect to the daily increase in oxygen saturation, a set of measurements taken at 11:00, 12:00 and 13:00 h on 20 May 2005 from transects laid out in the Pomeranian Bay coastal zone is shown in Figure 5. The records presented demonstrate the degree of oxygen supersaturation directly dependent on daily solar energy supply accumulated within the coastal area, especially from the water's edge to about 30 m off-shore. The oxygen saturation distribution measured at 11:00 showed only a slight increase towards the shore line, with a more pronounced oxygen supersaturation forming as time elapsed. The build-up of oxygen supersaturation was more pronounced in shallow water of c. 38 cm depth 30 m offshore: the oxygen supersaturation levels of 107, 112 and 118% were recorded at 11:00, 12:00 and 13:00 h, respectively. The corresponding increase in water temperature proceeded from 12.4°C at 11:00 to 12.6°C at 12:00 to 12.9°C at 13:00 h. Lower values of oxygen supersaturation were recorded in deeper waters (52–65 cm depth) 5–15 m off-shore (cf. Figure 5). The results indicate that, during typical spring conditions, the shallow coastal waters are effectively warmed and their oxygen content tends to increase during the midday increase in the solar energy supply. It has to be mentioned that cloudiness during the measurement events ranged from 2/8 at 11:00 to 5/8 at 13:00 h, while the wind speed ranged from 1.6 to 3.7 m/s; no breaking waves were observed.

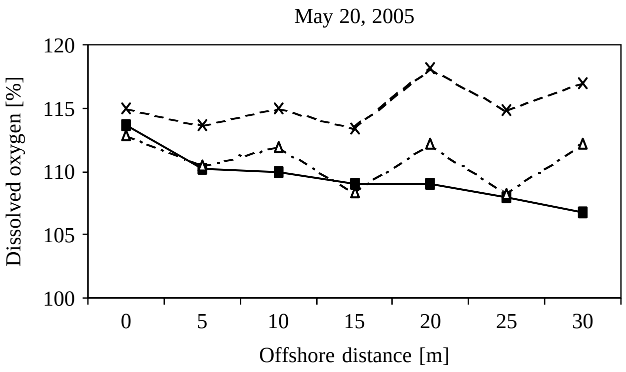

Figure 5 | Increase of oxygen saturation recorded in Pomeranian Bay during three successive hours (11.00, 12.00 and 13.00) on 20 May 2005.

Additional water temperature measurements were conducted at c. 1 and 10 mm below the sea surface as well as 1 and 10 mm above the sea bottom using a 1 m long pole, on which four thermocouples were mounted. Data were collected in Warszów (Pomeranian Bay) in May 2006 and 2007. Experiments indicated that, during periods of high solar energy, the water temperature measured at the sea sediment–water interface was usually higher than at the sea surface, exceeding even 2°C on occasion, within the shallow water bands of 10–50 cm depth. This indicates that solar energy warming of the sea bottom dominates over warming the water column; thus the portion of collected heat may become redistributed to warm the adjacent water layers. Such a significant degree of sea bed and interface water warming, compared to lower warming of the water column, directly impacts supersaturation of all dissolved gasses as well as enhancing sea bed photosynthesis. Thus both may cause an immediate oxygen rise in the shallow, light transparent inshore waters and coastal bands.

The results obtained indicate that, during spring and summer, the highly oxygen-supersaturated southern Baltic Sea coastal waters may serve as a substantial source of oxygen and related marine aerosol droplets, which may be of importance to the immediate, local micrometeorology, and to local air quality.

The results obtained also indicate that sunlight availability results in a time-lagged oxygen production in the coastal surface waters. Similar results were reported for near-shore oceanic waters at 5 m depth (13 m average depth of the water column) conducted off Martha's Vineyard, MA, USA during spring time (McNeil *et al.* 2006). In this case oxygen vertical fluxes measured at 5 m depth were primarily caused by changes in mixing conditions in the water column, thus air–sea gas transfer was found to play a secondary role in controlling vertical fluxes of oxygen. Experimental investigations by McNeil *et al.* (2006) include, among other parameters, a high resolution time series of dissolved CO_2 concentrations in the near-shore waters, indicating that dissolved CO_2 content of water covaried inversely with dissolved O_2. This indicates inverse coupling of both dissolved compounds incorporated into biological processes in shallow and coastal waters, which act as a source of O_2 and a sink for CO_2.

In general, the data collected show that the coastal waters are areas extremely active in terms of both solar energy accumulation and phytoplankton oxygen production. Both processes result in high dissolved oxygen supersaturation and may shift marine coastal systems to the oxygen supersaturation formed in the absence of breaking waves. As the surface water becomes oxygen-supersaturated, the oxygen water-to-air evasion may take place, especially within the active breaking wave areas. The combined effect of both solar energy accumulation and enhanced phytoplankton oxygen production is revealed by the oxygen saturation peaks recorded, as shown in Figures 3 and 5.

Since the number of datasets collected during the cold season was as low as 8, the presentation of results is restricted to those obtained in spring and summer. On the other hand, the cold season data show a much narrower range of oxygen saturation (96–104%), which indicates an almost uniform dissolved oxygen spatial distribution. A similar mean dissolved oxygen saturation range for the cold season was reported from the open water of the southern Baltic (Łysiak-Pastuszak & Trzosińska 1995).

In addition, it has to be pointed out that coastal oxygen production may be modified by coastal processes such as upwellings, along-shore currents, and freshwater discharge. If addition nutrient loads are supplied, phytoplankton activity and oxygen production may be enhanced, particularly during warm seasons. In contrast, oxygen depletion due to organic matter decomposition may dominate during the cold season.

BUBBLE FORMATION

Bubble formation was investigated in the actual sea water collected from the coastal zone of the Gulf of Gdańsk. The water collected was subjected to over-saturation by warming in the laboratory. A total of 50 water samples were collected and thermally stabilised at dissolved oxygen saturation levels of 105, 110 and 120%. The results obtained indicated that increasing percentage oxygen saturation was accompanied by a higher number of bubbles (spontaneously effervesced in still water) and their shift towards large sizes. For example, when the oxygen saturation increased from 105 to 110 and then to 120%, most of the bubbles had a characteristic radius of 50, 60 and 70 μm, respectively. In addition, the range of the measured bubble sizes increased from 10–70 to 20–90 and then to 30–110 μm as the oxygen saturation increased from 105 to 110 and then to 120%, respectively (Table 1). It has to be stressed that the results presented concern all the gases dissolved in the thermally supersaturated sea water sampled, but were here indicated by percent oxygen saturation.

Considering the data collected on 11 September 1995 in Lubiatowo (Figure 3) and recalculating the decrease in oxygen content from its maximum value of 132% (12.98 mg/l), as measured 75 m offshore (with no breaking waves) to 124% (12.18 mg/l) recorded 5 m offshore (with active breaking waves), the calculated oxygen evasion from 1 m^3 of water is 0.56 dm^3. Since most of the oxygen bubbles measured at 120% were represented by 70 μm radius ones, the approximate number of such bubbles formed in 1 m^3 of water is 7×10^8, hence the estimated air–water interfacial area of that bubble stock is 23 m^2. It is thus directly demonstrated that bubbles provide an extraordinarily expanded interface for the exchange between the two media. Considering, however, that the number of small bubbles found under real conditions exceeds the number of large ones, the real bubble concentration as well as the associated interfacial area may be higher.

Taking into account that about 50% of kinetic wave energy is used to generate bubbles (Terray *et al.* 1996), their abundant stock produced in the coastal waters under oxygen supersaturation has to be regarded as an important factor in protecting the coast from erosion. Due to the substantial eutrophication of the southern Baltic water, the increased oxygen supersaturation might be regarded as an additional

Table 1 | Bubble size distribution measured in thermally supersaturated seawater drawn from the Gulf of Gdańsk coastal zone

	Bubble radius (μm)			
Oxygen (%)	Smallest	Largest	Size spectrum width	Peak of abundance
105	10	70	60	50
110	20	90	70	60
120	30	110	80	70

factor that protects coastal areas during the warm seasons. However, the opposite effects may become operative during the cold season, when oxidation of organic matter may deplete oxygen and suppress bubble formation. Under such conditions, a slightly higher wave energy, which dissipates at the coastal barriers, may eventually be available for interaction with the bottom, thus causing more effective dislocation of coastal barriers. If such mechanisms are involved, the river discharge-associated organic pollution load in the coastal areas might be regarded as an additional factor responsible for more enhanced erosion acting over geological timescales.

CONCLUSIONS

The direct supply of solar energy into the southern Baltic Sea coastal zone effectively warms up the sea bed and shallow waters within a c. 100 m wide band, especially in spring and summer time and stimulates phytoplankton-related oxygen production. Both processes are gradually shifting the Baltic Sea coastal aquatic system to the state of oxygen supersaturation. Since the biological production of oxygen is inversely coupled to the dissolved carbon dioxide content of water, the shallow coastal waters of the southern Baltic Sea might also be regarded as a significant sink of carbon during the spring and summer time.

The oxygen which supersaturates the surface sea water tends to evade into the atmosphere. The main evasion mechanism is associated with active bubble generation in the coastal breaking wave areas, forming sub-bands parallel to the coast. The bubbles generated within those sub-bands substantially extends the air–water interface by providing a bubble-induced interfacial area.

The number of bubbles and their sizes as well as the related water-to-air oxygen evasion increases with the increase in percent oxygen supersaturation.

The gas supersaturation of the surface water enhances direct production of bubbles in the water, whereby it may affect the related aerosol droplets and humidity fluxes into the marine boundary layer.

In general, marine coastal waters might be regarded as the most effective zone of exchange and equilibration of the airborne and waterborne constituents. While during the spring and summer conditions coastal waters acts as significant source of gaseous constituents during the cold seasons they may act as a potential sink for gases including air pollutants.

ACKNOWLEDGEMENTS

The author is grateful to Dr. Krystyna Kruczalak for her friendly assistance in taking coastal measurements. The author would also like to thank Mr. Michał Bugajny and Ms Natalia Brzezowska for their assistance in collecting data from the Pomeranian Bay. Investigations conducted in the Pomeranian Bay were supported by the Polish National State Committee for Scientific Research under grant no. PZB-KBN-086/P04/2003 (505-2410000-84415). The editorial support of Dr. Teresa Radziejewska is gratefully acknowledged.

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First received 1 August 2007; accepted in revised form 7 January 2008