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Effect of phytoplankton growth on air bubble residence time in seawater

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[1] Laboratory experiments were carried out in a seawater mesocosm tank to investigate the influence of marine phytoplankton growth on air bubble residence time (BRT). Air bubbles of 10–1000 μm in diameter were injected by flushing a water jet into the top of the tank and BRT was determined acoustically. The tank was filled with seawater containing a natural phytoplankton population and growth stimulated by irradiating with artificial fluorescent light. A second experiment was conducted using a monoculture of the diatom *Cylindrotheca closterium*. BRT and several phytoplankton growth-related parameters (chlorophyll concentration, dissolved inorganic nutrients, dissolved organic carbon (DOC), oxygen saturation and bacteria numbers) as well as the water viscosity were monitored over periods of up to 24 days. BRT showed a statistically significant covariation with oxygen saturation (r = 0.69, α = 0.01 for natural phytoplankton; r = 0.93, α = 0.01 for the *Cylindrotheca closterium*) and chlorophyll concentration (r = 0.69, α = 0.05 natural phytoplankton; r = 0.76, α = 0.01 *Cylindrotheca closterium*) during phytoplankton growth periods. Increases in BRT of a factor >2 were found during the chlorophyll maximum, when the water was sufficiently supersaturated with oxygen ($\sim$>110%). No clear relationship was evident between BRT and measurements of DOC or water viscosity. Model experiments with highly oxygen-supersaturated water and artificial polysaccharide compounds indicated that oxygen supersaturation alone is not the main factor causing increased BRT during phytoplankton growth, but it is most likely a combination of the degree of gas saturation and the composition of the organic exudates derived from the microalgal population.

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1.   Introduction

[2] Air bubbles in the upper layer of the ocean play an important role in several physical processes of biogeochemical significance [*Thorpe*, 1982; *Woolf*, 1997] and act as a vehicle for the transport of material to the surface microlayer [*Scott*, 1975; *Gershey*, 1983; *Wallace and Duce*, 1978]. The primary mechanism by which organic particles are transported upward across the boundary between the ocean and the atmosphere is associated with the production of aerosol particles which in turn is the result of bubbles bursting at the sea surface [*Blanchard and Woodcock*, 1957; *Blanchard*, 1963; *Deane and Stokes*, 2002; *Monahan and Dam*, 2001]. Air bubbles are also involved in the exchange of gases between the atmosphere and the ocean [*Merlivat and Memery*, 1983; *Asher et al.*, 1996; *Woolf*, 1995; *Nightingale and Liss*, 2004]. *Wallace and Wirick* [1992]

found that increased wave action results in increased oxygen concentrations in the sea via bubble entrainment and they reviewed the importance of air bubbles in the cycling and global budget of trace gases. Air bubbles, especially those produced in the wakes of ships by propeller cavitation, are also of great interest to those involved in naval operations as they may interfere with the successful function of acoustic devices by scattering and absorbing sound due to their large acoustic cross section [*Trevorrow et al.*, 1994].

[3] It is known that air bubbles remain in the water column for different periods of time [*Graham et al.*, 2004]. Reasons for the differences in residence time of air bubbles have been found mainly to be due to the physical and chemical properties of seawater such as water temperature [*Thorpe*, 1986; *Thorpe and Hall*, 1987; *Hwang et al.*, 1991], salinity [*Scott*, 1975; *Peltzer and Griffin*, 1988; *Craig et al.*, 1993; *Wang and Monahan*, 1995] and the level of gas saturation [*Ramsey*, 1962; *Harris and Detsch*, 1991; *Woolf and Thorpe*, 1991; *Keeling*, 1993; *Bowyer and Woolf*, 2004].

[4] It is assumed, that biological factors in the ocean, especially phytoplankton, also have a major effect on the residence time of air bubbles through their influence on the gas saturation of seawater [*Sandler et al.*, 1982; *Zakharkov*

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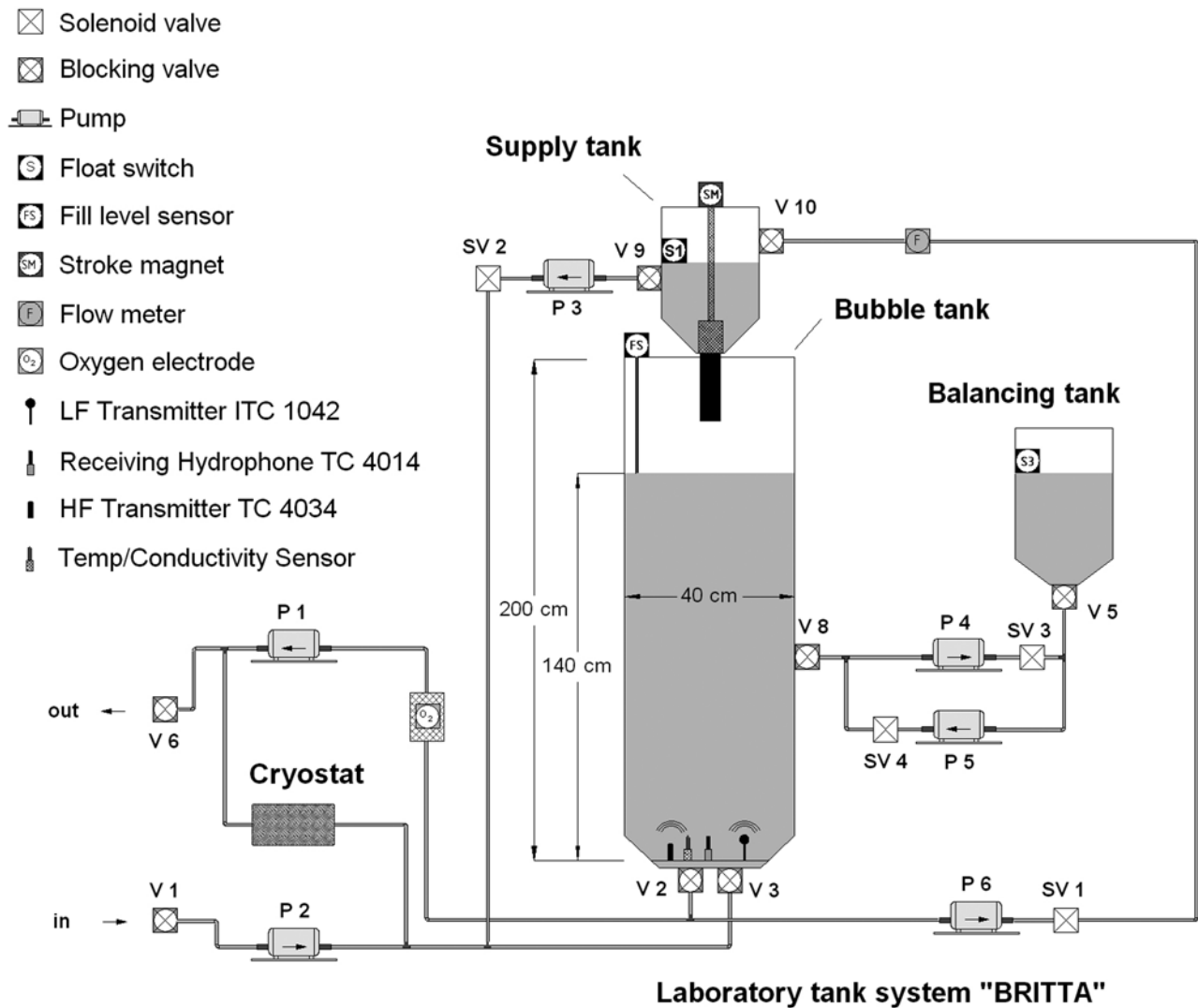[3]Forschungsanstalt der Bundeswehr für Wasserschall und Geophysik, Kiel, Germany.

Figure 1. Schematic diagram of laboratory experimental tank system.

et al., 1991] and through the release of organic substances such as polysaccharides [Leppard, 1995; Mopper et al., 1995; Myklestad, 1995]. These organic substances may result in changes in bubble surface tension [Nägeli and Schanz, 1991; Slauenwhite and Johnson, 1996] and the viscosity of seawater [Petkov and Bratkova, 1996] and may thus alter the rise speed of bubbles [Detwiler, 1979; Thorpe et al., 1992; Patro et al., 2001] as well as the diffusion of gas to and from the bubble [Thorpe et al., 1992].

[5] In regions of high biological production, spring-, summer- and early autumn phytoplankton blooms may influence bubble characteristics in near surface waters such as the residence time and the number of bubbles formed. Visual evidence for the extended residence times of air bubbles in the wakes of ships can sometimes be seen in Kiel Firth for example, when surface foam lines are visible for long periods after a ship has passed during low wind speed and calm weather conditions. However, not much is known about the relationship between the residence time of bubbles in seawater and biological activity.

[6] The aim of this work was to investigate if phytoplankton abundance, growth and their metabolic products of dissolved oxygen and dissolved organic material (DOM) can influence the mean residence time of gas bubbles in seawater. The main objectives were (1) to determine if bubble residence time (BRT) changes during different growth phases of phytoplankton populations, using a monoculture of the diatom *Cylindrotheca closterium* and mixed species in natural seawater, (2) to investigate the effect of phytoplankton abundance on seawater viscosity and compare this with bubble residence time, and (3) to determine the causes of changes in BRT in relation to phytoplankton particle abundance, oxygen production and phytoplankton exudates, that may act as surfactants in seawater.

2. Methodology

2.1. Laboratory Tank System

[7] Experiments were carried out in a specially designed laboratory experimental tank system (Figure 1) fitted with an acoustic detection system. The large bubble tank consisted of a 200 cm long, transparent plexi-glass tube, 40 cm
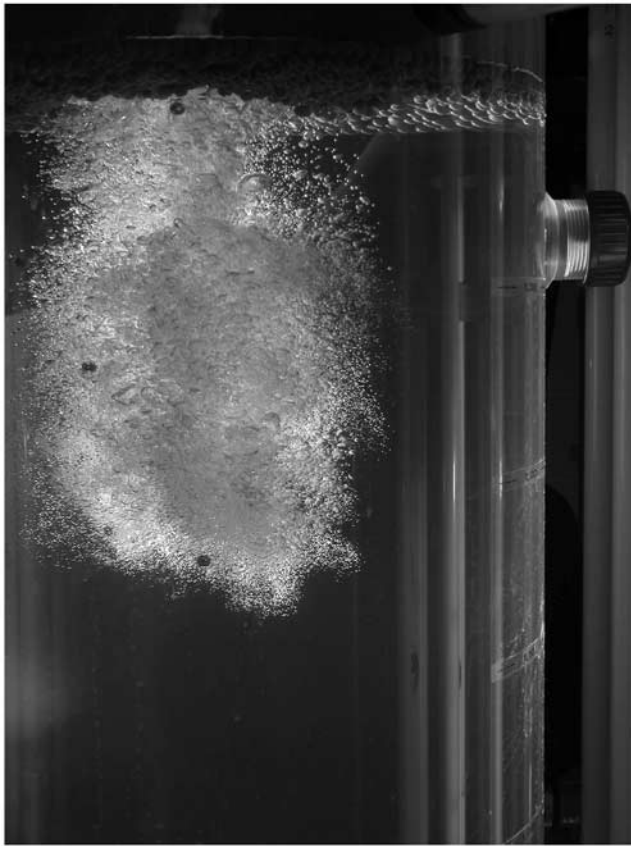
Figure 2. Injection of bubble cloud into the tank system by a water splash.

in diameter. The top of the tank was covered by a lid containing two holes, 8 cm in diameter, for air exchange with the atmosphere. The water surface was covered with small plastic balls (6 mm in diameter), that served to optimize the acoustic signal reflection from the surface. A small supply tank was mounted on top of the plexi-glass tube. From this supply tank, a water volume of 0.8 l was injected into the bubble tank, producing the bubble cloud (Figure 2). The size range of bubbles produced was between $10-1000$ μm in radius. The size of the largest bubbles was determined by photographing the bubble cloud. The size of the smallest bubbles could not be directly determined via the measurement set-up but is assumed to have been not <10 μm in radius according to *Vagle and Farmer* [1992]. A balancing tank at the side of the tank system acted as a water level equilibrator. All tanks were interlinked via Teflon tubing, covered with opaque foam insulation. The water circulation system included a cryostat (Aquamedic) to maintain a constant water temperature in the bubble tank and the supply tank. A total of 6 membrane pumps and 5 solenoid valves enabled the circulation of water between the different tanks as well as through the cryostat (Figure 1). Pumps and valves were operated via a relay matrix by the control software developed using Matlab. A tungsten fill level sensor in the large tank adjusted the water level. A temperature/conductivity probe (WTW Cond 340i) as well as an oxygen sensor (WTW Profi Line Oxi 197) were integrated into the tank system to monitor temperature,

salinity and dissolved oxygen. A flowmeter controlled the water volume that was injected into the bubble tank by the water jet. The bubble cloud was monitored using two transmitting hydrophones (ITC 1042 band = 0.01−100 kHz, resonance frequency = 79 kHz and TC 4034 band = 1 Hz−470 kHz, resonance frequency = 300 kHz) and one receiving hydrophone (TC 4034 band = 15 Hz−480 kHz) attached to the base of the bubble tank. The tank system was illuminated by 12 special plant fluorescent tubes (Osram L58 W/77), which were fitted on two opposite sides of the bubble tank to stimulate phytoplankton growth. The experimental tank system was operated automatically via the control software.

2.2. Measurement Cycle

[8] The measurement cycle was the time interval between successive measurements of BRT. Measurements of BRT were always carried out at constant water temperature. The duration of a measurement cycle varied between 1 and 1.5 h, depending on the pre-selected water temperature. Measurements of BRT were carried out with frequencies ranging from 40 to 400 kHz, subdivided into two frequency bands (40−180 kHz and 180−400 kHz). For a measurement cycle, only one frequency band could be sampled. A measurement cycle began with the adjustment of the water level in the large tank to a height of 140 cm and the filling of the supply tank, followed by the turbulence-and-cooling phase, when the water in the bubble tank was pumped through the cryostat, until the predefined measurement temperature was reached. Once the set measurement temperature was achieved, a 20 min quiescent phase commenced after which the acoustic sampling began. Following a 30 s initial period of acoustic sampling, the bubble cloud was produced by the water jet (duration 2 s, 0.8 l). The acoustic sampling then continued for another 19.5 min.

2.3. Determination of Bubble Residence Time

[9] Initially, the reference backscatter level was defined, comprising the first 30 s of the acoustic measurement phase before the release of the water jet. A mean reference value was calculated for all acoustic pings for every frequency. A standardization was then carried out for the remaining pings (from the time the water jet was released until the end of the acoustic measurement phase) with the corresponding reference value. The backscatter level was plotted over time and depth (Figure 3). A value of BRT for a certain frequency was then determined by applying a detection threshold. The detection threshold was set in the near surface layer to a level of 3 dB. BRT was then defined as the time when the backscatter level near the water surface fell below the detection threshold.

[10] In this paper, BRT values are presented for a frequency of 120 kHz only as previous observations of in situ bubble clouds by FWG (unpublished data) have shown strongest damping at this particular frequency.

2.4. Sampling

[11] Collection of water samples for measurements of chemical, biological and physico-chemical parameters was carried out once a day. Samples were drawn from a tap fitted mid way up the bubble tank. Triplicate 120 ml volumetric glass bottles were filled for the determination
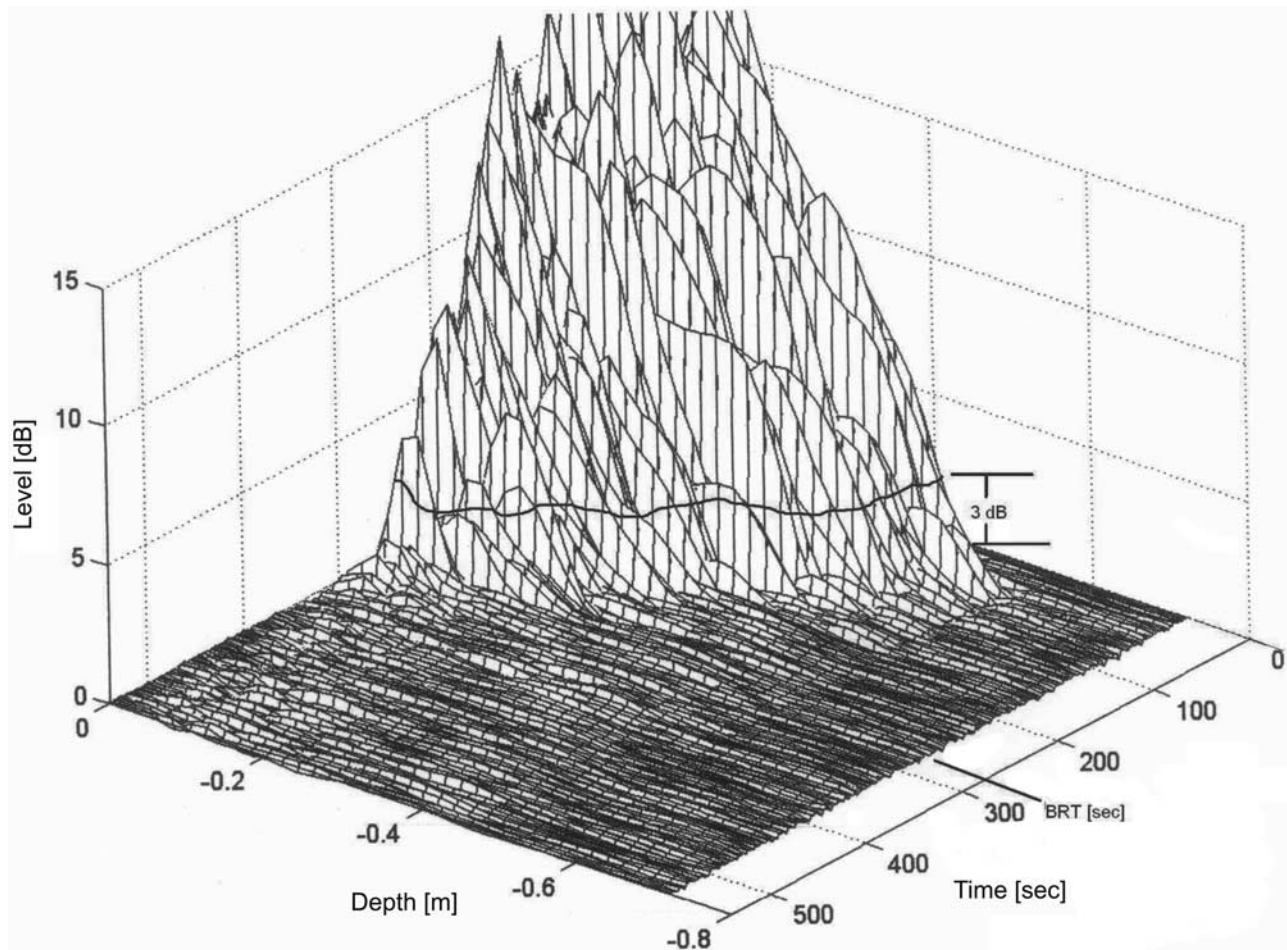
Figure 3. Backscatter level of the acoustic signal at 120 kHz over time and for different water depths of the tank system. The black line along the backscatter signal indicates the 3 dB threshold. The BRT is indicated on the time-axis at 280 s.

of dissolved oxygen and 1 ml of each Winkler reagent (manganese (II) chloride and alkaline iodide solution) added. Samples were analyzed using the Winkler procedure as described by *Grasshoff et al.* [1999] and a Hydro Bios titration system. A sample for filtration and further analysis of dissolved organic carbon (DOC) was poured directly from the tap into a 500 ml Schott glass flask, which had been pre-rinsed with the sampling water and was closed with a Teflon-lined lid. A large volume of about 1.5 l of tank water was poured into a plastic measuring jug for later sub-sampling for dissolved inorganic nutrients, chlorophyll *a*, phytoplankton cell counts, bacteria cell counts, and viscosity measurements.

[12] Samples for analysis of chlorophyll *a* were filtered in triplicate through Whatman glass fiber filters (GF/F) with a vacuum of between 0.2–0.3 bar. Filters were frozen at −40°C, then extracted in 90% acetone overnight and analyzed using a Turner GAT TD 10AU fluorometer as described by *Welschmeyer* [1994]. Samples for the analysis of dissolved inorganic nitrate, nitrite, phosphate and silicate were filtered in triplicate through Whatman GF/F filters and frozen in 100 ml plastic bottles at −40°C. Dissolved inorganic nutrients were analyzed according to the method described by *Grasshoff et al.* [1999]. Samples for the analysis of DOC were filtered through pre-combusted

(500°C for 12 h) GF/F filters with a pressure filtration system at 0.5 bars. The filtrate was decanted into 40 ml pre-combusted glass vials in triplicate, spiked with 150 μl 50% $H_3 PO_4$ and closed with Teflon-lined caps. Determination of dissolved organic carbon was done by high temperature catalytic oxidation [*Sharp*, 1973], using a Shimadzu TOC 5000A organic carbon analyzer (for the natural Kiel Firth phytoplankton experiment) and a Shimadzu TOC-V$_{CSN}$ organic carbon analyzer (for the experiment with *Cylindrotheca closterium*).

[13] 50 ml samples for bacteria counts were decanted into clean brown glass bottles and fixed with 1 ml of 37% pre-filtered formaldehyde. Samples were then filtered through black polycarbonate filters, stained with acridine orange [*Hobbie et al.*, 1977] and counted using a Zeiss Axioplan epifluorescence microscope with HBO 50 mercury vapor light and a blue-filter (450–490 nm).

[14] Samples for phytoplankton cell counts were placed into 250 ml clean brown glass bottles and fixed with 5 ml of Lugol's iodine solution (Merck). Phytoplankton cells were counted following the method described by *Utermöhl* [1958] with a Zeiss inverted microscope.

[15] A 3 ml sample was decanted into an Ostwald capillary glass viscometer (capillary diameter = 0.4 mm)

for the determination of bulk water viscosity. The principle of this method is based on the time taken for a fluid to pass a given distance through a small capillary, from which the kinematic viscosity (which is an indication of the internal friction of a fluid) is calculated using:

$$v = K \bullet t, \tag{1}$$

where v is the kinematic viscosity, K the capillary constant (0.01 for a capillary with diameter = 0.4 mm) and t is the time (in seconds) it takes for the fluid to pass a certain distance through the capillary. Viscosity measurements were made in a temperature controlled water bath (Lauda) at the same water temperature that was selected for the experimental tank system. 10 replicate measurements were made on every sample.

2.5. Preparation and Implementation of the Kiel Firth Nutrient Enriched Seawater Experiment

[16] 300 l of Kiel Firth water were pumped into plastic containers (the containers had previously been rinsed with deionized water) in January 2004 at the Kiel lighthouse on board the research vessel "Polarfuchs". A Johnson membrane pump was used to pump the water from approximately five meters below the sea surface. The water was transferred into the tank system on the same day it was sampled and the measurement software was started. The water temperature in the tank was set to 12°C. The fluorescent tubes were operated on a 12/12 h light/dark cycle (only 6 tubes were used). Initially the water jet was suppressed for a period of two days to let the water degas. Following this, the jet was switched on and bubble residence time measurements began. After four measurement cycles, 50 ml NaNO$_3$, 50 ml Na$_2$HPO$_4$ and 50 ml Na$_2$SiO$_3$ stock solution as well as 50 ml of Vitamin Mix and 5 ml of each metal stock solution of F/2 nutrient medium were added to the water to stimulate algal growth and BRT measurements were made for 13.5 consecutive days. Daily samples for the analysis of biological, chemical and physico-chemical parameters were taken from day 0.5.

2.6. Preparation of the Cylindrotheca Closterium Culture

[17] A non-axenic stock culture of *Cylindrotheca closterium* was subcultured into five 100 ml sterile glass flasks, filled with F/10 nutrient medium [*Guillard and Ryther*, 1962], made up from 1 l filtered (GF/F), sterile seawater (salinity 31) spiked with 200 μl of NaNO$_3$, 200 μl of Na$_2$HPO$_4$, 200 μl of Na$_2$SiO$_2$ stock solutions as well as 1 ml of vitamin mix stock solution and 100 μl of each metal stock solution. The initial ratio of stock culture and F/10 nutrient medium was approximately 1:10. All culture flasks were sealed with sterile cellulose stoppers and covered with aluminum foil. Algae were grown in a temperature controlled room at 18°C and were illuminated by fluorescent tubes for 12 h per day. The diatom cultures were left to grow for seven days, until they showed a distinct, slightly brownish color. The cultures were then transferred into five 300 ml sterile glass flasks and filled up with fresh F/10 nutrient medium. After a further seven days, the cultures were transferred into two 6 l glass flasks, each containing 5 l of fresh F/10 nutrient

medium. The cultures were then left to grow until they showed a distinct brownish coloring.

2.7. Preparation and Implementation of the Monoculture Growth Experiment With Cylindrotheca Closterium

[18] The aim of this growth experiment was to investigate the influence of *Cylindrotheca closterium* on BRT in the tank system, as this particular species is well known for its production of mucilagineous material [*Revelante and Gilmartin*, 1991].

[19] The tank system was filled with filtered (GF/F) aged North Sea water in October 2004 and measurements of BRT were started immediately at 18°C with the fluorescent tubes switched off. After one day, 40 ml NaNO$_3$, 40 ml Na$_2$HPO$_4$ and 40 ml Na$_2$SiO$_3$ stock solution as well as 135 ml of Vitamin Mix and 20 ml of each metal stock solution of F/2 nutrient medium were added to the tank followed by 10 litres of a dense monoculture of the diatom *Cylindrotheca closterium*. Daily samples for the analysis of biological, chemical and physico-chemical parameters were taken from day 1.5. After addition of the culture, six fluorescent tubes were operated on a 12/12 h light/dark cycle and measurements of BRT as well as sampling for all other parameters were carried out for a further 22 days. From day 12 to day 14, the light/dark interval of the fluorescent tubes was changed in error to 24 h and was set back to 12 h from midday on day 14 until the end of the experiment.

2.8. Preparation and Implementation of the Oxygen Supersaturation Experiment

[20] BRT measurements were made using deionized water, which had been in the tank system for several days at a temperature of 18°C. After 1.5 days, the deionized water was bubbled with pure oxygen from a pressurized bottle via a wooden frit, increasing the oxygen saturation of the tank water from 96.8% to 170%. BRT measurements were then carried out for a further 1.2 days.

2.9. Preparation and Implementation of the Experiment With Xanthan Gum

[21] The tank system was filled with deionized water and BRT measurements were started at a temperature of 18°C. After four days, a solution of the polysaccharide Xanthan Gum (Sigma) was added to the water, resulting in a Xanthan Gum concentration of approximately 0.008 g l^{-1}. After one day, the oxygen saturation of the tank water was increased to 143% by bubbling with oxygen from a pressurised bottle. After a further measurement cycle, the concentration of Xanthan Gum was increased to approximately 0.08 g l^{-1}. Kinematic viscosity of the tank water was measured several times throughout the experiment. After the second addition of Xanthan Gum, measurements of BRT were carried out for a further 6 days.

3. Results
3.1. Nutrient Enriched Kiel Firth Water

[22] A growth experiment with water from Kiel Firth, containing a natural plankton population dominated by diatoms was of particular interest as diatoms are known to
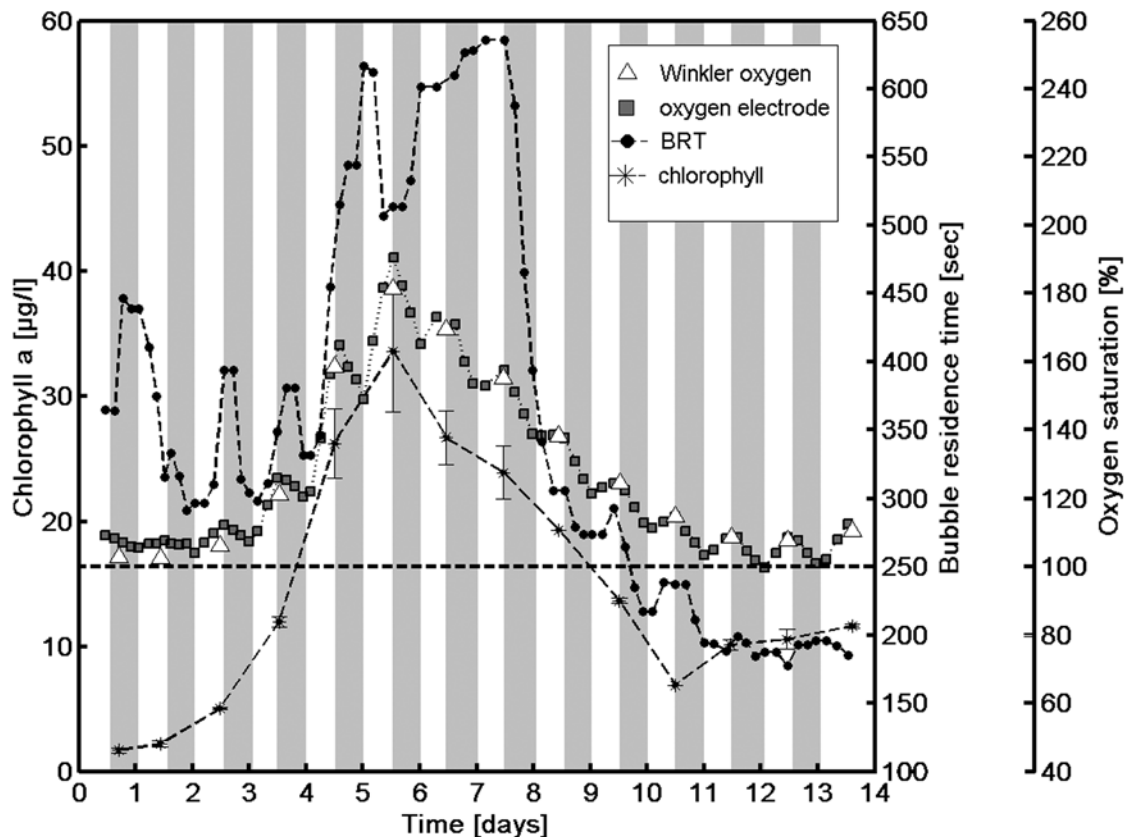
Figure 4. Changes in chlorophyll *a* concentration, BRT and oxygen saturation (%) with time for a growth experiment with nutrient enriched Kiel Firth water. The grey shaded bars indicate periods when the tank illumination was switched off, the white bars indicate the times when the tank system was illuminated. The black dashed line indicates the 100% oxygen saturation threshold.

release large quantities of surface active organic compounds [*Mopper et al.*, 1995] and therefore likely to influence BRT in the tank system.

[23] Water was collected from Kiel Firth on the day the experiment was started and an addition of nutrient medium made on day 0.7, with initial nutrient concentrations being 219 μmol l^{-1} NO_3^-, 12 μmol l^{-1} PO_4^{3-} and 50 μmol l^{-1} SiO_4. The removal ratio of NO_3^- : PO_4^{3-} was usually less than the Redfield ratio of 16 (2 between days 2.5–3.5 and 7.4 between days 3.5–4.5). The growth limiting nutrient was silicate, which became depleted to <2 μmol l^{-1} on day 5.5. Chlorophyll *a* concentration in the tank increased exponentially from 1.7 μg l^{-1} to a maximum of 33.6 μg l^{-1} on day 5.5 (Figure 4) indicating that the tank system supported good phytoplankton growth. After day 5.5, the chlorophyll concentration decreased again to 6.9 μg l^{-1} on day 10.5 followed by another slight increase to 10.5 μg l^{-1} on day 12.5. The standard deviation of mean chlorophyll concentrations calculated from triplicate samples was usually below 10% with a standard deviation of around 4% for most values.

[24] The phytoplankton in the tank system were dominated by diatoms, with the most abundant species being *Thalassionema nitzschioides*, *Skeletonema costatum*, *Thalassiosira* sp. and *Cylindrotheca closterium*. On day 0.5, the most dominant species was *Thalassionema nitzschioides*

(2.7×10^5 cells l^{-1}) followed by *Skeletonema costatum* (1.0×10^5 cells l^{-1}), *Thalassiosira* sp. (3.8×10^4 cells l^{-1}) and *Cylindrotheca closterium* (1.7×10^4 cells l^{-1}). *Skeletonema costatum* showed the highest specific growth rate during the exponential phase (1 division per day between days 0.5–4.5), and dominated the mixed diatom population while *Thalassionema nitzschioides*, *Cylindrotheca closterium* and *Thalassiosira* sp. had lower specific growth rates. The increase in chlorophyll concentration was accompanied by a rapid increase in oxygen saturation of the water from an initial supersaturation of 102% (values from oxygen electrode) to a maximum of 190% on day 5.5, when the chlorophyll concentration was at maximum (Figure 4). The accuracy of the oxygen data from the electrode (recorded 6–7 times per day) was monitored by daily Winkler titrations and the data showed good agreement. The light and dark changes in oxygen saturation as shown on Figure 4 varied by a difference of 10% between the dark phase minimum and the light phase maximum at the beginning of the phytoplankton growth period (day 2.0) to a maximum difference of approximately 40% between days 4.0 and 6.0, when chlorophyll concentrations were maximum. Once the chlorophyll concentration started to decline from day 6.5, the oxygen supersaturation decreased and light-dark differences diminished, with the light-phase rate of in-
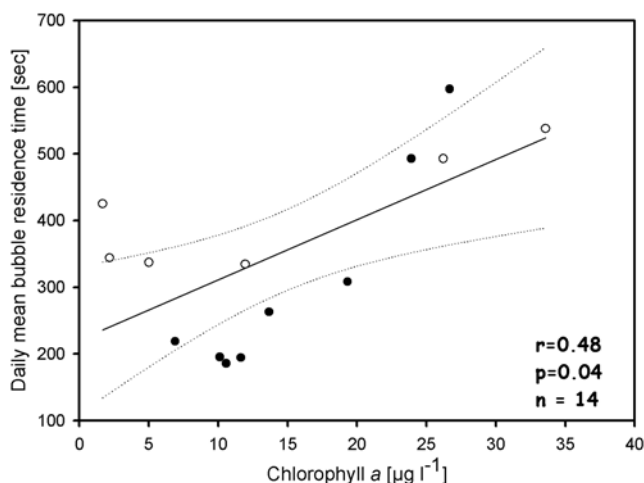
Figure 5. Chlorophyll *a* concentration versus mean daily BRT for Kiel Firth water growth experiment. Black solid line = linear regression; black dotted lines = 95% confidence intervals; open symbols = data points during chlorophyll increase; filled symbols = data points during chlorophyll decrease. Averaging intervals were between 5–7 BRT measurement points depending on the number of measurements made per day.

crease in oxygen saturation being less than the rate of decline during dark phase. After 13 days, the oxygen saturation had reduced back to its initial value of just over 100%.

[25] During the first two days of the experiment, when chlorophyll concentrations were still low ($\sim$2 μg l^{-1}) BRT decreased from 450 s to just less than 300 s (Figure 4). This initial decrease in BRT may have been due to organic material from the bulk fluid being scavenged by bubbles. When the bubbles burst on the water surface, the resulting jet droplets may have carried much of this organic material into the head space of the tank, where a fraction was deposited on the tank walls. As the amount of organic material in the bulk water was reduced by this process, subsequent bubbles remained "cleaner" for longer periods of time and thus rose more rapidly for a greater time until they collected enough organic material to make them "dirty" and thus slow their rise down. During days 2.0 to 4.0, BRT increased to 400 s during the light phase and decreased to 300 s during dark phase, indicated by the shaded areas in Figure 4. From day 4–5.5, when chlorophyll concentration was 25–33 μg l^{-1}, oxygen supersaturation increased rapidly and the rate of increase during light phase was also high, BRT increased to a maximum value of over 620 s on day 5.0, followed by a decline on the same day to 500 s and a further increase between days 6.0–8.0. Between days 4.5 and 9.0, when the water was highly supersaturated with oxygen, a clear light and dark cycle in BRT was not detectable. From days 9.0–10.5, when chlorophyll concentration and oxygen saturation both declined to 6 μg l^{-1} and $\sim$105% respectively, BRT decreased to 200 s. Between days 9.0–11.0, when oxygen saturation and BRT declined, BRT showed again some indication of following the light and dark phases indicated by the grey and white shaded areas on Figure 4. Daily chlorophyll concentration

and daily mean BRT did not show a particularly strong correlation over the 14 day period of the experiment with a correlation coefficient r = 0.48, a p-value of 0.04, n = 14, (correlation is significant at an α-level of 0.05, Figure 5). BRT showed a general covariation with oxygen saturation and both parameters were highly correlated (Figure 6; r = 0.69; p-value = 0.00; n = 77; α-level = 0.01). DOC concentration in the tank remained fairly constant during the exponential growth phase (days 2–6) with values around 260–270 μmol l^{-1} (Figure 7). As the chlorophyll concentration reached its maximum on day 5.5 and then began to decrease, the DOC concentration in the tank increased steadily up to 340 μmol l^{-1} on day 13.5. DOC concentration did not show any obvious trend with BRT.

[26] Bulk water viscosity did not show a detectable change over time during the experiment (Figure 7). The range of values of viscosity were between 1.197 mm^2 s^{-1} and 1.201 mm^2 s^{-1} with an average standard deviation of 0.004 mm^2 s^{-1}. Bacterial abundance did not show any obvious relationship with BRT with cell concentrations around 6 $\times$ 10^6 cells ml^{-1} except for days 6–9, when bacterial numbers increased up to 18 $\times$ 10^6 cells ml^{-1}.

3.2. Monoculture Growth Experiment With Cylindrotheca Closterium

[27] The aim of this experiment was to investigate the influence of the growth of the mucilaginous producing diatom Cylindrotheca closterium [*Revelante and Gilmartin*, 1991] on BRT in the tank system. Nutrients and algae were added to filtered North Sea water on day 1.5 of the experiment, giving initial nutrient concentrations of 320 μmol l^{-1} NO$_3^-$, 11.5 μmol l^{-1} PO$_4^{3-}$ and 25.0 μmol l^{-1} SiO$_4$. The ratio of nitrate to phosphate uptake was close to Redfield from days 1.5–2.5 (removal ratio $\sim$11) and days 3.5–4.5 (removal ratio $\sim$15). Between days 2.5–3.5, nitrate was removed more rapidly than phosphate (nutrient removal ratio of $\sim$6) and later during the experiment (days 4.5–8.5) phosphate was taken up more rapidly (removal ratios >26).
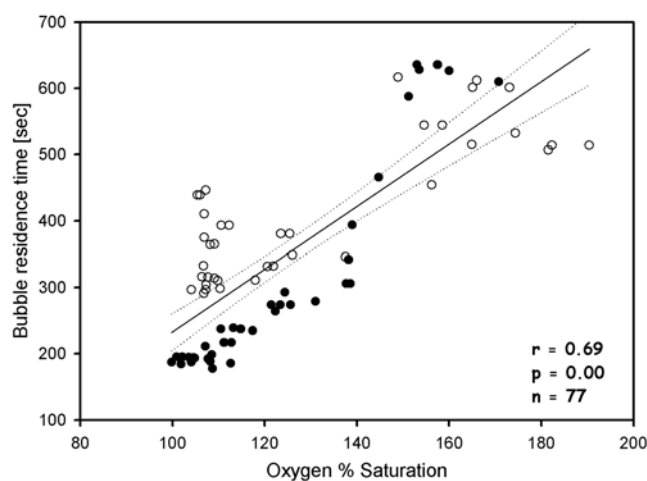

Figure 6. Oxygen saturation versus BRT for the Kiel Firth water growth experiment. Black solid line = linear regression; black dotted lines = 95% confidence intervals; open symbols = data points during oxygen saturation increase; filled symbols = data points during oxygen saturation decline.
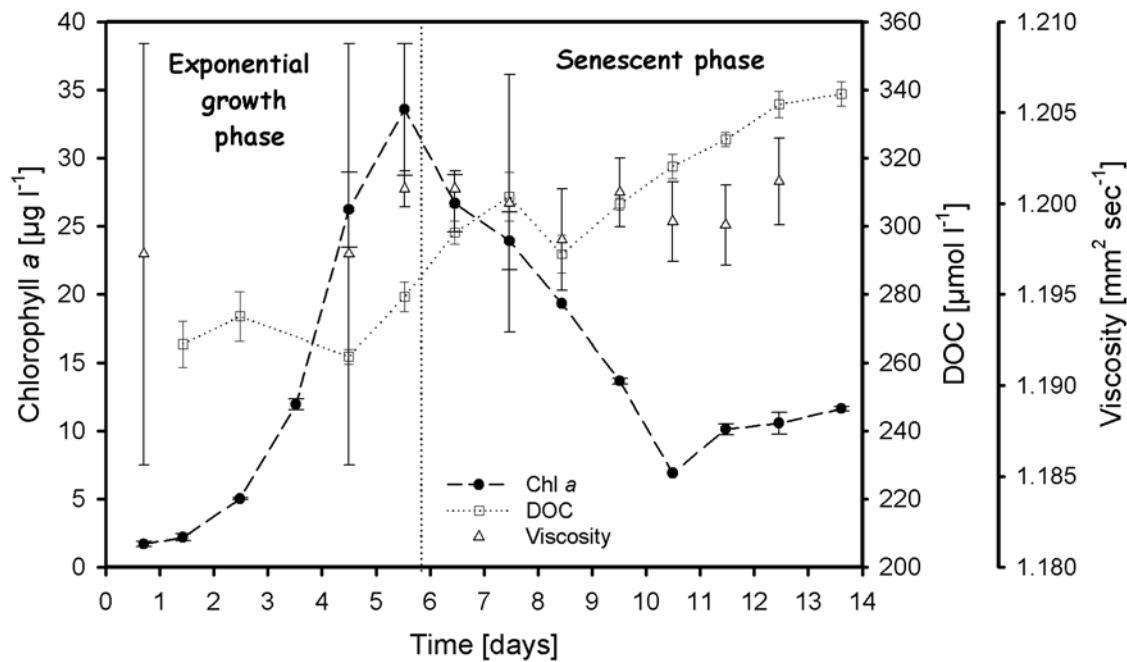
Figure 7.   Changes in chlorophyll *a* concentration, DOC and viscosity with time for the Kiel Firth water growth experiment. DOC error bars: $\pm 0.2 - 11$ μmol l^{-1}, chlorophyll error bars $\pm 0.2 - 2.8$ μg l^{-1}; viscosity error bars: $\pm 0.001 - 0.01$ mm^2 s^{-1}. The vertical dotted line indicates change from exponential to senescent growth phase.

However, the diatom population was not limited by inorganic nutrient availability throughout the experiment.

[28]   Chlorophyll concentration declined from an initial value of 21 μg l^{-1} to about 10 μg l^{-1} between days 1.5 and 2.5 (Figure 8) due to sedimentation of some cells onto the base of the tank. From day 2.5 to 9.5, the chlorophyll concentration increased to 24 μg l^{-1} and between days 9.5 and 12.5, chlorophyll concentration remained fairly constant at approximately 25 μg l^{-1} ($\pm$ 2). A drop in chlorophyll concentration to 17.4 μg l^{-1} ($\pm$ 1) occurred on day 13.5 followed by a further increase to 23 μg l^{-1} on day 14.5. Chlorophyll concentration began to decline from day 16.5 reaching a value of 1.4 μg l^{-1} on day 21.5.

[29]   Oxygen saturation measured (21–23 times per day) by the electrode and Winkler oxygen data showed close agreement (Figure 8). Before the addition of nutrients and diatom culture, oxygen saturation of filtered North Sea water was 96% between days 0.5 and 1.5. Shortly after the addition of nutrients and the *Cylindrotheca closterium* culture (from day 2.5), oxygen saturation began to increase, showing distinct light phase increases and dark phase decreases (Figure 8). Between days 2.0 and 6.5, oxygen saturation increased from 96% to a maximum of 150% with up to 22% increase during the light phase and 11% decrease during the dark phase. Saturation remained constant during days 6.5–11.5 (maximum of 150% during light phase, minimum of 132% during dark phase). Between days 11.5–12.5, when the tank illumination was switched off for a period of 24 h in error, oxygen saturation decreased from 150% to 118%. Between days 12.5–13.5, when the tank system was illuminated for 24 h, saturation increased again to 142%. From days 13.5 to 16.5 (again 12/12 h light dark cycle), oxygen saturation declined slightly from a

maximum of 142% to 135%, still showing distinct light-dark changes. From day 17.5, the light/dark changes became much smaller until they ceased completely from days 18.0 to 23.5, when saturation declined to a minimum of 63%.

[30]   Following the filling of the tank with filtered North Sea water on day 0.5, BRT decreased from 240 to 220 s during the first day (Figure 8). Then with the addition of algae and nutrient medium, BRT stabilized at about 220 s. With increasing chlorophyll concentration and oxygen saturation, BRT increased consistently from 220 to 350 s on day 5.5. From days 4.0 to 18.0, BRT showed distinct light-dark fluctuations with increases during light periods, when the oxygen saturation also increased, and decreases during darkness, when the saturation decreased. Differences in the BRT values between dark phase and light phase were about 80 s at the chlorophyll and oxygen saturation maximum ($\sim$25 μg l^{-1} and 150% respectively) during days 8.0 to 12.0, when BRT reached maximum values of 420 s during light phase. On days 11.5 and 12.5, when the light dark cycle was changed to 24 h, the strong decrease in oxygen saturation during dark phase (150–117%) co-varied with a strong decline in BRT from 400 to 225 s. During the following 24 h light phase, the increase in oxygen saturation was accompanied by an increase in BRT to 400 s by the end of the light phase. From days 14.0–17.0, both oxygen saturation and BRT declined slightly, however, the light dark fluctuations were still clearly visible until day 18.0. Between days 18.0 and 23.5, when chlorophyll concentration and oxygen saturation declined rapidly, BRT decreased to a mean value of approximately 170 s.

[31]   Chlorophyll concentration and daily mean BRT were highly correlated (r = 0.76, p-value = 0.00 and n = 21) and Figure 9 shows a clear linear relationship. BRT and oxygen
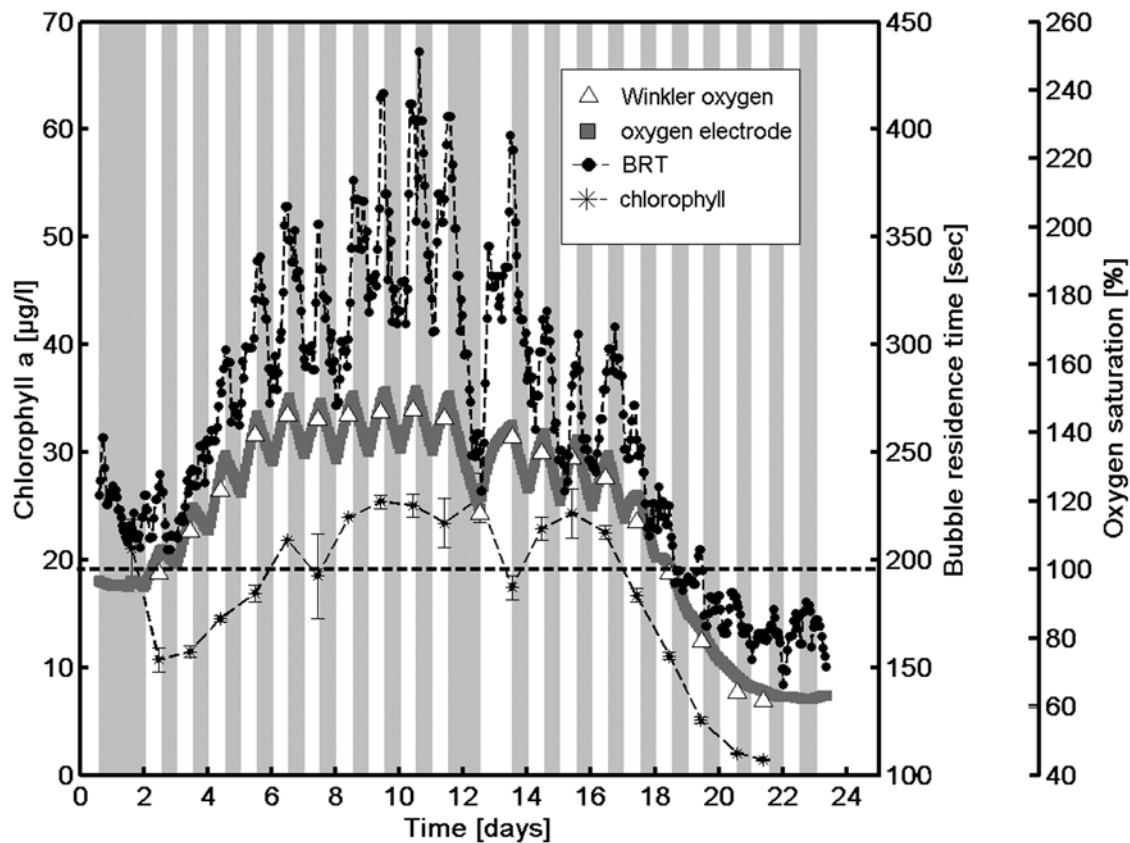
Figure 8. Changes in chlorophyll *a* concentration, BRT and oxygen saturation with time for the growth experiment with *Cylindrotheca closterium*. The grey shaded bars indicate periods when the tank illumination was switched off, the white bars indicate the times when the tank system was illuminated. The black dashed line indicates the 100% oxygen saturation threshold.
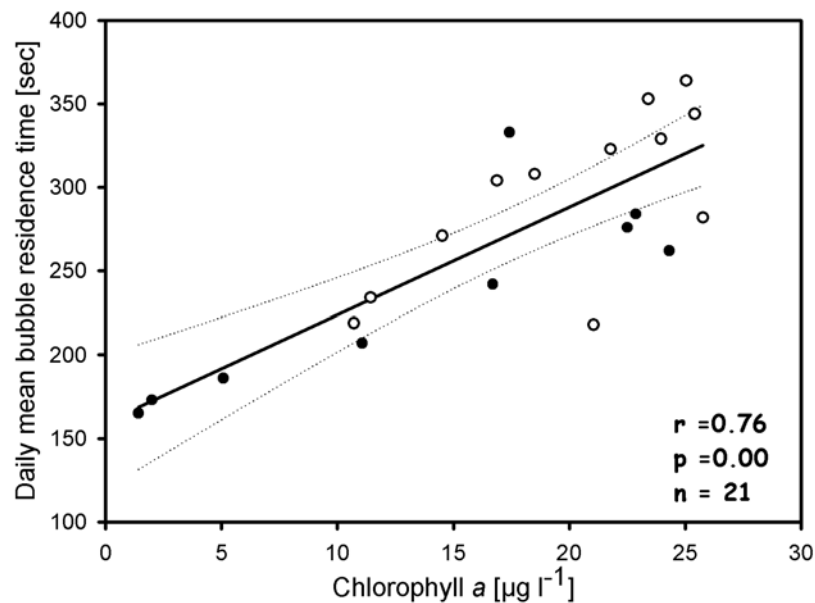

Figure 9. Chlorophyll *a* concentration versus mean daily BRT for the *Cylindrotheca closterium* growth experiment. Black solid line = linear regression; black dotted lines = 95% confidence intervals; open symbols = data points during chlorophyll increase; filled symbols = data points during chlorophyll decrease. Averaging intervals were between 21–23 BRT measurement points depending on the number of measurements made per day.
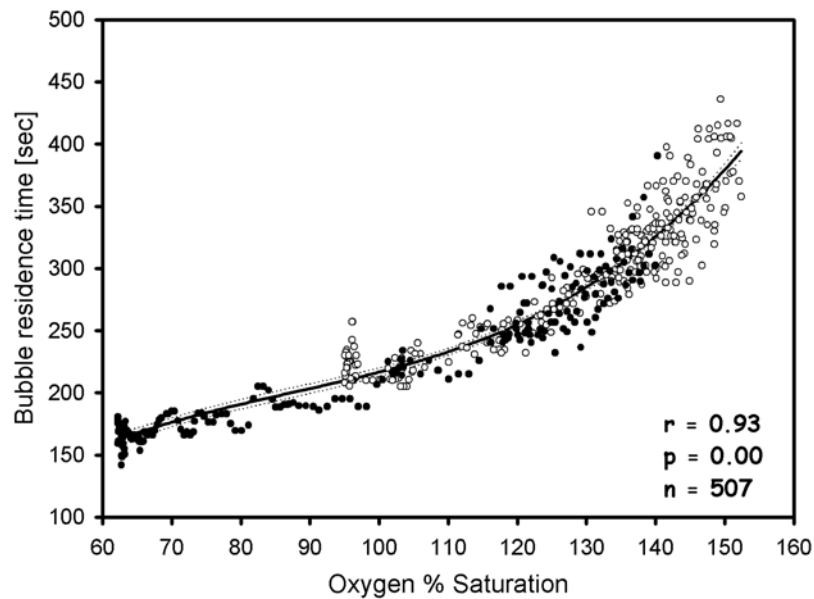
Figure 10. Oxygen saturation versus BRT for the *Cylindrotheca closterium* growth experiment. Black solid line = quadratic regression; black dotted lines = 95% confidence intervals; open symbols = data points during oxygen saturation increase; filled symbols = data points during oxygen saturation decline.

saturation also showed a strong correlation (Figure 10; r = 0.93, p-value = 0.00 and n = 507).

[32] DOC values did not change significantly during the exponential growth phase ($\sim$135 μmol l^{-1}; Figure 11) but during the stationary phase (days 7.0–17.0), DOC increased to 195 μmol l^{-1} and continued to increase during the senescent phase of the culture (days 17.0–21.5) to 245 μmol l^{-1}. Bulk water viscosity showed some increase (0.905 mm^2 s^{-1} to 0.910 mm^2 s^{-1}) during the exponential growth phase between days 1.5 and 7.0, when the chlorophyll concentration increased (Figure 11). A further increase in viscosity

occurred between days 7 and 13 (increase to 0.915 mm^2 s^{-1}), however, the range of measured viscosity values was very small (0.905 mm^2 s^{-1}–0.915 mm^2 s^{-1}) and the standard deviation large compared to the small range of values ($\pm$0.0018–0.0082 mm^2 s^{-1}).

[33] No apparent co-variation between the total bacteria concentration and BRT was evident. The total bacteria number per ml in the tank water increased between days 1.5 and 5.5 from 3.4 $\times$ 10^6 to 9.3 $\times$ 10^6 cells ml^{-1}, followed by a decrease between days 6.5 and 8.5 to 1.2 $\times$ 10^6 cells ml^{-1}. From day 9.5 to day 13.5, the total bacteria

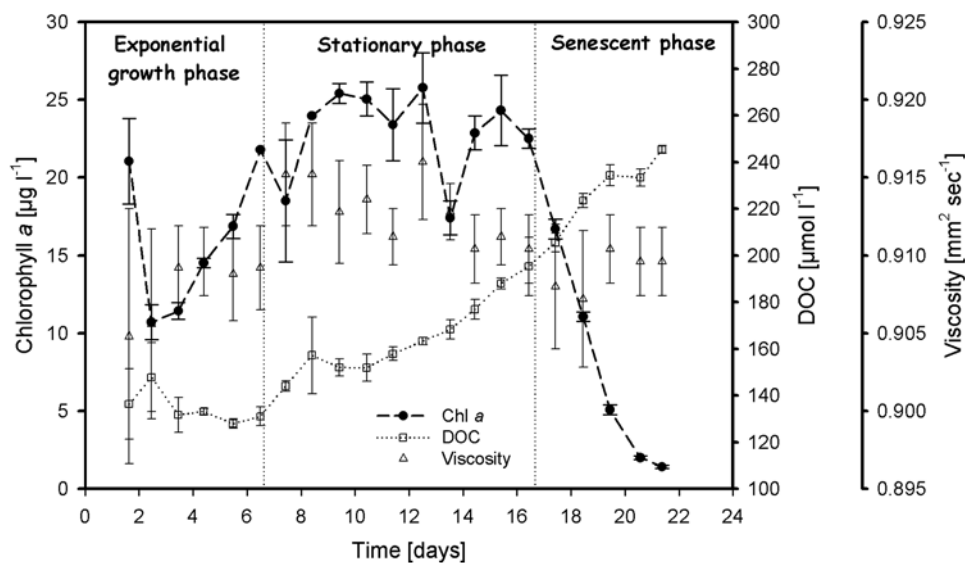**Figure 11.** Changes in chlorophyll *a* concentration, DOC and viscosity with time for the *Cylindrotheca closterium* growth experiment. DOC error bars: $\pm$1.4–16.4 μmol l^{-1}, chlorophyll error bars $\pm$0.1–2.7 μg l^{-1}; viscosity error bars: $\pm$0.0018–0.0082 mm^2 s^{-1}. The vertical dotted lines indicate changes from exponential to stationary to senescent growth phases.
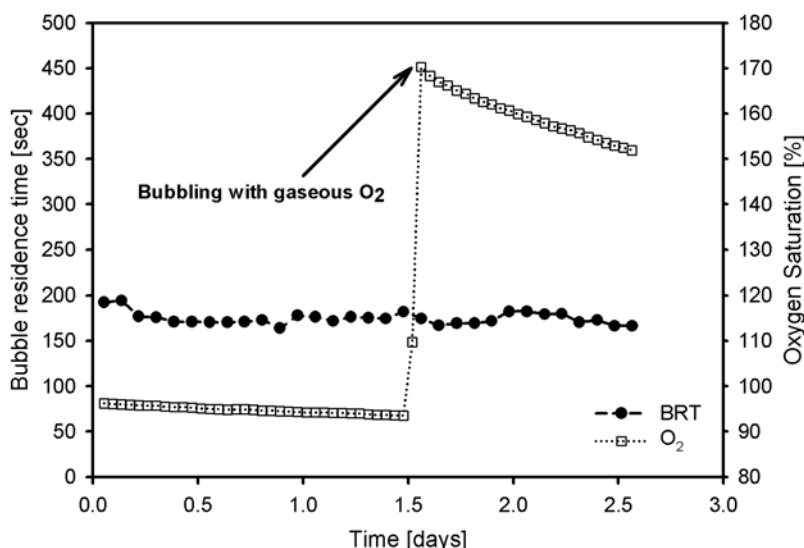
Figure 12. Changes in bubble residence time and oxygen saturation during the control saturation experiment using deionized water.

number increased to 5.5×10^6 cells ml^{-1}. Between days 15.5 and 18.5, a further increase to 9.8×10^6 cells ml^{-1} was followed by another decline (days 19.5 and 20.5) to 3.6×10^6 cells ml^{-1}. The average standard deviation of total bacteria counts was $\sim\pm25\%$.

3.3. Oxygen Supersaturation of Deionized Water

[34] Results from the phytoplankton growth experiments described in the previous sections suggest that the main influence on BRT appears to be the degree of oxygen saturation of the water as a result of phytoplankton photosynthesis. The amount of organic exudates seem to have little or no direct effect on BRT as no correlation was evident between DOC concentration and BRT. To verify the influence of oxygen saturation on BRT, the oxygen saturation of water in the absence of growing phytoplankton was physically manipulated. The bubbling of deionized water with pure oxygen for 2 min on day 1.5 resulted in an oxygen supersaturation of 170% (Figure 12), which then gradually declined over the following 2 days. However, no significant change in BRT occurred, while the water was highly supersaturated with oxygen and average BRT remained at approximately 180 s throughout the experiment.

3.4. Model Dissolved Organic Substance–Xanthan Gum

[35] As shown by the results of the previous experiment, oxygen supersaturation on its own was not the dominant factor causing the observed increases in BRT during the phytoplankton growth experiments with a natural phytoplankton population from Kiel Firth water and a *Cylindrotheca closterium* culture. Therefore it was investigated whether deionized water artificially enriched with a polysaccharide compound could have (i) an effect on the bulk water viscosity and (ii) an effect on BRT. Additionally, both oxygen saturation and concentration of the model polysaccharide were enhanced and the effect on BRT investigated.

[36] The average BRT of deionized water was approximately 140 s, while oxygen saturation gradually increased from 55% to 70% within the first 4.5 days of the experiment

(Figure 13). Kinematic viscosity was 0.868 mm^2 s^{-1}. With the addition of Xanthan Gum to a concentration of 0.008 g l^{-1} on day 4.6, kinematic viscosity increased slightly to 0.900 mm^2 s^{-1}, however, no detectable increase in BRT occurred. On day 5.68, oxygen saturation was increased by bubbling with oxygen from a pressure bottle to 142%, however, BRT showed only a very slight increase to 160 s. The addition of Xanthan Gum to a concentration of 0.08 g l^{-1} on day 5.72 however resulted in an increase in viscosity to 1.272 mm^2 s^{-1} and an increase in BRT to ~ 280 s. For the remaining period of the experiment, BRT, oxygen saturation as well as bulk water viscosity gradually declined.

4. Discussion

4.1. Air Bubble Residence Time in Relation to the Phytoplankton Growth Related Parameters Chlorophyll Concentration and Oxygen Saturation

[37] A significant correlation was found between chlorophyll concentration, oxygen saturation and bubble residence time for both phytoplankton growth experiments. During both experiments BRT increased simultaneously with increasing chlorophyll concentration and thus, increasing oxygen saturation. However, the experiments differ significantly with respect to the order of magnitude of initial and maximum chlorophyll concentration, oxygen saturation and BRT, as is summarized in Table 1. The maximum chlorophyll concentrations reached in both growth experiments were high in comparison to those typically measured in coastal waters. *Osterroth et al.* [1985] reported chlorophyll *a* concentrations during the spring bloom in Kiel Bight of 1982 to have reached $5-17$ μg l^{-1} and during autumn blooms, chlorophyll *a* ranged between $10-20$ μg l^{-1}. However, in highly eutrophic regions of the Baltic Sea, mean levels during spring 2004 averaged around 114 μg l^{-1} [*Schumann et al.*, 2005].

[38] Despite an initial lower chlorophyll concentration, higher maximum chlorophyll concentrations, oxygen saturation and BRT values were reached during the Kiel Firth water experiment than during the experiment with the
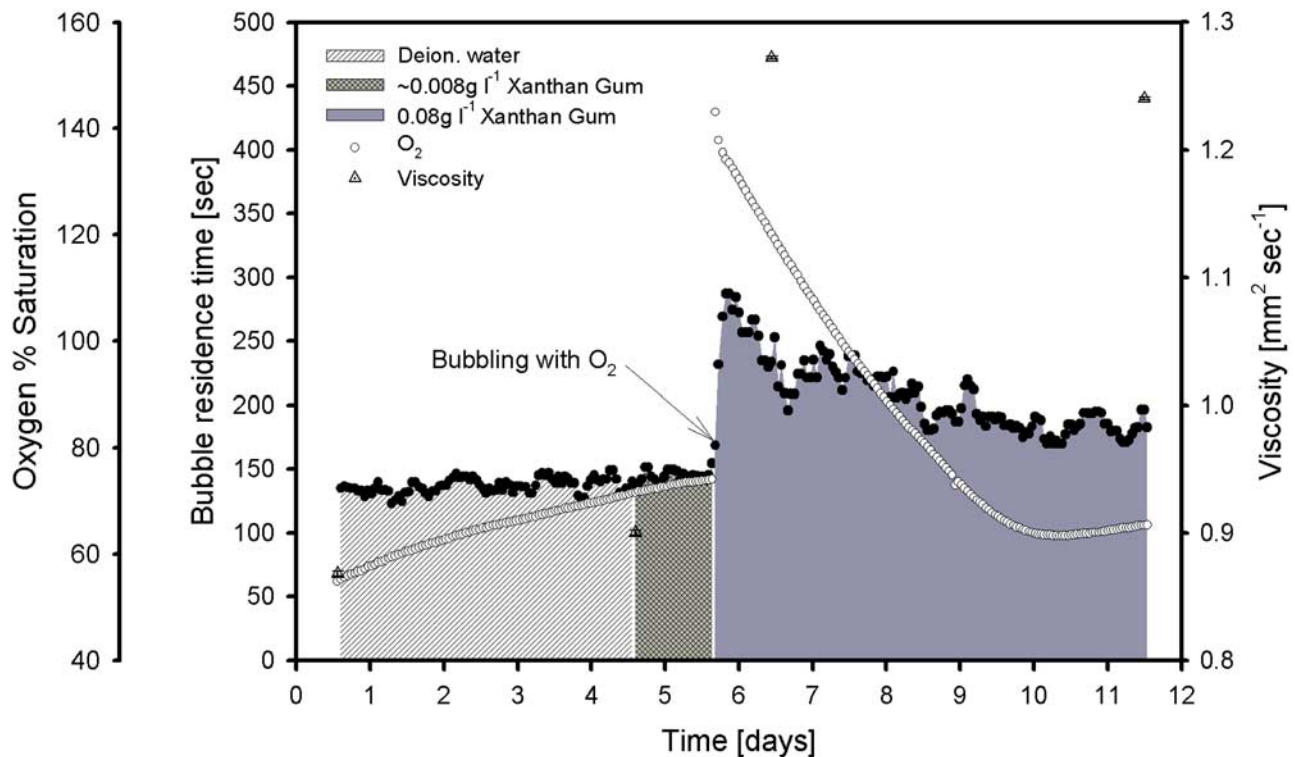
Figure 13. Changes in bubble residence time (black symbols), oxygen saturation and viscosity with time for different concentrations of Xanthan Gum and oxygen saturation.

culture of *Cylindrotheca closterium*. Reasons for the variation in the maxima of these parameters may be explained by the different species compositions for the two experiments.

[39] The close covariation between chlorophyll concentration and BRT for both growth experiments and the strong correlation between chlorophyll concentration and BRT for the *Cylindrotheca closterium* experiment suggest that increases in BRT may be linked to increases in the number of particles present in the tank system. However, data from other phytoplankton growth experiments using the tank system (not included here) have shown that despite high chlorophyll levels of up to 70 μg l^{-1}, no major change in BRT occurred if the water remained undersaturated with respect to oxygen [*Kuhnhenn-Dauben*, 2005]. Thus it is likely that the increasing particle concentrations represented by increases in chlorophyll concentration were a co-factor causing increased BRT, possibly by means of a reduction in bubble rise velocity as has been described by *Thorpe* [1982] and *Patro et al.* [2001] via their accumulation on the surfaces of the bubbles [*Kepkay*, 1994; *Slauenwhite and Johnson*, 1996; *Patro et al.*, 2001].

[40] It is also possible that the phytoplankton were acting as bubble nucleation sites and when the tank was supersaturated with respect to oxygen, a large number of small bubbles with low rise velocities may have formed about the phytoplankton particles, giving rise to the longer BRTs observed during the growth experiments. This may also be the reason why no increases in BRT were observed in the absence of phytoplankton particles during the oxygen supersaturation control experiment with deionized water.

[41] The data from the two growth experiments show that a certain threshold in oxygen saturation must be reached before major changes in BRT become apparent (Figures 4 and 8); this threshold being around 110%. A similar saturation threshold was reported by *Bowyer* [1992] and *Keeling* [1993] to be linked to the dissolution of small bubbles, which is in turn dependent on the level of gas saturation and its influence on the stable existence, growth

Table 1. Initial (Beginning of Growth Phase) and Maximum (Following Growth Phase) Chlorophyll *a* Concentration, BRT and Oxygen Saturation for Both Growth Experiments

	Kiel Firth Water	*Cylindrotheca Closterium*
Initial chl *a* concentration, μg l^{-1}	1.7 (day 0.5)	10.7 (day 2.5)
Maximum chl *a* concentration, μg l^{-1}	33.6 (day 5.5)	25.5 (day 9.5)
Initial BRT, s	~400 (day 0.5)	219 (day 2.5)
Maximum BRT, s	620 (day 5.5)	400 (day 9.5)
Initial oxygen saturation, %	102.8 (day 0.5)	104 (day 2.5)
Maximum oxygen saturation, %	190 (day 5.5)	150 (day 9.5)

Table 2. Total Gas Pressure of Tank Water, Laplace Pressure and Total Bubble Pressure for Bubbles at and Close to Resonance[a]

Oxygen Saturation, %	Pressure, Pa	
100	101325	
110	103352	
120	105378	
130	107405	
140	109431	
160	113484	
180	117537	
190	119564	
Laplace Pressure, Pa		
r = 20 μm	r = 30 μm	r = 40 μm
7300	4866	3650
Total Bubble Pressure, Pa		
118710	116275	115060

[a]Total bubble pressure was calculated after *Woolf and Thorpe* [1991]. The total gas pressure was calculated estimating a constant partial pressure of nitrogen of 0.8 atmospheres. r is the bubble radius.

or disappearance of bubbles in near surface waters [*Ramsey*, 1962; *Harris and Detsch*, 1991]. Bubbles lose gas by dissolution when the internal bubble pressure exceeds the total gas pressure in the water and they tend to gain gas when the opposite is true. *Bowyer* [1992] and *Stramska et al.* [1990] report that for increasing saturation of water with dissolved gas (in this case, oxygen), the smallest bubbles that can exist show a tendency toward a lower radius. Table 2 provides an estimate of the theoretical gas pressure in the tank water with increasing oxygen saturation as well as the Laplace pressures and total bubble pressures of bubbles at and close to resonance for a frequency of 120 kHz [*Vagle and Farmer*, 1992] calculated after *Woolf and Thorpe* [1991]:

$$\Sigma p_b = P_a + \rho_w \cdot g \cdot z + 2\sigma/r \qquad (2)$$

where p_b is the total pressure inside the bubble, P_a is the atmospheric pressure (101325 Pa), ρ_w is the density of seawater ($\sim$1028 kg m^{-3}), g = 9.81 m s^{-2}, z is the maximum depth of bubble plume (1 m), σ is the bubble surface tension ($\sim$73 mN m^{-1}) and r is the bubble radius.

[42] This calculation was made assuming constant nitrogen saturation in the tank water although it is possible that the nitrogen saturation also changed during phytoplankton growth. Even at high oxygen supersaturations of 160–180%, resonant bubbles (radius = 20 μm for 120 kHz) and those close to resonance (r = 15–40 μm) were still not in equilibrium with the surrounding water, a condition that *Woolf and Thorpe* [1991] have reported as normal due to hydrostatic pressure and surface curvature of bubbles. As the total gas pressure in the bubbles at 1 m depth exceeds the gas pressure of the surrounding water, diffusion of gas should still take place from the bubbles into the water. However, at first, the process is decelerated with increasing oxygen saturation, thus bubbles dissolve more slowly, resulting in longer residence times. Secondly, some gases compressed inside a bubble are much more soluble than others (e.g., CO_2) and will equilibrate more rapidly,

decelerating the net flux of gas [*Woolf and Thorpe*, 1991] and thus bubble dissolution. For microbubbles in deeper layers, dissolution may occur much faster (e.g., z = 1.5 m), whereas microbubbles in the near surface layer may dissolve even more slowly (e.g., z = 0.5 m). As the bubbles rise through the water column, the decrease in hydrostatic pressure will also lead to a reduction in total bubble pressure and thus decelerate dissolution [*Bowyer and Woolf*, 2004].

[43] In both microalgal growth experiments there were periods when phytoplankton photosynthesis during light phases increased the oxygen saturation and respiration during dark phases decreased the oxygen saturation in the tank water. These periods of increase and decrease in O_2 saturation coincided with similar relative changes in BRT. This coincidence was very clearly apparent during most of the growth experiment with *Cylindrotheca closterium* but less apparent during the experiment with Kiel Firth water with coincidence only noticeable during days 1.5–4.5 and days 8.5–11.0 (Figure 4). Assuming that oxygen saturation was the dominant factor responsible for the observed changes in BRT during light and dark phase in the *Cylindrotheca closterium* growth experiment, it is perhaps surprising that these differences are much less obvious throughout the Kiel Firth water experiment. One explanation for this could be the considerably higher oxygen saturations reached during the Kiel Firth water experiment (up to 190%) compared to the *Cylindrotheca closterium* experiment (up to 150%). This would imply that oxygen saturation had reached a level between day 4.5 and 8.5 where even during dark phases the oxygen saturation was high enough for the smallest bubbles not to attain dissolution. Another factor that may account for the less obvious light and dark changes in BRT during the chlorophyll maximum of the Kiel Firth water experiment is the difference in salinity of the water used in both experiments (31 for *Cylindrotheca closterium* culture water and 16 for Kiel Firth water). The growth of the diatom *Cylindrotheca closterium* in higher salinity water may have resulted in slightly different (i.e., smaller) bubble sizes as a result of reduced coalescence [*Craig et al.*, 1993; *Wang and Monahan*, 1995]. In turn, smaller bubbles may have been more sensitive to the degree of oxygen saturation compared to slightly larger bubbles and therefore they may have dissolved earlier, especially when the oxygen saturation was slightly lower. As the set-up of the tank system and the methodology of BRT determination did not allow for bubbles to be optically monitored, information on their abundance, size and dissolution is unavailable.

[44] The experimental data from the phytoplankton growth experiments as well as the argument for the importance of gas/oxygen saturation with respect to bubble dissolution and bubble growth supported by other authors at first suggests oxygen saturation as the main factor responsible for the observed increases and decreases in BRT over a phytoplankton growth period.

[45] However, supersaturating deionized water with oxygen from a pressurized bottle showed that oxygen saturation alone may not have been the main cause of the observed changes in BRT during phytoplankton growth. This artificial supersaturation did not coincide with a change in BRT, an unexpected result, as *Stramska et al.* [1990] and *Asher and Farley* [1995] have shown that increasing concentra-

tions of dissolved gases resulted in higher bubble concentrations. However, the nitrogen saturation was not measured in our experiments and it may be that bubbling the tank water with oxygen resulted in most of the dissolved nitrogen being stripped out. The oxygen would thus have only replaced the nitrogen and not increased the total gas pressure of the tank water. Considering that bubble residence time is a function of the total gas pressure [*Woolf and Thorpe*, 1991], this could be an explanation why bubbling with oxygen did not result in increasing BRT. From the phytoplankton growth experiments it follows that sufficient saturation of water with oxygen is a precondition for major changes in BRT to occur as a result of the net diffusive flux of gases across the air bubble- water interface. This flux is proportional to the concentration gradient of a gas between water and the overlying air [*Woolf and Thorpe*, 1991]. Also *Bowyer* [1992] stated that for a certain degree of gas saturation, the initial radius of a bubble is important with respect to its lifetime. If this initial radius is below a certain threshold, the bubble will collapse immediately after formation as a result of the Laplace pressure. In order for bubbles not to dissolve immediately after their formation but to grow, gas must diffuse into the bubble from the surrounding water [*Bowyer*, 1992]. As the exchange of gas is always from high to low concentration, gas, respectively oxygen will diffuse into the bubble only if the water is supersaturated with oxygen. This will then result in stabilization and growth of the bubble, enabling it to reside in the water for a longer period of time. However, as stated by *Bowyer and Woolf* [2004] bubble gasdynamics are non-linear, and interdependencies exist between the exchange of gas across a bubble's surface, its resulting size and further gas exchange.

4.2. Dissolved Organic Material

[46] A consistent covariation between BRT and DOC concentration was not shown in either phytoplankton growth experiments. For both growth experiments, DOC increased with increasing chlorophyll concentration, but the concentrations and rates of increase became significantly higher during the stationary and senescent phases. These results generally agree with the findings of other studies conducted by *Lee and Wakeham* [1989], *Williams* [1990], and *Norrman et al.* [1995], who also reported that DOC accumulation rates were higher during the senescent phase of a phytoplankton bloom compared to the exponential growth phase. The increase of DOC concentration during the senescent phase of the phytoplankton growth experiments may be attributed to nutrient stress as already discussed by *Jensen* [1984] and *Williams* [1990]. Bacterial induced cell lysis of phytoplankton cells during the senescent phase, described by *Imai et al.* [1993] as well as bacterial release of DOC from capsular material [*Stoderegger and Herndl*, 1998] were likely to have contributed to the higher DOC levels measured during senescent phases. However, despite the lack of a covariation between DOC concentration and BRT, it is highly likely that some fractions of the DOM released by phytoplankton throughout the growth experiments, influenced BRT to some extent. Diatoms can release large amounts of polysaccharides during all stages of growth, [*Hoagland et al.*, 1993; *Zutic et al.*, 1981; *Mopper et al.*, 1995; *Zhou et al.*, 1998] and some of these compounds are known to be surface active. In his investigations of algal mucilages, *Leppard* [1995] showed that the chemical composition determines the surface activity of DOM. Studies by *Leppard* [1995] and *Lancelot* [1995] indicate that a large fraction of the DOC produced by phytoplankton are reactive, surface active polysaccharides. It is highly likely that the chemical composition of DOC as well as its surface activity varies on a diurnal scale [*Shinomura et al.*, 2005] as well as over the growth phase of a phytoplankton culture [*Metaxatos et al.*, 2003] and additionally, is species specific [*Mingazzini et al.*, 1995; *Metaxatos et al.*, 2003]. This may also have been the case during the phytoplankton growth experiments with Kiel Firth water and *Cylindrotheca closterium*. It is possible, that during light periods, the DOC produced by the phytoplankton was more surface active than during dark periods, thus contributing to the diurnal variation in BRT. Furthermore, the DOC produced during the senescent phase may have been less surface active than during the exponential growth phase and combined with decreasing oxygen saturation may have led to a reduction in BRT, even though the overall DOC concentration increased during the later phases of the culture. The presence of organic surfactants released by phytoplankton has a significant influence on the state of the bubbles' surfaces, affecting the diffusion of gas and particles to and from the bubbles, as well as their rise speed and their surface tension [*Detwiler*, 1979; *Woolf and Thorpe*, 1991; *Thorpe et al.*, 1992; *Slauenwhite and Johnson*, 1996; *Leifer et al.*, 2000]. This could explain why initial BRT at the beginning of the phytoplankton growth experiments were higher than BRT in the deionized water, as bubbles in deionized water rose like clean bubbles [*Woolf and Thorpe*, 1991], whereas bubbles in the water containing phytoplankton rose like dirty bubbles. Unfortunately, rise speed of bubbles could not be measured with the experimental set-up. However, *Thorpe* [1982] states that the rise speeds of dirty bubbles of r $\leq$ 80 μm are closely proportional to r^2. Thus a 20 μm bubble would rise approximately 0.04 cm s^{-1} and take 2500 s to rise to the tank surface from a depth of 1m. As BRTs in the phytoplankton growth experiments are much shorter, dissolution must be the dominant process.

4.3. Bulk Water- and Surface Shear Viscosity

[47] The range of bulk water viscosity values showed differences between the two growth experiments, which mainly resulted from the difference in water temperature and salinity. However, species specific differences may have also influenced the viscosity such as the nature of the organic material released by phytoplankton cells as well as the density and nature of the cells themselves. Species specific differences of bulk water viscosity also with respect to different water temperatures have been identified by *Myklestad* [1972] and *Petkov and Bratkova* [1996]. However, as no significant change in bulk water viscosity was detected over the duration of the Kiel Firth water experiment, and also not with certainty over the growth phase of the *Cylindrotheca closterium* experiment, it is unlikely that this factor had a major influence on BRT.

[48] The experiment with the model polysaccharide Xanthan Gum showed that a large change in bulk water viscosity can affect BRT. The polysaccharide concentrations used during the experiment were however highly exagger-

ated compared to natural DOM concentrations in seawater. This suggests that the concentrations of organic material produced in the phytoplankton growth experiments were too low to have a measurable effect on bulk water viscosity. Investigations recently carried out by *Kuhnhenn et al.* [2006] have shown that some phytoplankton species can have a significant influence on the surface shear viscosity. They showed that the diatom *Cylindrotheca closterium*, a species which occurred in both growth experiments included in this study, had a marked effect on measured surface shear viscosity whereas a number of other diatom species tested showed no effect on surface shear viscosity. *Kuhnhenn et al.* [2006] found that *Cylindrotheca closterium* particularly influenced measured surface shear viscosity during the exponential growth phase of cultures. This supports the assumption made earlier that the surface-active nature of organic material released by phytoplankton varies over different stages of the growth curve. It also corresponds well with the strong increase in BRT, which occurred during the exponential growth phase for both phytoplankton growth experiments.

[49] Unfortunately, our experimental set-up did not provide a direct way of investigating the influence of surface shear viscosity on BRT. However, the relationship between surface shear viscosity and BRT could be explained as follows. Increased surface shear viscosity could have led to a decrease in bubble coalescence as a result of the mechanical resistance at the bubbles surface. This in turn would have resulted in longer residence times at high oxygen supersaturation (when small bubbles did not dissolve immediately), as smaller bubbles rise more slowly than larger bubbles. The formation of a rigid cap on the surface of the bubbles, resulting from compact mechanical structures as described by *Dukhin et al.* [1998] would have led to essential deceleration of the bubble rise velocities, thus contributing to increasing BRT. Furthermore, the formation of polymer networks on the surface of the bubbles possibly reduced the diffusion of gas from bubbles into the surrounding water.

5. Conclusions

[50] The results of this study have shown that phytoplankton growth can have a significant influence on air bubble residence time in seawater. The parameter that was directly influenced by phytoplankton photosynthesis and that was identified as a necessary precondition for major changes of BRT was the oxygen saturation of the water. Furthermore, during the course of growth experiments, changes in BRT closely corresponded with the photosynthesis-respiration (light-dark cycle) induced changes in oxygen saturation, for oxygen saturations below 150%, emphasizing the dependency of BRT on the oxygen saturation of the water. The results of the saturation experiments with deionized water however indicate that oxygen supersaturation on its own in a non biological, particle-free system does not show any significant influence on BRT. Therefore it can be concluded, that a combination of factors including oxygen saturation as well as phytoplankton exudates were responsible for the increases and decreases in BRT observed during the phytoplankton growth experi-

ments. The results from these experiments suggest that a certain threshold in oxygen saturation has to be achieved for major changes in BRT to occur, so that small bubbles do not dissolve immediately after their formation but can remain in the water for longer periods of time. This threshold was found to be between 110–140% oxygen saturation and is considered to be specific with respect to the species composition of the phytoplankton.

[51] Additionally, the actual phytoplankton cells and the organic material produced during blooms influence BRT, most likely through a change in bubble rise velocity and gas diffusion. Taking into account the results obtained by other authors, it is highly likely that some surface active material was produced during these experiments although it was not possible to directly characterize these compounds.

Notation

α	level of significance
BRT	bubble residence time, s
dB	Decibel
DOC	dissolved organic carbon, μmol l^{-1}
DOM	dissolved organic material
FWG	Forschungsanstalt der Bundeswehr für Wasserschall und Geophysik
g	acceleration due to gravity, m s^{-2}
K	capillary constant
kHz	kilo Hertz
n	number of data points
ν	kinematic viscosity, mm^2 s^{-1}
p	P value
P_a	atmospheric pressure, Pa
p_b	total bubble pressure, Pa
r	correlation coefficient
r	bubble radius, μm
ρ_w	density of water, kg m^{-3}
sp.	Species
σ	surface tension, mN m^{-1}
t	time, s
z	depth, m

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