



# Using Avrami equation in the studies on changes in granulometric composition of algal suspension

Magdalena Kuśnierz · Janusz Łomotowski

Received: 18 June 2014 / Revised: 6 April 2015 / Accepted: 17 April 2015 / Published online: 29 April 2015  
© The Author(s) 2015. This article is published with open access at Springerlink.com

**Abstract** In recent years, it has been recognized that the laser diffraction gives valuable information on particle size distribution for all types of dry inorganic or even organic materials. With use of the laser diffraction and the laser granulometer, this paper presents the changes occurring in the granulometric distribution of algal agglomerates and the changes in values of percentiles 10, 50 and 90%, determined basing on volume distribution. While assessing the granulometric composition, the existence of a proportional relationship between the diameter values corresponding to the percentile of 10, 50 and 90% was observed. What is more, the obtained results give insight into the possibility of application of the general Avrami equation to describe the granulometric composition of the algal suspension through the analogy of crystals formation from saturated solutions. The analysis shows that the model described by the modified Avrami equation adequately matched the regression to the experimental data on the granulometric composition of algal suspensions. The values

of the correlation coefficients were close to 1, which proves that the regression model explained nearly all cases by the dependent variable  $V_i = F(d_i)$ .

**Keywords** Avrami equation · Laser granulometer · Algal suspensions · Particle size distribution PSD

## Introduction

Human waste materials production, plant and animal materials, erosion minerals, organic and inorganic compounds affect the surface water quality. One of the symptoms of the ecological imbalance of surface water is the change of water colour caused by massive growth of algae. During seasonal water blooms, the algae cover large areas of open reservoirs forming multi-dispersive suspension systems. It is relatively hard to rapidly describe their particle size and shape in proportion to their natural state without the use of precise microscopes connected with image analysers (Rolinski et al., 2013). As for now size-related changes of algal biovolume are still estimated on the base of cell shape and calculated using appropriate for the geometric shape formula (Morin et al., 2008; Sitoki et al., 2012; Kaggwa et al., 2013; Mazur-Marzec et al., 2013). The sizes of individual algal cells may vary by up to 100  $\mu\text{m}$  (Stoyneva et al., 2007), and their shapes may take different forms. However, microscopy technique used for biovolume calculations may possess several limitations. Regarding detection, inaccurate evaluation of cell shape or size and

---

Handling editor: Judit Padisák

---

M. Kuśnierz (✉) · J. Łomotowski  
Institute of Environmental Engineering, Wrocław  
University of Environmental and Life Sciences, Plac  
Grunwaldzki 24, 50-363 Wrocław, Poland  
e-mail: magdalena.kusnierz@up.wroc.pl

J. Łomotowski  
e-mail: janusz.lomotowski@up.wroc.pl

the application of an incorrect formula for the calculation of cell volume or the lack of a relevant calculation formula in the case of new, unidentified species constitute the restrictions of this approach.

Algal cell size, biovolume, chlorophyll-a, or growth rate parameter are necessary to produce forecasts of algal bloom dynamics and determining the trophic interactions within water quality (Cloot & Pieterse, 1999; Flynn, 2003; Morin et al., 2008; Mao et al., 2009). The change in the algal size structure can be presented as the surface area to volume ratio ( $S/V$ ) (Dokulil et al., 2007; Stoyneva et al., 2007), percentage chlorophyll-a contribution to total biovolume (Dokulil et al., 2007), or calculated as total biovolume/total density (Souza et al., 2008). In many studies cell size/algal growth rate relationships are sought (Morin et al., 2008). Growth of algae is influenced by a variety of biological and non-biological factors, and the ecosystem models incorporates such factors as transparency, temperature, pH, BOD, electrolytic conductivity nitrate and phosphate (Kozak, 2005; Souza et al., 2008; Mao et al., 2009; Lehman et al., 2010; Yao et al., 2011; Lyche-Solheim et al., 2013).

The algae structure and biomass is hardly accessible by one method alone. Wollschläger et al. (2015) presented overview of methods based on optical and molecular biological approaches which enable analysis of phytoplankton. Currently, it is possible to evaluate the particle size distribution (PSD) of organic suspensions with use of a laser granulometer (Burszta-Adamiak et al., 2010). Laser granulometer does not allow for particle shapes assessment, but it shows the changes occurring in the suspensions system in a rapid and reproducible manner. The differences in sizes of individual particles obtained as a result of granulometric tests may be presented in the form of various variability functions, depending on the substitute mean diameter of the particles ( $d_i$ ) (Burszta-Adamiak et al., 2012). The PSD is generally accepted as an important physical property for water and wastewater characterization (Li et al., 2004; Wu et al., 2009; García-Mesa et al. 2010). This method is rarely applied in studies on phytoplankton, although Cho et al. (2010) and Xiao et al. (2015) have incorporated PSD for organic sediment assessment. Organic sediments are ubiquitous in aquatic systems and can contain orders of magnitude higher indicator organisms than the overlying water (Droppo et al., 2011) and they physically behave similarly as algae.

Data obtained from laser granulometer do not involve shape nor particle character description nevertheless authors of this study assumed that it could be useful method for the size description of small plant and animal organisms, which float or drift in great numbers. Moreover, the authors found that information on the obtained cumulative PSD  $F(d_i)$  may constitute a basis for the analysis of the process of changes occurring in the growth of the particles creating the suspension. The aim of this study was to investigate whether the Avrami equation describing the kinetics of the formation of crystals in a saturated solution can be used as a modified approach to uneven growth of algae particles characterised by PSD derived from laser granulometer. Measurements of the increases in crystal volume or mass during crystallization with use of a laser granulometer were also taken by Judge et al. (1995) quot. Bluma et al. (2009).

### Crystallization process

The creation of algal agglomerates may be initiated by single algal cells creating colonies and producing mucus that increases their adhesion capability at the same time improving the adhesion to the subsequent cells. The extent of changes in the size of algal agglomerates can be linked to the pace of growth of individual grains of the substances remaining in a dissolved state during the crystallization process.

The crystallization process is based on the formation of crystallization nuclei understood as material points of the solid phase, followed by the growth of nuclei and the creation of a super-particular structure in the given system in the time  $t$ . It is worth noting that the differentiation and separation of the nucleation process (the formation of nuclei) from the nucleic growth process still remains a subject of research (Khalil et al., 2012). So far, crystallization kinetics has been widely studied in research on polymers (Lu et al., 1998; Martins & Cruz Pinto, 2002; Krumme et al., 2004), alloys (Vázquez et al., 2000; Liu et al., 2002), kaolinite (Fiore et al., 2011), oil-in-water emulsion (Khalil et al., 2012) or even milk fat fraction and chocolate (Herrera et al., 1999; Fernandes et al., 2013). The general Avrami equation was applied in the process of crystals formation of any shape and uses substitute spherical diameters. Avrami equation is

taking into consideration a constant nucleation rate and constant linear growth in 1–3 dimensions (Lorenzo et al., 2007). The Avrami equation was developed to describe isothermal conditions of crystallization processes (Supaphol, 2001; Krumme et al., 2004) but as it turns out it can be also applied to the description of non-isothermal processes and analytical data (Di Lorenzo & Silvestre, 1999; Martin, 2010). According to Málek (1995), the description of non-isothermal processes is possible only in a limited number of special cases. What is more, for studies on the crystallization of non-isothermal and isothermal conditions thermal analysis and techniques such as DSC (Differential Scanning Calorimetry) have become more popular (Lorenzo et al., 2007; Ovono Ovono et al., 2012). According to Khalil et al. (2012) and Stelzer et al. (2013), tests on the formation of crystals can be also carried out with use of light transmittance, polarized light microscopy, viscosimetry, diffusive light scattering, time-resolved synchrotron X-ray diffraction, ultrasound velocity measurements and laser-polarized light turbidimetry.

## Materials and methods

### Sampling

Studies on changes in the granulometric composition of the algal suspension were conducted since March 2007 until March 2009 on water samples collected from an accurately prepared laboratory bench (a specially made aquarium). Waters used to supply the laboratory bench originated mainly from the pond located in the Stanisław Tołpa memorial park (51°7′11.46″N, 17°3′16.87″E) in the City Centre district of Wrocław (Poland). This small park pond of the surface area of 5600 m<sup>2</sup> is a relic of a branch of the Odra river. The flora of blue algae and algae existing in the pond was analysed in the years 2001–2010, among others by Richter (2013) and Richter & Matuła (2012).

Water from the pond, in the amount of 10 dm<sup>3</sup>, was collected in March during the phase of invisible algae development. After introduction of the water to the bench and supplementing it with tap water to the volume of 50 dm<sup>3</sup>, cultivation was continued in a controlled way with respect to abiotic factors (lighting, temperature, nutrients) and in an uncontrolled way with respect to biotic factors (competition). Above the

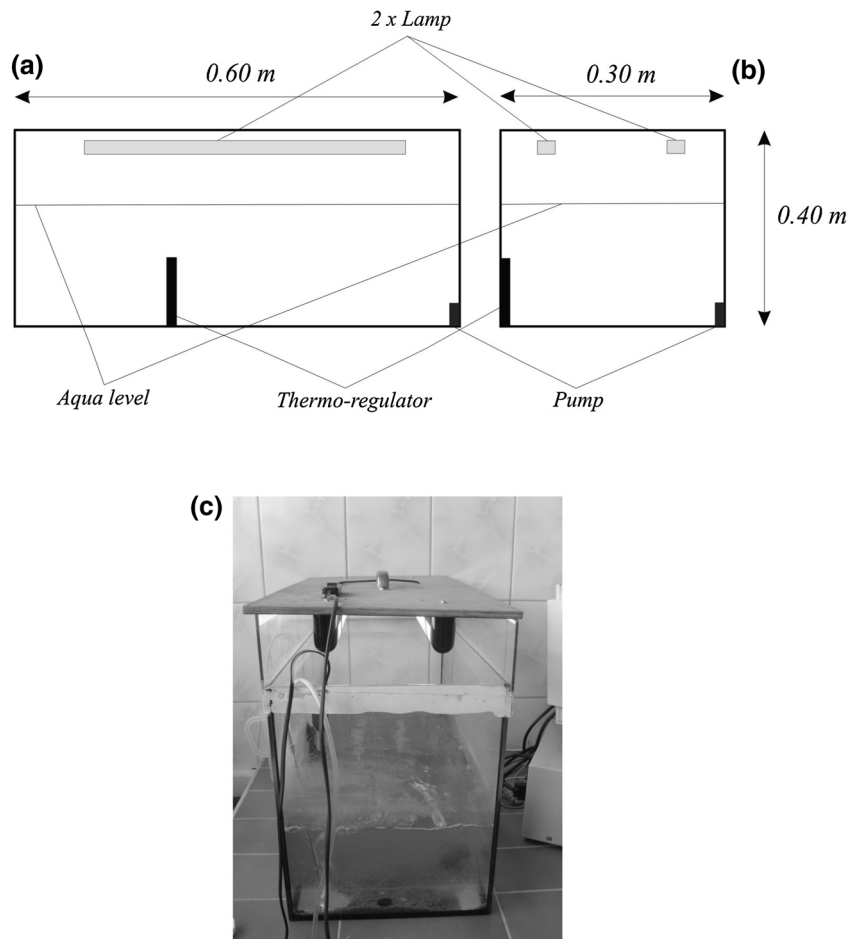
water surface of the tank overhead lighting was installed, with a 12-h cycle of lighting. Constant water temperature was maintained on the level of 22°C. The mixing of water in the tank occurred as a result of movements of inflowing air generated by a pump at defined 93 time intervals set by the programmer. The view of the tank is presented in Fig. 1a–c.

The structure of the algae has been observed through scanning electron microscopy LEO 435 VP. Macroscopic observation revealed biodiversity in species which obstructed identification; however, this fact does not adversely affect the quality of results presented in this article. The performed microscopic analyses of the developing algae demonstrated that the dominant species in the bench were *Bacillariophyceae*: c.f. *Navicula* sp., c.f. *Eumotia* sp., c.f. *Synedra* sp., c.f. *Pinnularia* sp. and *Oscillatoriales*.

### Particle size distribution

The algae were examined using laser granulometer Mastersizer 2000 Malvern Instruments Ltd. with a measurement scope from 0.01 to 2000 μm. This instrument is equipped with an optical system consisting of red and blue light sources, a set of detectors, and a measurement cell. In the measurement cell, particles of substance that remain in the suspension scatter and absorb light rays falling in their direction. Three sets of appropriately placed detectors allow for the measurement of the scattered light intensity nearly in the full range of angles. The central detector enables the identification of large particles, side detectors are used for the determination of micro-suspension size, and reverse detectors identify colloidal particles. Total sample volume for one measurement was about 600–700 dm<sup>3</sup>; however, several samples had to be diluted, as too high a concentration of sample did not allow proper values of laser light obscuration (from 10 to 20%) to be obtained in the measurement cell of the granulometer. If the particles are well dispersed, we measure the scattering from each particles and avoid multiple reflection. Bizi & Baudet (2006) and Bushell (2005) attempted to maintain similar obscuration values in their experiments. Macroscopic observations demonstrated that algae may appear as agglomerated particles and for that reason measurements with stirring were needed. In order to keep the sample suspended, dispersed stirring energy was applied to the sample.

**Fig. 1** Schematic description and the image of the experimental tank; **a** side view, **b** front view, **c** image of the experimental tank in April 2008



Stirring coped with particle–particle and particle–wall collisions and allowed them to be separated. Other laser diffraction measurement uncertainty has been well presented by Sperazza et al. (2004).

The tests were conducted for the optical properties determined basing on the studies by Quirantes & Stewart (2004; 2006). The absorbing properties of algal populations were 0.1 and the refractive index 1.05.

#### Modification of the Avrami equation

For the creation of crystals of any shape and for the application of substitute spherical diameters, the Avrami equation in the form (Todinov, 2000) is used:

$$\phi_t = 1 - \exp\left[-\frac{\pi \times G^3 \times L_z}{3} \times t^4\right], \quad (1)$$

where  $\phi_t$  is the volume share of the crystalline fraction in the solution after time  $t$ ;  $L_z$  is the number of nuclei

from which the crystals are created;  $G$  is the linear pace of crystal growth, linking the crystal diameter  $r$  with the duration of crystallization:

$$r = G \times t. \quad (2)$$

In practice, when developing the results of tests on the precipitation of substances from water solutions, the general Avrami equation is used (IUPAC, 1997):

$$V(t) = 1 - \exp(-k' \times t^{n'}), \quad (3)$$

where  $k'$  and  $n'$  are constant, while  $k'$  depends on the environmental conditions, where the phase transformation occurs, and the exponential  $n'$  is connected with the geometry of the emerging transformation products and may take values from the range [1; 4].

The Avrami equation was introduced in the year 1940 (quot. Yang et al., 2005), basing on the assumption that spherical particles emerge as a result

of the crystallization process. Using the relationship (2) and transforming the Eq. (3) results in:

$$V(d) = 1 - \exp\left(-\frac{2^n \times k}{G^n} \times d^n\right), \quad (4)$$

and after introducing the constant:

$$K = \frac{2^n \times k}{G^n}, \quad (5)$$

then, Eq. (4) takes the form:

$$V(d) = 1 - \exp(-K \times d^n), \quad (6)$$

which shows that the volumetric share of particles of the diameter  $d$  and smaller in the crystalline fraction may be described with use of a relationship analogical to that describing the kinetics of emergence of the crystalline fraction (3).

Equation (6) describes the total curve of the volumetric share of particles of the given diameter  $d$  together with smaller diameter particles with respect to the volume of all particles that exist in the analysed material. In the further sections of the study, the Eq. (6) will be referred to as the modified Avrami equation.

The non-linear estimation module of the Statistica 10 Pl software was applied to determine the empirical regression coefficients described by the Eq. (6). The calculations were performed with use of the least squares method with the Levenberg–Marquardt algorithm. The value of the sum of squares error (SSE) was adopted as the function of user losses, described by the relationship (7):

$$\text{SSE} = \sum_{i=1}^n (x_i - x')^2, \quad (7)$$

where  $x_i$  are independent values observed in the course of analysis, and  $x'$  are corresponding values calculated basing on non-linear regression models.

The accuracy of non-linear regression was evaluated basing on the value of the correlation coefficient.

## Results

The results of the analysis of the granulometric composition of algal suspension in form of the probability distribution function  $F(d_i)$  obtained during the culture growth are presented in Figs. 2, 3 and 4.

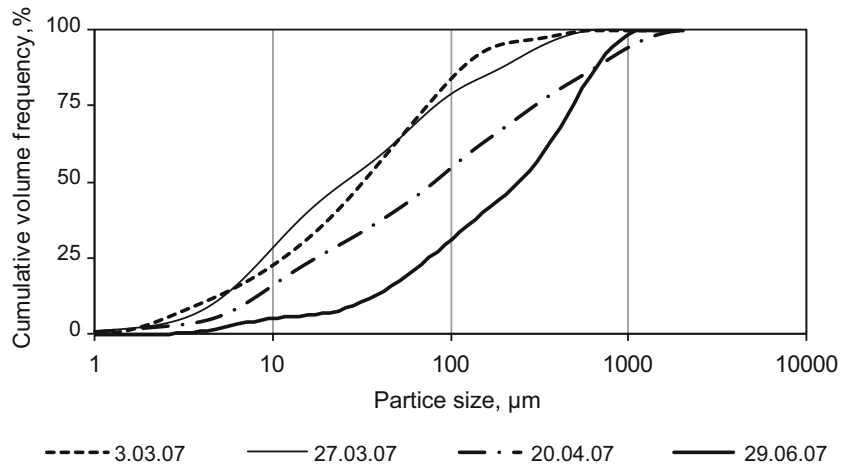
The data obtained during the first months did not offer clear results; however, situation has changed after several months. In the initial period of algal growth, the PSD had a multimodal course, and strong changeability of hydro biotic water components was observed. During this period, particles of suspension in the range 1–1200  $\mu\text{m}$  were identified (Fig. 2). As the experiment continued, a decrease in the share of particles below 10  $\mu\text{m}$  was observed. During the period from September to December 2007, no particles of a size smaller than 10  $\mu\text{m}$  were found in the suspension (Fig. 3), and the distributions were unimodal. Received distribution curves had microscope image confirmation. After 1 year, the share of particles up to 500  $\mu\text{m}$  accounted for less than 20% of the total volume of suspensions (Fig. 4).

Table 1 presents a list of selected values of diameters corresponding to the 10, 50 and 90% percentiles, determined basing on the volume distribution of particles creating the algal suspension. The lowest values of percentiles were noted in the initial period of creation of agglomerates in 2007, and the highest—in the middle of the test period—in October 2008. They reached, respectively, for  $d(0.1) = 235.99 \mu\text{m}$ ;  $d(0.5) = 990.94 \mu\text{m}$ ;  $d(0.9) = 1581.09 \mu\text{m}$ . Additionally, the existence of a proportional relationship between the diameter values corresponding to the percentile of 10, 50 and 90% (denoted respectively by  $d(0.1)$ ,  $d(0.5)$  and  $d(0.9)$ ) was observed. The correlations between the diameter values  $d(0.9)$  and  $d(0.5)$  is presented in Fig. 5. The level of the linear relationship between each of the variables was characterised by Pearson correlation coefficient with the value  $r = 0.954$ .

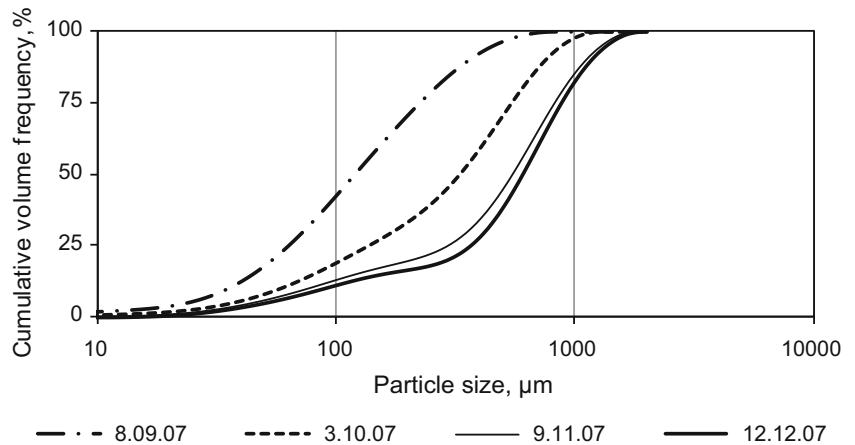
Proportional relationship between  $d(0.1)$ ,  $d(0.5)$  and  $d(0.9)$  is also observed in crystals precipitated from a saturated solution in the course of the crystallization process. Therefore, an attempt to describe the granulometric composition of algal suspensions with Avrami equation was undertaken. The substitution of a linear relationship of the pace of crystal growth, linking the radius of the crystals  $r$  to the crystallization time and the introduction of the constant  $K$  results in a modification of the Avrami Eq. (6).

Crystallization incorporates homogeneous and heterogeneous nucleation which involves the creation of a stable nucleus whose size and shape is governed by molecular interactions. The crystallization theory

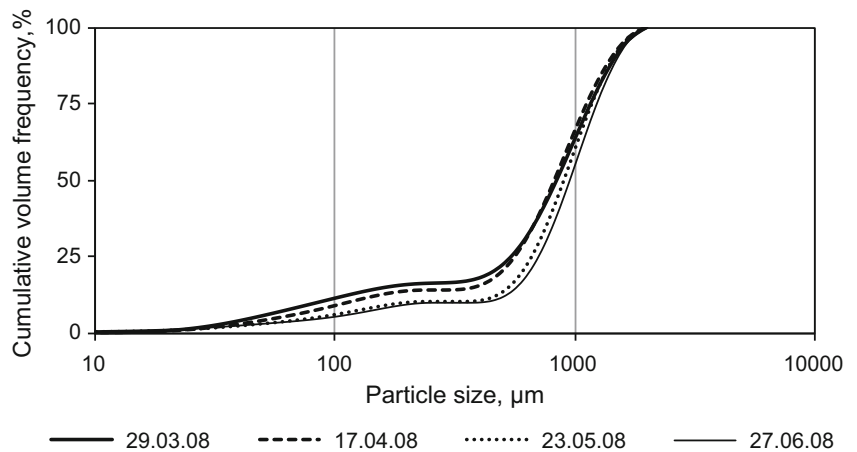
**Fig. 2** Functions  $F(d_i)$  of the suspensions determined for samples of water collected from the tank during the period March–June 2007



**Fig. 3** Functions  $F(d_i)$  of the suspensions determined for samples of water collected from the tank during the period September–December 2007



**Fig. 4** Functions  $F(d_i)$  of the suspensions determined for samples of water collected from the tank during the period March–June 2008

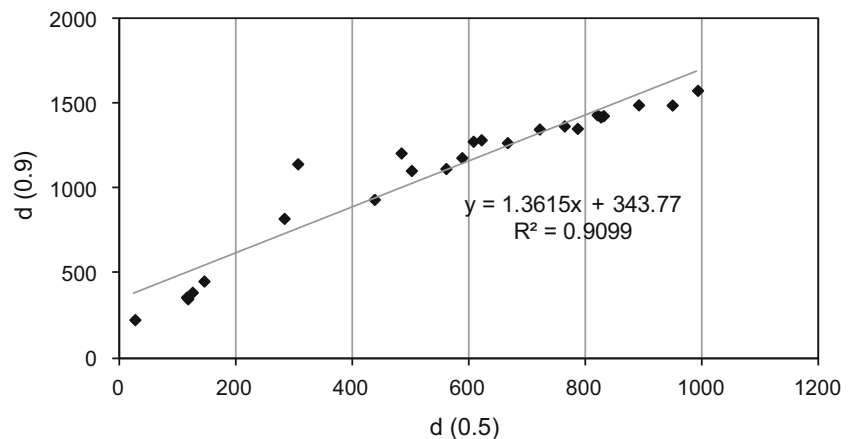


takes into account the random nature of the distribution of points in the given system that initiates the process of the creation of “grains” of a diameter  $d$  that are deposited in the spaces of the emerging structure.

**Table 1** Percentiles  $d(0.1)$ ,  $d(0.5)$  and  $d(0.9)$  determined basing on the function of changeability in the volume of particles in the algal suspension

Date	Values of specific percentiles ( $\mu\text{m}$ )		
	$d(0.1)$	$d(0.5)$	$d(0.9)$
27.03.2007	4.64	25.47	230.61
27.04.2007	7.53	304.86	1148.35
31.05.2007	13.22	124.00	391.59
19.06.2007	30.06	144.02	457.94
07.07.2007	26.84	281.58	826.86
28.08.2007	35.72	116.19	353.48
06.09.2007	33.02	114.09	362.90
17.10.2007	74.33	436.34	938.68
24.11.2007	89.17	586.40	1184.77
19.12.2007	99.40	664.64	1273.22
09.01.2008	110.18	719.51	1353.11
15.02.2008	137.25	818.52	1437.26
22.03.2008	126.41	784.64	1357.03
17.04.2008	114.71	824.48	1424.59
16.05.2008	138.23	829.36	1432.07
27.06.2008	235.99	947.42	1494.54
09.10.2008	138.92	990.94	1581.09
14.11.2008	85.79	762.30	1371.47
07.12.2008	54.50	559.16	1120.62
10.01.2009	57.64	619.76	1289.99
29.02.2009	86.75	605.92	1281.31
28.03.2009	70.63	499.94	1109.02

**Fig. 5** Linear regression between the diameters  $d(0.9)$  and  $d(0.5)$  for the results of analysis of granulometric composition of algal suspension



In the case of algal agglomerates, random nucleation was expected. Figures 6 and 7 present sample results of matching function (6) to the test results of algae granulometric composition.

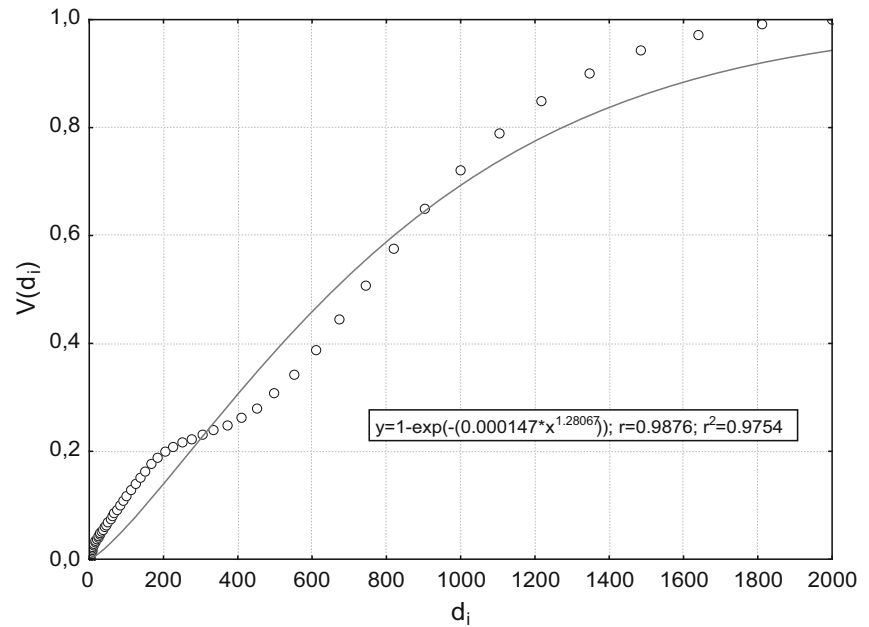
Table 2 presents the obtained selected values of the constants  $K$  and exponent  $n$  for Eq. (6) for models of the percentage share of particles from a given range of substitute mean diameters in the total volume of suspension. In all analysed cases, these constants were statistically significant on the level of 95%. The values of the correlation coefficients were close to one, which means that the regression model explained nearly all cases with use of the dependent variable  $V_i = F(d_i)$ . The values of the exponent  $n$  fell into the range from one to two, corresponding with the growth of nuclei in two dimensions. It was noted that for higher percentile values  $d(0.5)$  the exponent  $n$  reached higher values. The median of the data collection for the exponent  $n$  was 1.17, and the mean was 1.205.

The analysis of the influence of the value of the constant  $K$  and the exponent  $n$  on the course of the function  $V_i = F(d_i)$  (Figs. 8, 9) shows that the share of grains with small diameters increases with the increase in the  $K$  constant, while at lower values of the exponent  $n$  the function  $V_i = F(d_i)$  is characterised by a wider range of diameter changeability. A decrease in the value of constant  $K$  is observed at the increase of the exponent  $n$ .

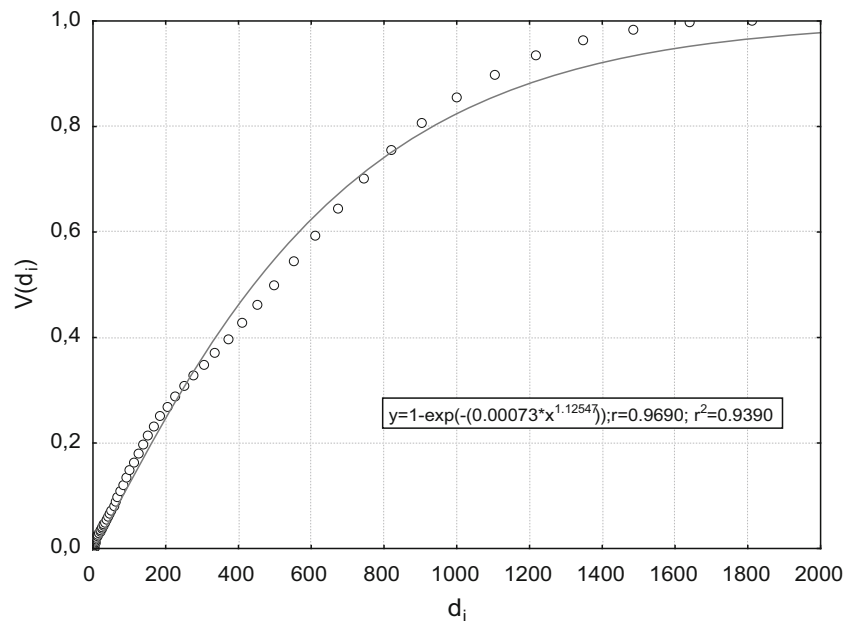
## Discussion

Aspects of ecological status are the underlying reasons why there is a need to study and model the algal bloom

**Fig. 6** Regression function described by Eq. (6), determined basing on the granulometric composition of the algal suspension analysed in the sample collected on the 9.11.2008. *Solid line* estimated regression function of the general Eq. (6); *dotted line* PSD determined in the course of the tests with use of laser granulometer



**Fig. 7** Regression function described by Eq. (6), determined basing on the granulometric composition of the algal suspension analysed in the sample collected on the 28.03.2009. *Solid line* estimated regression function of the general Eq. (6); *dotted line* PSD determined in the course of the tests with use of laser granulometer



dynamics. In many studies, it has been presented that the dynamics of nutrient consumption reflect the growth of organisms (Flynn, 2003), and little can be said about dynamics of algal size changes. Normally, studies of algal growth kinetics have been performed using deterministic water quality models which also simulate nutrient uptake and photosynthetic production (Mao

et al., 2009). Flynn (2003) presented that there are three main modelling strategies for phytoplankton growth: Monod, quota, and mechanistic. However, algal cells are able to assimilate nutrients much faster than what is required to support their metabolism. This is why biomass growth rate might not be directly related to the external concentration of the limiting substrate in the



medium (De la Hoz Siegler et al., 2011). The implication of this fact is that such models as Monod are not appropriate for modelling algal dynamics (De la Hoz Siegler et al., 2011).

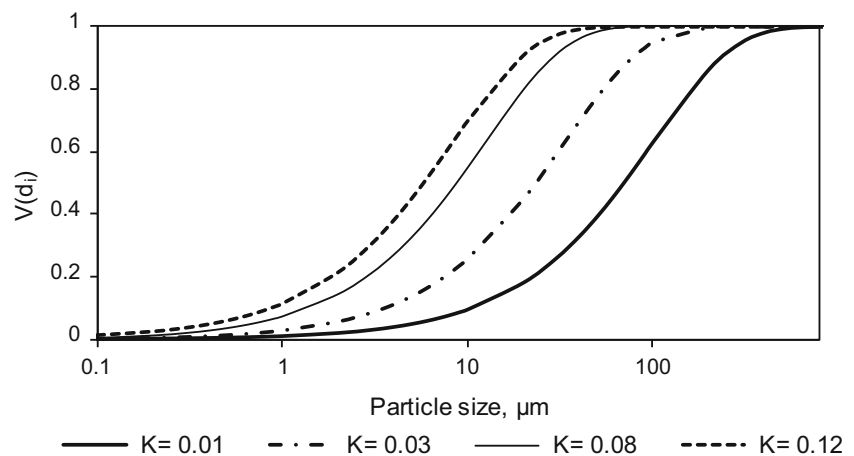
**Table 2** List of results of the calculation of constants for regression models of the granulometric composition

Date	Parameters in Eq. (6)		
	$K$	$n$	$r$
27.03.2007	5.24E-02	0.749	0.993
27.04.2007	3.47E-02	0.559	0.988
31.05.2007	6.67E-03	0.971	0.999
19.06.2007	3.08E-03	1.083	0.999
07.07.2007	8.86E-03	0.804	0.994
28.08.2007	1.25E-03	1.310	0.999
06.09.2007	1.80E-03	1.238	0.999
17.10.2007	2.50E-04	1.320	0.998
24.11.2007	9.20E-05	1.413	0.996
19.12.2007	–	–	–
09.01.2008	–	–	–
15.02.2008	–	–	–
22.03.2008	1.90E-06	1.924	0.991
17.04.2008	4.50E-06	1.789	0.988
16.05.2008	–	–	–
27.06.2008	–	–	–
09.10.2008	4.50E-06	1.748	0.981
14.11.2008	1.80E-04	1.273	0.987
07.12.2008	1.38E-03	1.019	0.992
10.01.2009	1.43E-03	0.995	0.992
29.02.2009	4.50E-04	1.170	0.997

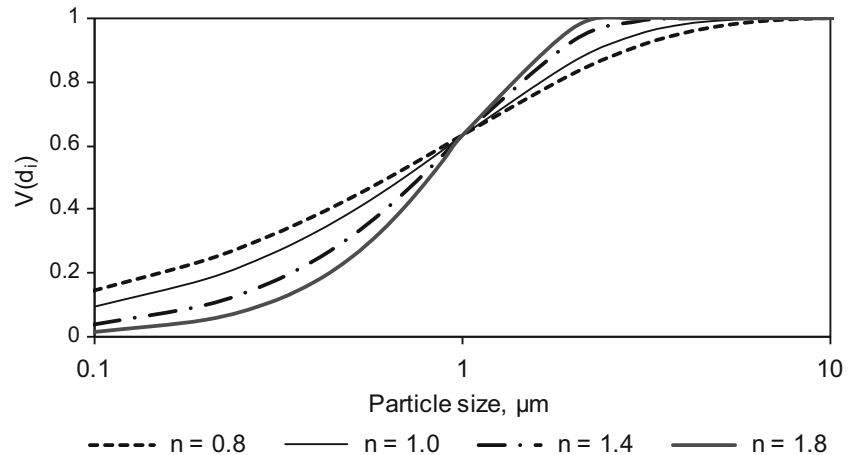
In this paper, it was demonstrated that the Avrami's theory could be applied in order to simulate the algal suspension formation, in laboratory test. Important difference laboratory conditions from the natural environment is the absence of mortality by grazing and concentrations of all necessary nutrients, vitamins, and trace metals (Berge et al., 2012). To our knowledge, no studies have attempted to model this phenomenon; however, Tran et al. (2013) proposed a kinetic modelling of colonization of mortar surface by green algae using Avrami's law. Additionally Tran et al. (2012) suggested that the Avrami's law is often use by other authors to express function  $f(X)$  when  $X(t)$  is a sigmoidal curve. Avrami's model is based on two processes nucleation and growth. The nucleation corresponds to the appearance of very small grains called nuclei and growth, and represents the increase in the size of nuclei during the time  $t$ . The first algal grains which were visible on the surface of the tank were detected after latency period lasted 30 days. A similar latency period was presented for mortar algae and lasted between 50 and 100 days (Martinez et al., 2014). Initially algal grains were very small and randomly distributed on the surface of the tank; however, after latency period exponential rapid growth was observed. The algal grains growth rate was independent of the appearance time. Considering all the measurements done on the algal samples three steps of growth was notice: nucleation, growth and stagnation just as suggested Tran et al. (2013).

The analysis shows that the model described by the modified Avrami Eq. (6) adequately matched the

**Fig. 8** Influence of the constant  $K$  on the degree of transformation  $V(d_i)$ , understood as the total volume of all grains of the suspension of substitute diameters equal or lower than  $d$  (diagrams were created for value  $n = 1$ )



**Fig. 9** Influence of the exponent on the degree of transformation  $V(d_i)$ , understood as the total volume of all grains of the suspension of substitute diameters equal or lower than  $d$  (diagrams were created for value  $K = 0.1$ )



regression to the experimental data on the granulometric composition of algal suspensions contained in nearly all the analysed samples, with the exception of those collected on the 19.12.2007, 09.01.2008, 15.02.2008, 16.05.2008 and 27.06.2008. That part of the test period was characterised by a dynamic process of growth of the algal culture, which led to the obtaining of the highest differentiation in the values of the empirical distribution for percentiles  $d(0.1)$ ,  $d(0.5)$  and  $d(0.9)$ . The differentiation of the dimensions of algae during periods of growth and in the prolonged time of cultivation caused a temporary mismatch of the model to the granulometric composition data. In addition, the PSD determined in the tests during the period of changes indicates the existence of various paces of algal growth, i.e. the existence of two cultures of algae—old and new one. This can be seen as a less accurate matching of the particle size composition to the mathematical formula of the model (dotted line shown in Fig. 6).

## Conclusions

The research on algae cultures grown in laboratory conditions showed that the laser granulometer allows for indirect identification of the dynamics of participation changes of suspension particles in the open expanses of standing water exposed to eutrophication and the granulometric composition of algal suspension can be described by the Eq. (6), analogous to Avrami equation.

Currently the changes in particle size are described with use of the general gamma function distribution equation, distribution functions by Rosin–Rammler–Bennett, Gamma, exponential,  $\chi$  with  $k$  degrees of freedom,  $\chi^2$  with  $k$  degrees of freedom. Apart from the Rosin–Rammler distribution function, the Gates–Gaudin–Schumann, Gaudin–Meloy and Harris models are often used for the linearization of the  $V(d_i)$  function. On the other hand, there is no universal description of changes  $V(d_i)$  that would take into account grain growth mechanisms. The modified Avrami equation is suitable for the modelling of changes in the  $V(d_i)$  functions due to several reasons. First, this is the only model for which it was possible to match the measurement data throughout the whole range of sizes, and second, it takes into account the random nature of spatial distribution of individual cells, their contacts, division, and the influence of these phenomena on the growth pace. The growth model described by the modified Avrami equation works well in the phase of initial rapid growth of algae, and in the period when the growth pace is stabilised. During the period of changes occurring in the population (dying of cells, aggregation resulting from the division and adhesion processes), the matching of the obtained PSD to the model is hindered. However, this is a transition phase. Algae stabilise their vital processes slowly and some of them die. The remaining organisms adapt to the new living conditions, they enter the growth or stabilisation phase, followed by dying. As a result of the changes occurring in the

population in certain periods of time, it is impossible to match the obtained data to the model.

The studies on the application of the modified Avrami equation are of a pioneering nature. The possibility to describe algal suspension by the modified Avrami equation raises the hypothesis that the mechanism of algal suspension formation is similar to the mechanism of the formation of crystals from saturated solutions. This research can serve as a base for future studies in this area. Currently, as a result of the existence of global algae industry, there is a need to develop the technical challenges for optimising the cultivation of algae. Additionally, the continuation of the analyses presented in our study increases the chances to introduce new cell size/algal growth parameter to the existing models of algal bloom dynamics.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

- Berge, T., N. Daugbjerg & P. J. Hansen, 2012. Isolation and cultivation of microalgae select for low growth rate and tolerance to high pH. *Harmful Algae* 20: 101–110.
- Bizi, M. & G. Baudet, 2006. Contribution of static light scattering to the textural characterization of large aggregates. *Journal of Colloid and Interface Science* 300: 200–209.
- Bluma, A., T. Höpfner, G. Rudolph, P. Lindner, S. Beutel, B. Hitzmann & T. Scheper, 2009. Adaptation of in-situ microscopy for crystallization processes. *Journal of Crystal Growth* 311: 4193–4198.
- Burszta-Adamiak, E., M. Kęszycka & J. Łomotowski, 2010. Structure and granulometric composition of suspensions in sewage sludge and activated sludge. Monography “Environmental Engineering III”. CRC Press, Boca Raton: 161–166.
- Burszta-Adamiak, E., M. Kuśnierz, J. Łomotowski & P. Wiercik, 2012. Badania składu granulometrycznego zawiesin zawartych w ściekach komunalnych i przemysłowych (Analysis of the granulometric composition of suspensions contained in municipal and industrial wastewaters). *Infrastruktura i Ekologia Terenów Wiejskich* 3: 43–54.
- Bushell, G., 2005. Forward light scattering to characterise structure of flocs composed of large particles. *Chemical Engineering Journal* 111: 145–149.
- Cho, K. H., Y. A. Pachepsky, J. H. Kim, A. K. Guber, D. R. Shelton & R. Rowland, 2010. Release of *Escherichia coli* from the bottom sediment in a first-order creek: experiment and reach-specific modeling. *Journal of Hydrology* 391: 322–332.
- Cloot, A. H. J. & A. J. H. Pieterse, 1999. Modelling phytoplankton in the Vaal River (South Africa). *Water Science and Technology* 40: 119–124.
- De la Hoz Siegler, H., A. Ben-Zvi, R. E. Burrell & W. C. McCaffrey, 2011. The dynamics of heterotrophic algal cultures. *Bioresource Technology* 102: 5764–5774.
- Di Lorenzo, M. L. & C. Silvestre, 1999. Non-isothermal crystallization of polymers. *Progress in Polymer Science* 24: 917–950.
- Dokulil, M. T., K. Donabum & K. Teubner, 2007. Modifications in phytoplankton size structure by environmental constraints induced by regime shifts in an urban lake. *Hydrobiologia* 578: 59–63.
- Droppo, I. G., B. G. Krishnappan, S. N. Liss, C. Marvin & J. Biberhofer, 2011. Modelling sediment-microbial dynamics in the South Nation River, Ontario, Canada: towards the prediction of aquatic and human health risk. *Water Research* 45: 3797–3809.
- Fernandes, V. A., A. J. Müller & A. J. Sandoval, 2013. Thermal, structural and rheological characteristics of dark chocolate with different compositions. *Journal of Food Engineering* 116: 97–108.
- Fiore, S., S. Dumontet, F. J. Huertas & V. Pasquale, 2011. Bacteria-induced crystallization of kaolinite. *Applied Clay Science* 53: 566–571.
- Flynn, K. J., 2003. Modelling multi-nutrient interactions in phytoplankton; balancing simplicity and realism. *Progress in Oceanography* 56: 249–279.
- García-Mesa, J. J., J. M. Poyatos, F. Delgado-Ramos, M. M. Muñoz, F. Osorio & E. Hontoria, 2010. Water quality characterization in real biofilm wastewater treatment systems by particle size distribution. *Bioresource Technology* 101: 8038–8045.
- Herrera, M. L., M. De León Gatti & R. W. Hartel, 1999. A kinetic analysis of crystallization of a milk fat model system. *Food Research International* 32: 289–298.
- IUPAC, 1997. *Compendium of Chemical Terminology*, 2nd ed. (the “Gold Book”). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford.
- Judge, R. A., M. R. Johns & E. T. White, 1995. Protein purification by bulk crystallization: the recovery of ovalbumin. *Biotechnology Bioengineering* 48: 316–323.
- Kagwa, M. N., M. Gruber, S. O. Oduor & M. Schagerl, 2013. A detailed time series assessment of the diet of Lesser Flamingos: further explanation for their itinerant behavior. *Hydrobiologia* 710: 83–93.
- Khalil, A., F. Puel, X. Cosson, O. Gorbachev, Y. Chevalier, J. M. Galvan, A. Rivoire & J. P. Klein, 2012. Crystallization-in-emulsion process of a melted organic compound: in situ optical monitoring and simultaneous droplet and particle size measurements. *Journal of Crystal Growth* 342: 99–109.
- Kozak, A., 2005. Seasonal changes occurring over four years in a reservoir’s phytoplankton composition. *Polish Journal of Environmental Studies* 14: 451–465.
- Krumme, A., A. Lehtinen & A. Viikna, 2004. Crystallisation behaviour of high density polyethylene blends with bimodal molar mass distribution. 1. Basic characteristics and

- isothermal crystallization. *European Polymer Journal* 40: 359–369.
- Lehman, P. W., S. J. Teh, G. L. Boyer, M. L. Nobriga, E. Bass & C. Hogle, 2010. Initial impacts of *Microcystis aeruginosa* blooms on the aquatic food web in the San Francisco Estuary. *Hydrobiologia* 637: 229–248.
- Li, X.-Y., J.-J. Zhang & J. H. W. Lee, 2004. Modelling particle size distribution dynamics in marine waters. *Water Research* 38: 1305–1317.
- Liu, L., Z. F. Wu & J. Zhang, 2002. Crystallization kinetics of Zr Cu Al Ni bulk amorphous alloy. *Journal of Alloys and Compounds* 339: 90–95.
- Lorenzo, A. T., M. A. Arnal, J. Albuerne & A. J. Müller, 2007. DSC isothermal polymer crystallization kinetics measurements and the use of the Avrami equation to fit the data: guidelines to avoid common problems. *Polymer Testing* 26: 222–231.
- Lu, M. G., M. J. Shim & S. W. Kim, 1998. Curing behavior of an unsaturated polyester system analyzed by Avrami equation. *Thermochimica Acta* 323: 37–42.
- Lyche-Solheim, A., C. K. Feld, S. Birk, G. Phillips, L. Carvalho, G. Morabito, U. Mischke, N. Willby, M. Søndergaard, S. Hellsten, A. Kolada, M. Mjelde, J. Böhmer, O. Miler, M. T. Pusch, C. Argillier, E. Jeppesen, T. L. Lauridsen & S. Poikane, 2013. Ecological status assessment of European lakes: a comparison of metrics for phytoplankton, macrophytes, benthic invertebrates and fish. *Hydrobiologia* 704: 57–74.
- Málek, J., 1995. The applicability of Johnson-Mehl-Avrami model in the thermal analysis of the crystallization kinetics of glasses. *Thermochimica Acta* 267: 61–73.
- Mao, J. Q., J. H. W. Lee & K. W. Choi, 2009. The extended Kalman filter for forecast of algal bloom dynamics. *Water Research* 43: 4214–4224.
- Martin, D., 2010. Application of Kolmogorov–Johnson–Mehl–Avrami equations to non-isothermal conditions. *Computational Materials Science* 47: 796–800.
- Martinez, T., A. Bertron, G. Escadeillas & E. Ringot, 2014. Algal growth inhibition on cement mortar: efficiency of water repellent and photocatalytic treatments under UV/VIS illumination. *International Biodeterioration & Biodegradation* 89: 115–125.
- Martins, J. A. & J. J. C. Cruz Pinto, 2002. Evaluation of the instantaneous nucleation density in the isothermal crystallization of polymers. *Polymer* 43: 3999–4010.
- Mazur-Marzec, H., K. Sutryk, J. Kobos, A. Hebel, N. Hohlfeld, A. Błaszczuk, A. Toruńska, M. J. Kaczkowska, E. Łysiak-Pastuszak, W. Kraśniewski & I. Jasser, 2013. Occurrence of cyanobacteria and cyanotoxin in the Southern Baltic Proper. Filamentous cyanobacteria versus single-celled picocyanobacteria. *Hydrobiologia* 701: 235–252.
- Morin, S., M. Coste & F. Delmas, 2008. A comparison of specific growth rates of periphytic diatoms of varying cell size under laboratory and field conditions. *Hydrobiologia* 614: 285–297.
- Ovono Ovono, D., S. Berre, P. Pradeau, M. Comte & G. Bruno, 2012. Study of the crystallization kinetics of LAS glass by differential scanning calorimetry, X-ray diffraction, and beam bending viscometry. *Thermochimica Acta* 527: 158–164.
- Quirantes, A. & B. Stewart, 2004. Light scattering by marine algae: two-layer spherical and nonspherical models. *Journal of Quantitative Spectroscopy & Radiative Transfer* 89: 311–321.
- Quirantes, A. & B. Stewart, 2006. Light-scattering methods for modelling algal particles as a collection of coated and/or nonspherical scatterers. *Journal of Quantitative Spectroscopy & Radiative Transfer* 100: 315–324.
- Richter, D., 2013. Analysis of changes in cyanobacterial and algal flora of selected water reservoirs in Wrocław between 1878 and 2010 (south-west Poland). *International Journal of Oceanography and Hydrobiology* 42: 379–397.
- Richter, D. & J. Matuła, 2012. Response of cyanobacteria and algae community from small water bodies to physico-chemical parameters. *International Journal of Oceanography and Hydrobiology* 41: 18–28.
- Rolinski, S., P. Pätz, K. Papendick, S. Jähnichen & N. Scheifhacken, 2013. Phytoplankton appearance in particle size spectra – deriving conversion functions between microscopic and particle counter measurements. *Water Research* 47: 1928–1940.
- Sitoki, L., R. Kurmayer & E. Rott, 2012. Spatial variation of phytoplankton composition, biovolume, and resulting microcystin concentrations in the Nyanza Gulf (Lake Victoria, Kenya). *Hydrobiologia* 691: 109–122.
- Souza, M. B. G., C. F. A. Barros, F. Barbosa, É. Hajnal & J. Padišák, 2008. Role of *atelmixis* in replacement of phytoplankton assemblages in Dom Helvécio Lake, South-East Brazil. *Hydrobiologia* 607: 211–224.
- Sperazza, M., J. N. Moore & M. S. Hendrix, 2004. High-resolution particle size analysis of naturally occurring very fine-grained sediment through laser diffractometry. *Journal of Sedimentary Research* 74: 736–743.
- Stelzer, T., D. Pertig & J. Ulrich, 2013. Ultrasonic crystallization monitoring technique for simultaneous in-line measurement of liquid and solid phase. *Journal of Crystal Growth* 362: 71–76.
- Stoyneva, M. P., J. P. Descy & W. Vyverman, 2007. Green algae in Lake Tanganyika: is morphological variation a response to seasonal changes? *Hydrobiologia* 578: 7–16.
- Supaphol, P., 2001. Application of the Avrami, Tobin, Malkin, and Urbanovici-Segal macrokinetic models to isothermal crystallization of syndiotactic polypropylene. *Thermochimica Acta* 370: 37–48.
- Todinov, M. T., 2000. On some limitations of the Johnson–Mehl–Avrami–Kolmogorov equation. *Acta Materialia* 48: 4217–4224.
- Tran, T. H., A. Govin, R. Guyonnet, P. Grosseau, C. Lors, D. Damidot, O. Deves & B. Ruot, 2013. Avrami’s law based kinetic modeling of colonization of mortar surface by alga *Klebsormidium flaccidum*. *International Biodeterioration & Biodegradation* 79: 73–80.
- Tran, T. H., A. Govin, R. Guyonnet, P. Grosseau, C. Lors, E. Garcia-Diaz, D. Damidot, O. Deves & B. Ruot, 2012. Influence of the intrinsic characteristics of mortars on biofouling by *Klebsormidium flaccidum*. *International Biodeterioration & Biodegradation* 70: 31–39.
- Vázquez, J., P. L. López-Alemán, P. Villares & R. Jiménez-Garay, 2000. Generalization of the Avrami equation for the analysis of non-isothermal transformation kinetics. Application to the crystallization of the  $\text{Cu}_{0.20}\text{As}_{0.30}\text{Se}_{0.50}$  alloy. *Journal of Physics and Chemistry of Solids* 61: 493–500.

- Wollschläger, J., K. H. Wiltshire, W. Petersen & K. Metfies, 2015. Analysis of phytoplankton distribution and community structure in the German Bight with respect to the different size classes. *Journal of Sea Research* 99: 83–96.
- Wu, J., X. Jiang & A. Wheatley, 2009. Characterizing activated sludge process effluent by particle size distribution, respirometry and modeling. *Desalination* 249: 969–975.
- Xiao, J., J. Fan, D. Zhai, R. Wen & X. Qin, 2015. Testing the model for linking grain-size component to lake level status of modern clastic lakes. *Quaternary International* 355: 34–43.
- Yang, Y., B. J. McCoy & G. Madras, 2005. Distribution kinetics of polymer crystallization and the Avrami equation. *The Journal of Chemical Physics* 122: 064901.
- Yao, J., P. Xiao, Y. Zhang, M. Zhan & J. Cheng, 2011. A mathematical model of algal blooms based on the characteristics of complex networks theory. *Ecological Modelling* 222: 3727–3733.