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MELIMEX, an experimental heavy metal pollution study: Particle size distributions in limno-corrals

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ABSTRACT

The particle size distributions in three limno-corrals, located in Baldeggersee, Switzerland, have been determined by means of a Zeiss Micro-Videomat image analyzer as a function of depth and time. The distributions were measured biweekly over a period of 1 year at depths of 0 m, 2.5 m, 5 m, 7.5 m and 10 m (= above bottom). Two of the limno-corrals were charged with heavy metals, whereas the third was uncharged and served as a reference. The shape of the distributions as well as the particle concentrations in the uncharged container did not differ from the ones in the charged limno-corrals. The distributions were found to be self-preserving and independent on heavy metal load, time, depth and particle concentrations. As an average, the dependence of the distributions on the particle diameter was found to be -1.5 to -2.5.

1. Introduction

The composition of natural waters is determined by a variety of chemical and physical processes, such as dissolution of gases and solids, adsorption and complexation of metal ions at surfaces of suspended solids, acid-base reactions, precipitations and interactions of solutes with the sediments. Among these processes the interactions of suspended solid matter with dissolved species is of particular importance, because suspended solids may take part via sedimentation in the process of transporting solutes from the water body into the sediments. Suspended solids consist of oxides, carbonates, silicates, clays as well as living and dead microorganisms and their decomposition products. An important parameter for the characterization of suspended solids is the particle size distribution. A change of the particle size distribution would be reflected in a change of the transportation characteristics. The limno-corrals used in the MELIMEX study [4] represent a suitable system to study particle size distributions in order to answer the following questions: a) What are the particle size distributions and the total particle concentration as a function of time and depth? b) What is the influence of an increased heavy metal load on the particle size distribution as well as on the total particle concentration? c) Are the particle size distributions self-preserving and independent of heavy metal load, time, depth and particle concentration?

Particle size distribution and coagulation are closely related. It is the purpose of this paper to discuss the particle size distributions in terms of coagulation phenomena. Coagulation determines largely the composition of the suspended phase in the water body. Since aqueous phase and solid phase are closely interrelated by equilibria which involve the solid phase, coagulation may affect the composition of the aqueous phase and vice versa.

2. The concept of self-preserving distributions

The concept of self-preserving distributions was developed in order to explain regularities in the particle size distribution of atmospheric aerosols, observed by Junge [8–10]. Swift and Friedlander [15] have shown that it is possible to find a distribution function which has the same shape at all times during a coagulation experiment, if the distribution is self-preserving. This distribution function satisfied the general equation for Brownian and shear coagulation.
Self-preserving distributions of particles have been found under laboratory conditions [14], as well as in the atmosphere [3] and in the ocean [7]. The existence of a self-preserving particle size distribution in the atmosphere has been explained on the basis of two assumptions: First, the upper end of the spectrum, i.e. particle diameter $a > 0.2$ µm, has attained a dynamic steady state between matter that enters the spectrum and matter which gets lost by sedimentation. Second, the form of the upper end of the spectrum is completely determined by coagulation of smaller particles and sedimentation.

3. Predictions on the functional dependence of the size distributions on the particle diameter

Assuming a dynamic steady state and by dimensional reasoning, Friedlander [2, 3] and Hunt [6] predicted the dependence of the particle size distributions on the particle diameter in the atmosphere and in seawater, respectively, by selecting subranges, at which either Brownian coagulation, shear coagulation, differential sedimentation coagulation or settling dominates. Hunts predictions in seawater are collected in table 1.

Table 1. Dependence of the particle size distribution on the particle diameter.
Tabelle 1. Abhängigkeit der Partikelgrössenverteilung vom Durchmesser der Partikel.

Dominating mechanism	Size distribution is dependent on	To be expected for
Brownian	$a^{-5/2}$	small particles
Shear	a^{-4}	medium size particles
Differential sedimentation	$a^{-9/2}$	large particles
Settling	$a^{-19/4}$	large particles

4. Experimental

4.1 *Sampling and sample preparation*

Samples were taken biweekly in all three limno-corrals at the following depths:

surface (= 0 m), 2.5 m, 5 m, 7.5 m and above bottom (= approx. 10 m). In order to increase contrast differencies between particles and background, the samples were stained by addition of several drops of an approx. 7% Gentiana-violet solution. After 1 hour, 1 to 1.5 ml of the samples were withdrawn and centrifuged with a Shandon-Elliot slide centrifuge[1]) in order to transfer the particles onto a microscope slide.

Initially, the results, obtained by the above sample preparation technique were compared with those, resulting from two different concentration techniques: Sedimentation and flow-through centrifuge[2]). Since no difference neither in particle size distribution nor in particle concentration was observed, the Shandon-Elliot slide centrifuge was used for all subsequent measurements because of its simple and fast operation.

4.2 *Counting and sizing*

The particles were counted and sized, using a Zeiss Micro-Videomat as described by Kavanaugh et al. [11]. The size spectrum was divided into 14 different size classes, ranging from 1 to 100 µm. The individual class sizes are shown in table 2:

Table 2. Division of the size spectrum into different size classes. The increase of the mean size to the higher size class is $\sqrt{2}$.
Tabelle 2. Unterteilung des Partikelgrössenspektrums in einzelne Grössenklassen. Die Mittel der einzelnen Klassen unterscheiden sich durch einen Faktor von $\sqrt{2}$.

Class interval µm	Mean size µm	Class interval µm	Mean size µm
0.85–1.2	1.025	9.6– 13.6	11.6
1.2 –1.7	1.45	13.6– 19.2	16.5
1.7 –2.4	2.05	19.2– 27.2	23.2
2.4 –3.4	2.9	27.2– 38.4	32.8
3.4 –4.8	4.1	38.4– 54.3	46.3
4.8 –6.8	5.8	54.3– 76.7	65.5
6.8 –9.6	8.2	76.7–108.0	92.35

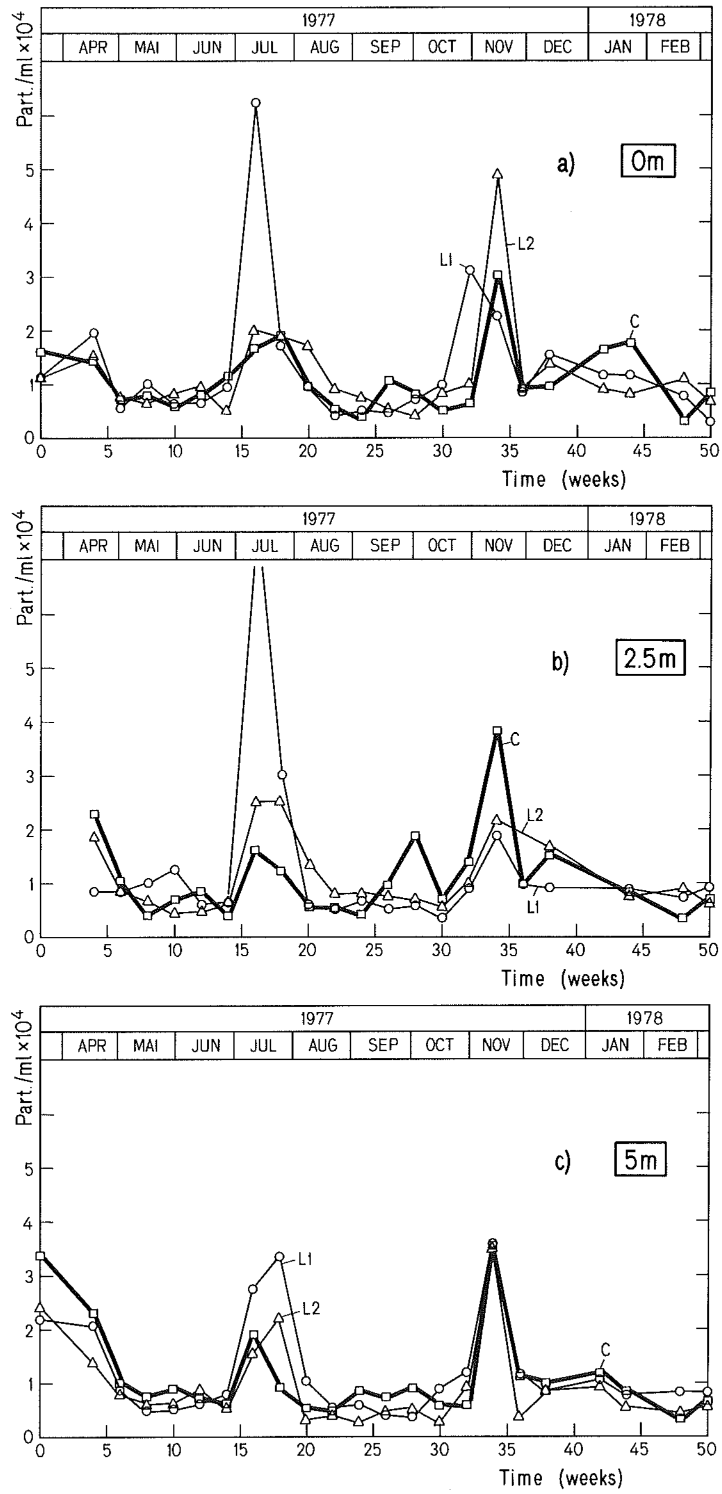
The precision of the total number count, as well as the number length mean diameter $\bar{a}$ is approx. 10%, indicated as coefficient of variation. However, the precision of particle counting in each size class strongly depends on the class size. In the size classes 1.025 µm, 4.1 µm and 65.5 µm, the precision, again as coefficient of variation, is 28%, 9% and 245%, respectively [11].

5. Results and discussion

5.1 *Particle concentrations*

Figure 1 shows the particle concentrations in the three corrals as a function of time. Whereas corral C is uncharged with respect to heavy metals and serves as a refer-

1) Shandon Labortechnik GmbH, Frankfurt, German Federal Republic.
2) 'CEPA' centrifuge, from Carl Padberg, Zentrifugenbau GmbH, 763 Lahr, German Federal Republic.


1977
1978
APR
MAI
JUN
JUL
AUG
SEP
OCT
NOV
DEC
JAN
FEB
Part./ml×10⁴
a)
0m
L1
L2
C
Time (weeks)
b)
2.5m
C
L2
L1
c)
5m
L1
L2
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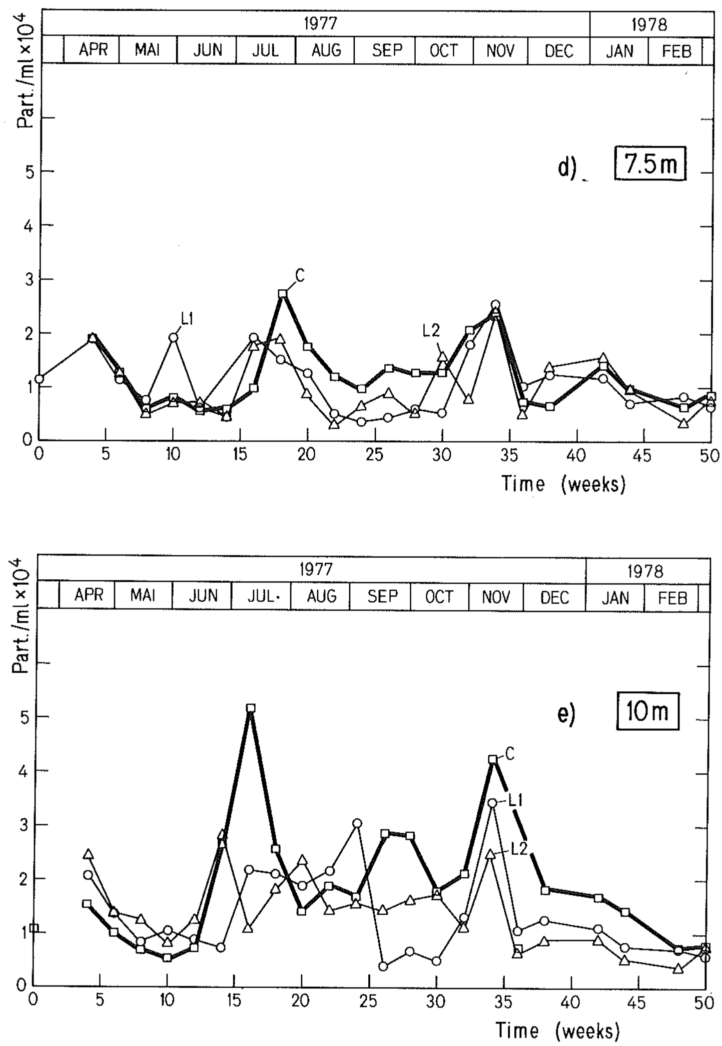


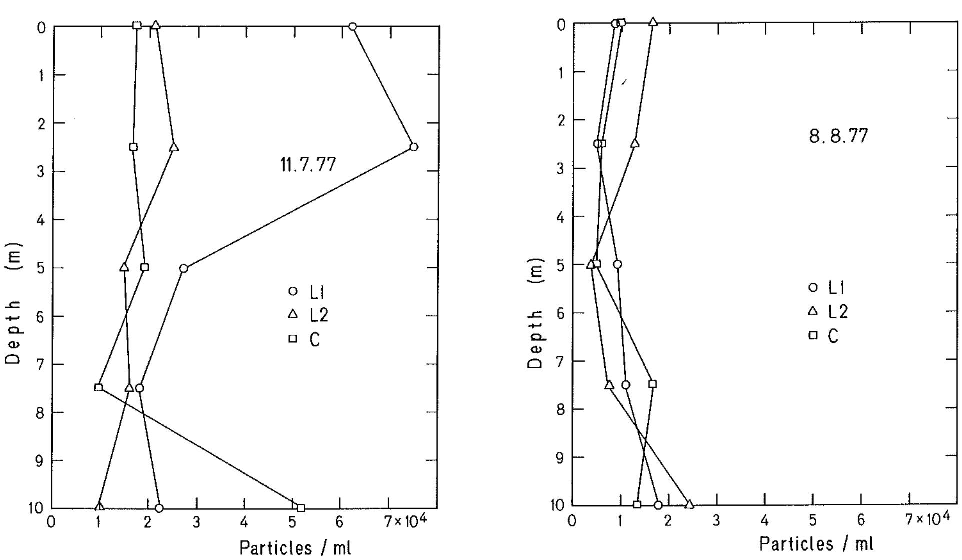
Figure 1. Total number of particles per milliliter as a function of time. Corral C is uncharged, corrals L1 and L2 are charged with heavy metals. a) depth = 0 m; b) depth = 2.5 m; c) depth = 5 m; d) depth = 7.5 m; e) depth = 10 m.

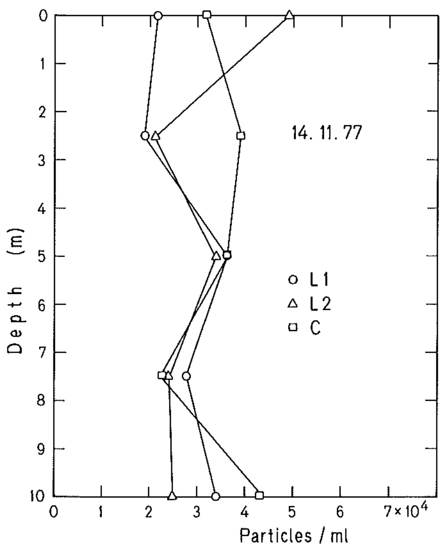
Abb. 1. Die totale Partikelzahl pro Milliliter als Funktion der Zeit. Die Modellseen L1 und L2 wurden mit Schwermetallen belastet, der Modellsee C blieb unbelastet. a) Tiefe = 0 m; b) Tiefe = 2,5 m; c) Tiefe = 5 m; d) Tiefe = 7,5 m; e) Tiefe = 10 m.

ence, corrals L1 and L2 are charged with heavy metals, according to the 'Verordnung über Abwassereinleitungen vom 8. Dezember 1975' (Ordinance on the content of wastewater input into water systems, 8 December 1975), which gives upper limits for the concentrations of potentially toxic heavy metal ions in rivers and lakes. The concentration of particles in the three corrals fluctuates drastically with time, whereby concentration changes are largest in the upper layers of water, i.e. 0 m < depth < 5 m. In the winter months December, January and February the particle concentration as well as the fluctuations are generally lower in all three containers than in the other months of the year. This indicates, that the production of biomass might be the main source of particles in the containers.

No clear cut difference in particle concentration can be observed between the charged limno-corrals L1 and L2 and the uncharged control C. However, Lang [12] and Gächter [5] have found that sedimentation, production of biomass as well as concentration of intact algae is significantly higher in corral C than in the loaded corrals L1 and L2. A comparison between the concentrations of intact algae, measured by the above authors and our total particle concentrations shows that the number of intact algae per milliliter is much smaller than the total particle concentration. At a ration algae:debris = (2 to 10):100 it becomes apparent that differencies in algae concentrations of 100 to 300% in L1, L2 and C are not necessarily reflected in the total particle concentration. The concentration fluctuations seem to occur accidentally, which is evidence for the fact, that temporarily high or low particle concentrations in the containers are due to single events, occurring in the water body.

Figure 2 shows typical particle concentrations in the three corrals as a function of depth for 4 different days, chosen randomly over 1 year. The smallest particle concentrations are observed at a depth of approx. 5–7 m. The largest concentrations were measured at a depth of 0–2.5 m and at 10 m. This might be due to production of biomass and/or input of airborn particles at the surface and disturbance of the water-sediment layer by emanating gas bubbles from the sediments, respectively.





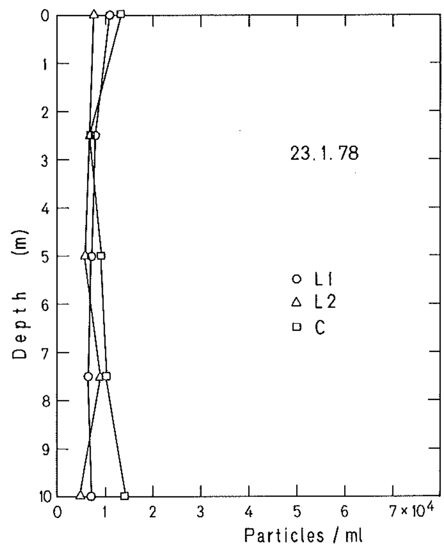
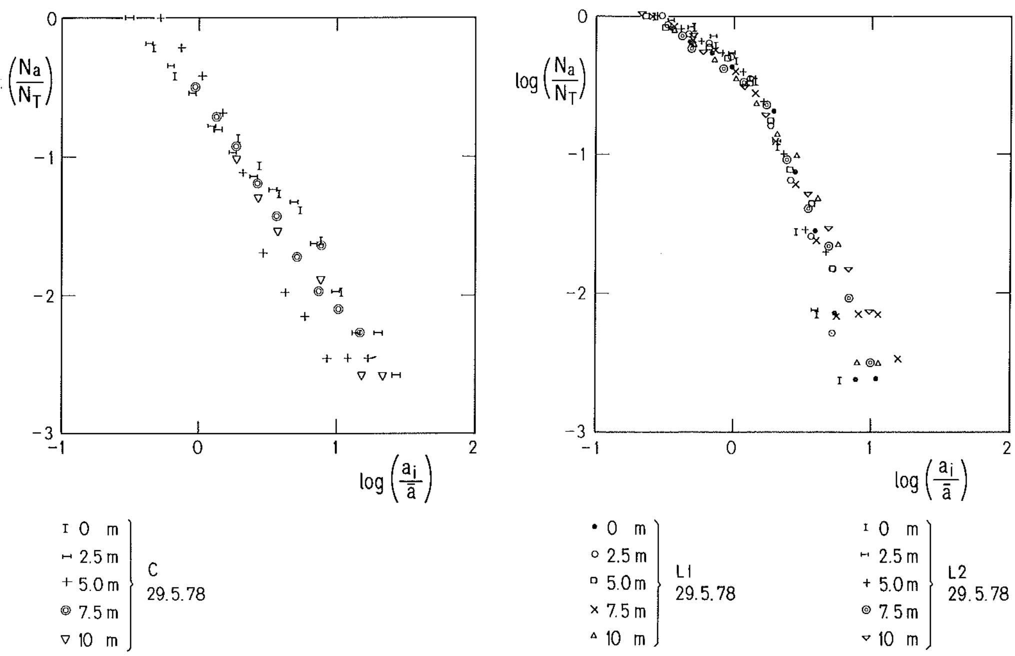
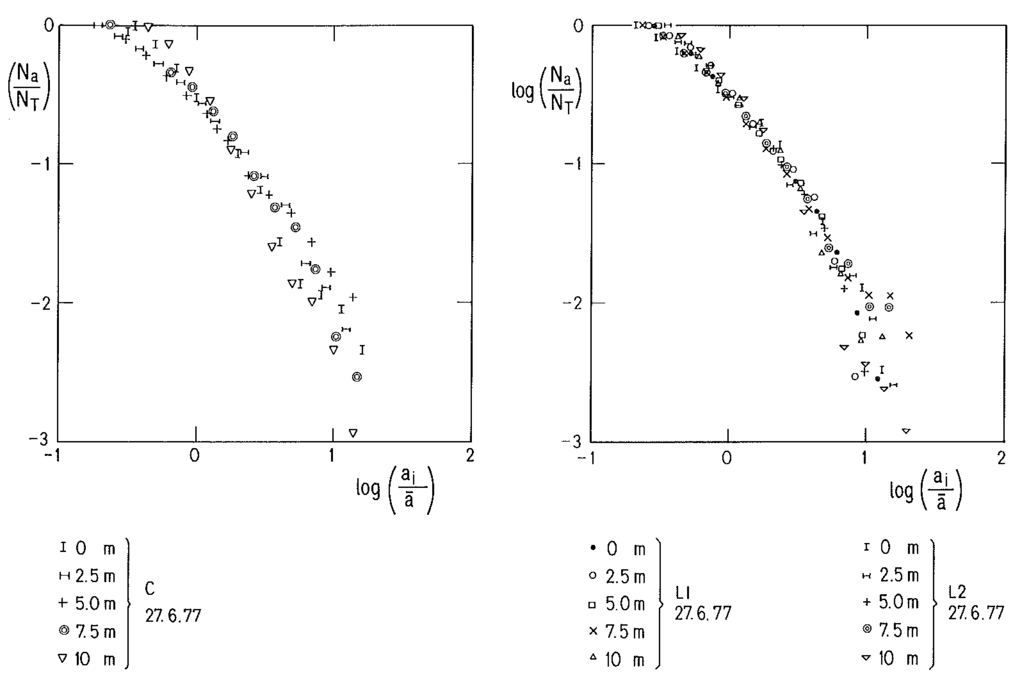


Figure 2. Total number of particles per milliliter as a function of depth at various days of the year. a) 11 July 1977; b) 8 August 1977; c) 14 November 1977; d) 23 January 1978.
Abb. 2. Die totale Partikelzahl pro Milliliter als Funktion der Tiefe an verschiedenen Jahrestagen. a) 11. Juli 1977; b) 8. August 1977; c) 14. November 1977; d) 23. Januar 1978.

5.2 *Self-preserving distributions*

Test for self-preserving distributions is done by plotting the dimensionless parameter $\eta_i = a_i/\bar{a}$ against N_a/N_T. N_a is the cumulative number of particles equal to or larger than a_i. N_T is the total number of particles per milliliter. η_i represents the ratio between the actual diameter a_i of the particle in a given size range i and the number length mean diameter $\bar{a}$. If the plot shows the same functional dependence at various locations and at various times, then the distributions are self-preserving. Figure 3 shows for 3 randomly selected days that the distributions have the same functional dependence on the dimensionless parameters η and N_a / N_T for the charged corrals as well as for the uncharged one. Furthermore, the same dependence is observed at various depths. At the upper end of the particle spectrum, i.e. $\log \eta > 0.8$, the points are more scattered around the curve than at the lower end of the spectrum. This is due to experimental uncertainties: The counted number of large particles is small, compared to the counted number of small particles. Thus the statistical error becomes large (see experimental part). The distributions appear to be self-preserving, independent of depth, day and container.
Figure 4 shows the test for self-preservation as a function of time in corral C at a depth of 0 m. Again, the same functional dependence is observed for various times. As can be seen from figures 1 and 2, the particle concentrations change markedly with depth and time. This, however, is not reflected in the self-preserving forms of


log $\left(\frac{N_a}{N_T}\right)$
log $\left(\frac{a_i}{\bar{a}}\right)$
0 m
2.5 m
5.0 m
7.5 m
10 m
C
29.5.78
L1
29.5.78
L2
29.5.78


log $\left(\frac{N_a}{N_T}\right)$
log $\left(\frac{a_i}{\bar{a}}\right)$
0 m
2.5 m
5.0 m
7.5 m
10 m
C
27.6.77
L1
27.6.77
L2
27.6.77

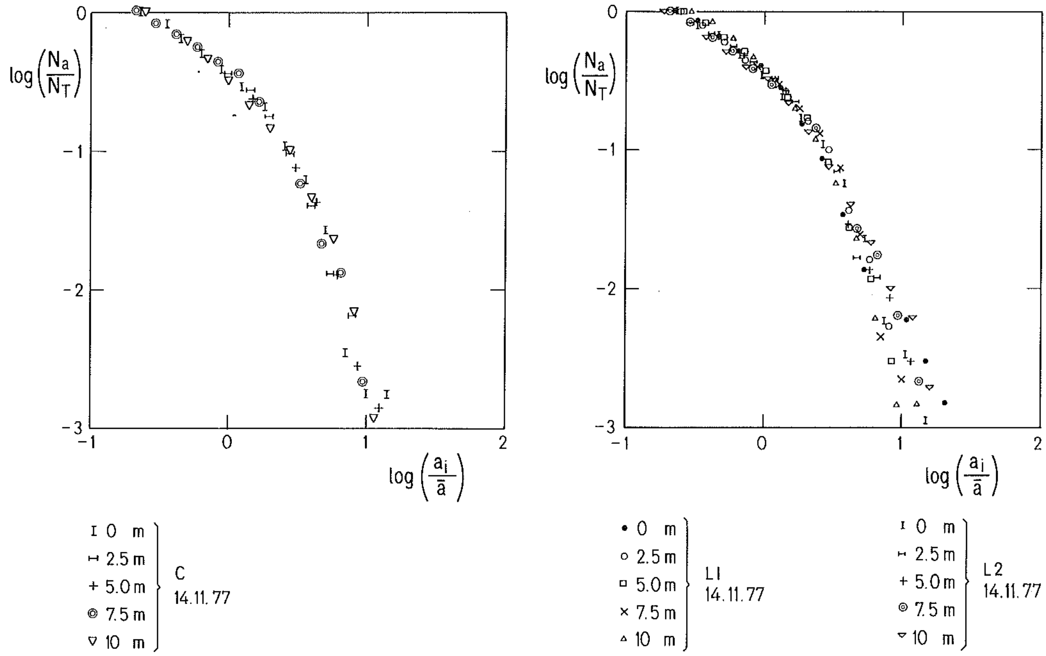


Figure 3. Test for self-preserving distributions as a function of depth at various days of the year. a) 29 May 1978, uncharged corral C; b) 29 May 1978, charged corrals L1 and L2; c) 27 June 1977, uncharged corral C; d) 27 June 1977, charged corrals L1 and L2; e) 14 November 1977, uncharged corral C; f) 14 November 1977, charged corrals L1 and L2.

Abb. 3. Test, ob die Partikelgrössenverteilungen der 3 Modellseen selbsterhaltend (self-preserving) im ganzen Tiefenprofil an verschiedenen Jahrestagen sind. a) 29. Mai 1978, unbelasteter Modellsee C; b) 29. Mai 1978, belastete Modellseen L1 und L2; c) 27. Juni 1977, unbelasteter Modellsee C; d) 27. Juni 1977, belastete Modellseen L1 und L2; e) 14. November 1977, unbelasteter Modellsee C; f) 14. November 1977, belastete Modellseen L1 und L2.

the distributions, i.e. the shapes of the distributions are independent of the particle concentrations. This was expected by Swift and Friedlander [15] and confirmed by Hunt [7].

5.3 *Distributions*

Figure 5a shows some particle size distributions in the uncharged limno-corral C at the surface, approx. equally distributed over 1 year. Figure 5b contains the respective distributions in the loaded corral L1. Our interest is focused on the average slopes of the distributions. As immediately can be seen, the average slopes of the distributions scatter between -1.5 and -2 and hardly exceed -2.5. This result is most surprising, since the slopes are far below what would be expected according to the predictions by Hunt. They are even below the smallest slope of -2.5 which is expected for a Brownian coagulation mechanism. Since figure 5 shows 16 different distributions, measured in different containers and during different seasons, there is

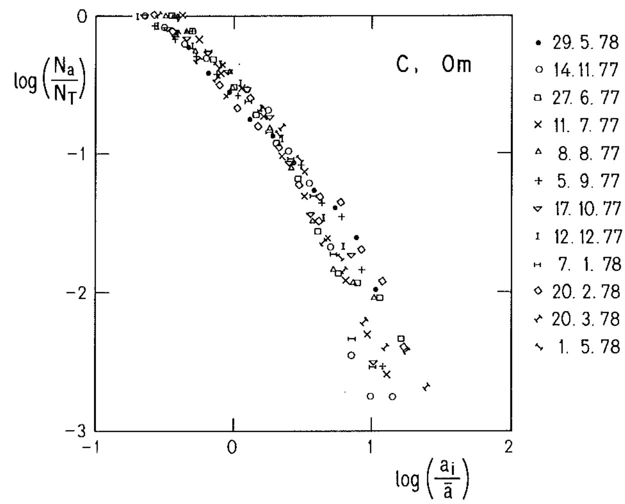


Figure 4. Test for self-preserving distributions as a function of time in the uncharged container C at a depth of 0 m.
Abb. 4. Test, ob die Partikelgrössenverteilungen des mit den Schwermetallen unbelasteten Modellsees C innerhalb eines Jahres selbsterhaltend (self-preserving) sind. Tiefe = 0 m.

no doubt that these distributions with small slopes are not accidentally occurring. On the other hand, as shown in figures 3 and 4, the distributions are self-preserving, which indicates that there is a common factor which finally leads to similar particle size distributions. A closer look to the figures shows that in particular the slopes for larger particles, i.e. a >20 µm are too small, or in other words, there are too many large particles. A reasonable explanation for this is the fact, that a noticeable part of the particles may consist of living organic matter (phytoplankton, zooplankton). It is known that plankton is capable to act against gravitational forces (sedimentation) and thus maintains a given depth in the water body. If we therefore exclude settling and differential sedimentation as dominating coagulation mechanisms for large particles, there is still the shear coagulation mechanism, for which a diameter-dependence of -4 is predicted. Since it is difficult to measure shear rates in such a container system, estimates must be used instead. Hunt used a value of $G = 3\ sec^{-1}$[3]) as an average shear rate in coastal waters. In these containers, which represent a kind of a closed system, the shear rates may be much lower. We may therefore assume that the shear rate, as well as turbulence are so small that Brownian motion becomes the dominant factor for coagulation. Then the slopes should be -2.5 which is closer to what was measured.

At the lower end of the spectrum, i.e. a <2 µm, there are too few particles. Comparing measurements with Coulter Counter on identical samples reveal higher particle concentrations in the size range 1–2 µm [14]. This is in agreement with the reported tendency of the Zeiss Micro-Videomat to underestimate particle counts below 1 µm and to overestimate above this limit [11].

3) G is the mean advection velocity gradient perpendicular to the flow, $G = dU_x/dz$.

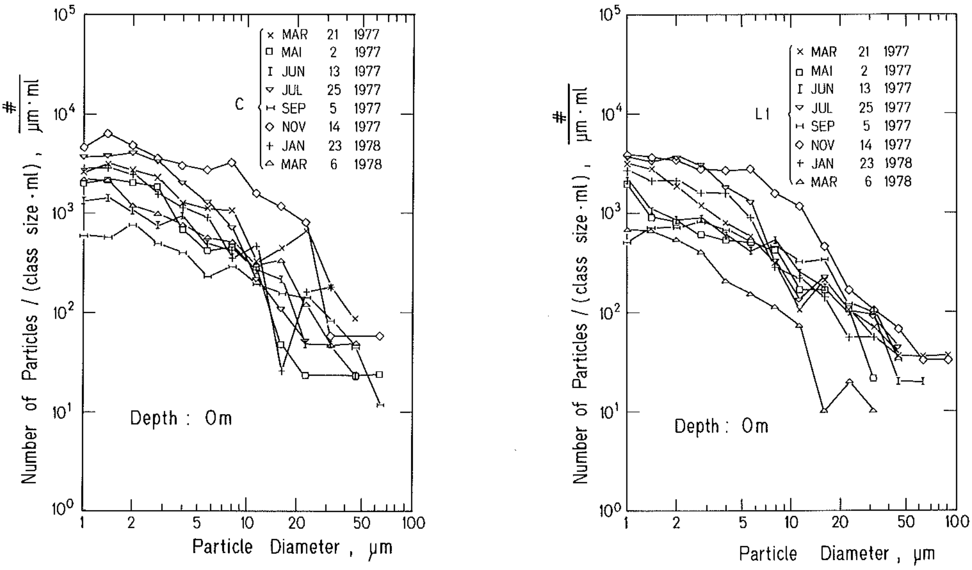


Figure 5. Measured particle size distributions, approx. equally distributed over the period of one year. a) Uncharged control-corral C, depth = 0 m; b) charged corral L1, depth = 0 m.

Abb. 5. In der Zeitperiode eines Jahres gemessene Partikelgrössenverteilungen. a) Unbelasteter Modellsee C, Tiefe = 0 m; b) belasteter Modellsee L1, Tiefe = 0 m.

Faisst [1] and Peterson [13] measured particle size distributions in sludge and coastal waters, respectively, by means of Coulter Counter. The agreement between predicted and observed slopes is much better, although the medium subrange still has a flatter slope than predicted.

The nature of the mechanism which finally results in the observed flat particle size distributions needs some improvement which shall be subject of further investigations.

ZUSAMMENFASSUNG

Die Partikelgrössenverteilungen in drei Modellseen, die im Baldeggersee, Schweiz, verankert waren, wurden als Funktion der Tiefe und Zeit mit dem elektronischen Bildschirmanalysator Zeiss Micro-Videomat bestimmt. Die Verteilungen wurden jede zweite Woche im Laufe eines ganzen Jahres gemessen. Die Probenahme erfolgte in den Tiefen 0 m, 2,5 m, 5 m, 7,5 m und 10 m (über dem Seeboden). Zwei der Modellseen wurden mit Schwermetallen belastet, der dritte blieb unbelastet und diente als Vergleich (Kontrolle). Die Form der Verteilung und die Partikelkonzentration im unbelasteten Modellsee unterschieden sich nicht von den Verhältnissen in den belasteten Seen. Es wurde festgestellt, dass die Verteilungen selbsterhaltend (self-preserving) und trotz variierender Partikelkonzentration unabhängig von der Zeit, Tiefe und Schwermetallbelastung sind. Die Steigungswerte in den logarithmischen graphischen Darstellungen der gemessenen Partikelgrössenverteilungen variierten zwischen −1,5 und −2,5.

RÉSUMÉ

Les distributions des tailles de particules dans trois limno-corrals ancrés sur le Baldeggersee, lac suisse, ont été déterminées en fonction de la profondeur et du temps avec l'écran électronique Zeiss Micro-

Videomat. Les distributions ont été mesurées tous les quinze jours pendant une année. L'échantillonnage a été effectué à des profondeurs de 0 m, 2,5 m, 5 m, 7,5 m et 10 m (au-dessus du fond). Deux des limno-corrals ont été additionnés de métaux lourds tandis que le troisième, non additionné, servait de référence. La forme des distributions ainsi que les concentrations de particules dans le limno-corral non additionné ne différaient pas de celles contenues dans les limno-corrals additionnés. Les distributions se sont avérées autopréservatrices (self-preserving) et indépendantes des apports de métaux lourds, du temps, de la profondeur ainsi que des concentrations de particules. On a trouvé qu'en moyenne les distributions dépendantes du diamètre des particules variaient entre − 1,5 et − 2,5.

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