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On Fluctuations and Mean Relations of Chemical Parameters in the Northwestern North Sea

By FRIEDRICH SCHOTT and MANFRED EHRHARDT

Über Veränderlichkeit und mittlere Zusammenhänge chemischer Parameter in der nordwestlichen Nordsee (Zusammenfassung): Auf drei Schnitten und während einer Dauerstation wurden chemische Parameter (PO_4 , SiO_4 , NO_3 , NO_2 , NH_3 , O_2) aus Schöpferproben bestimmt. Trotz relativer Konstanz der hydrographischen Faktoren zeigten einige Parameter starke Fluktuationen. Mit verankerten Strommessern wurde das Stromfeld um die Dauerstation gemessen. Aus dem Stromfeld und den an der Dauerstation gemessenen Fluktuationen der chemischen Parameter konnten horizontale Konzentrationsgradienten bestimmt werden. Die relativen Änderungen der chemischen Konzentrationen betragen bis zu 50% auf weniger als 500 m. Mit Hilfe der Diffusionstheorie werden Schätzwerte über die Zeitskala biochemischer Prozesse gegeben.

Die insgesamt ca. 400 chemischen Meßwerte ergaben eine lineare Beziehung zwischen Phosphat und Silikat. Sowohl die nichtlineare Relation zwischen Phosphat bzw. Silikat und Nitrat als auch diejenige zwischen Nitrat und dem Sauerstoffdefizit lassen Nitrat als den wachstumslimitierenden Faktor erscheinen. Aus den mittleren Oxydationsverhältnissen von Phosphat, Nitrat und Silikat ergab sich folgende Kombination:

$$\Delta \text{AOU} : \Delta \text{P} : \Delta \text{N} : \Delta \text{Si} = 276 : 1.2 : 14.7 : 7.2$$

Summary: Along three sections and at a one day permanent station chemical parameters (PO_4 , SiO_4 , NO_2 , NO_3 , NH_3 , and O_2) were determined from NANSEN bottle samples. Significant fluctuations of some of these parameters were observed. From a moored current meter array the current field was determined. It was coupled to the concentrations observed at the permanent station. The horizontal gradients of chemical components showed values up to 50% in less than 500 m distance. By use of the diffusion theory some estimates on the time scale of biochemical processes are presented.

From the entire set of about 400 observations the mean relation between phosphate and silicate was found to be linear. Nitrate seemed to be the growth limiting factor. The mean relations between phosphate and nitrate and silicate and nitrate respectively differ considerably from a linear function. The oxidative ratios for nitrate, phosphate and silicate have been calculated and the following combination has been found from these regressions:

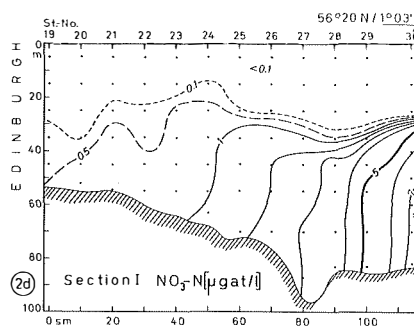
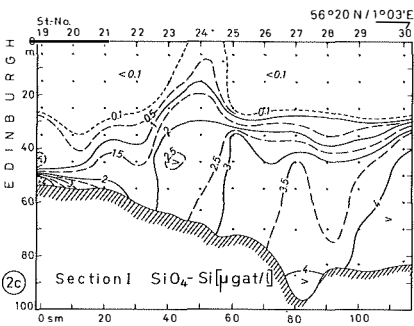
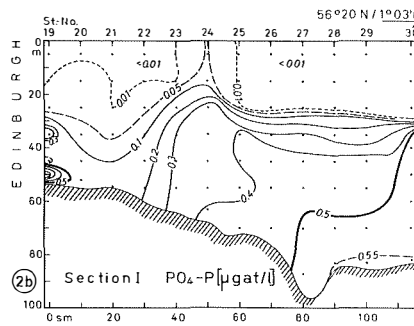
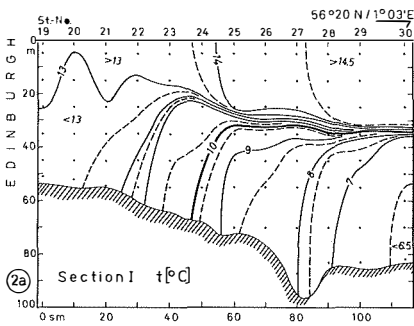
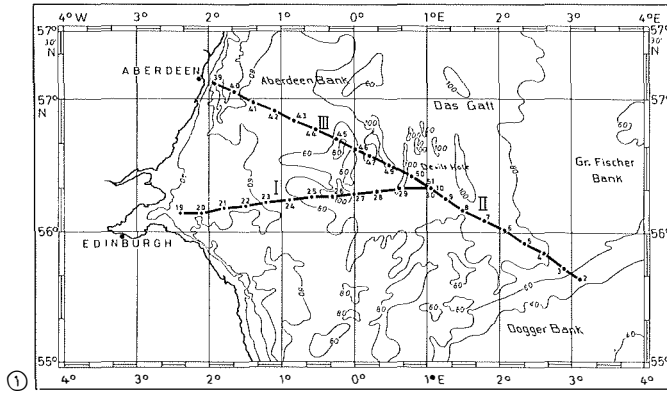
$$\Delta \text{AOU} : \Delta \text{P} : \Delta \text{N} : \Delta \text{Si} = 276 : 1.2 : 14.7 : 7.2$$

1. Observational and analytical methods

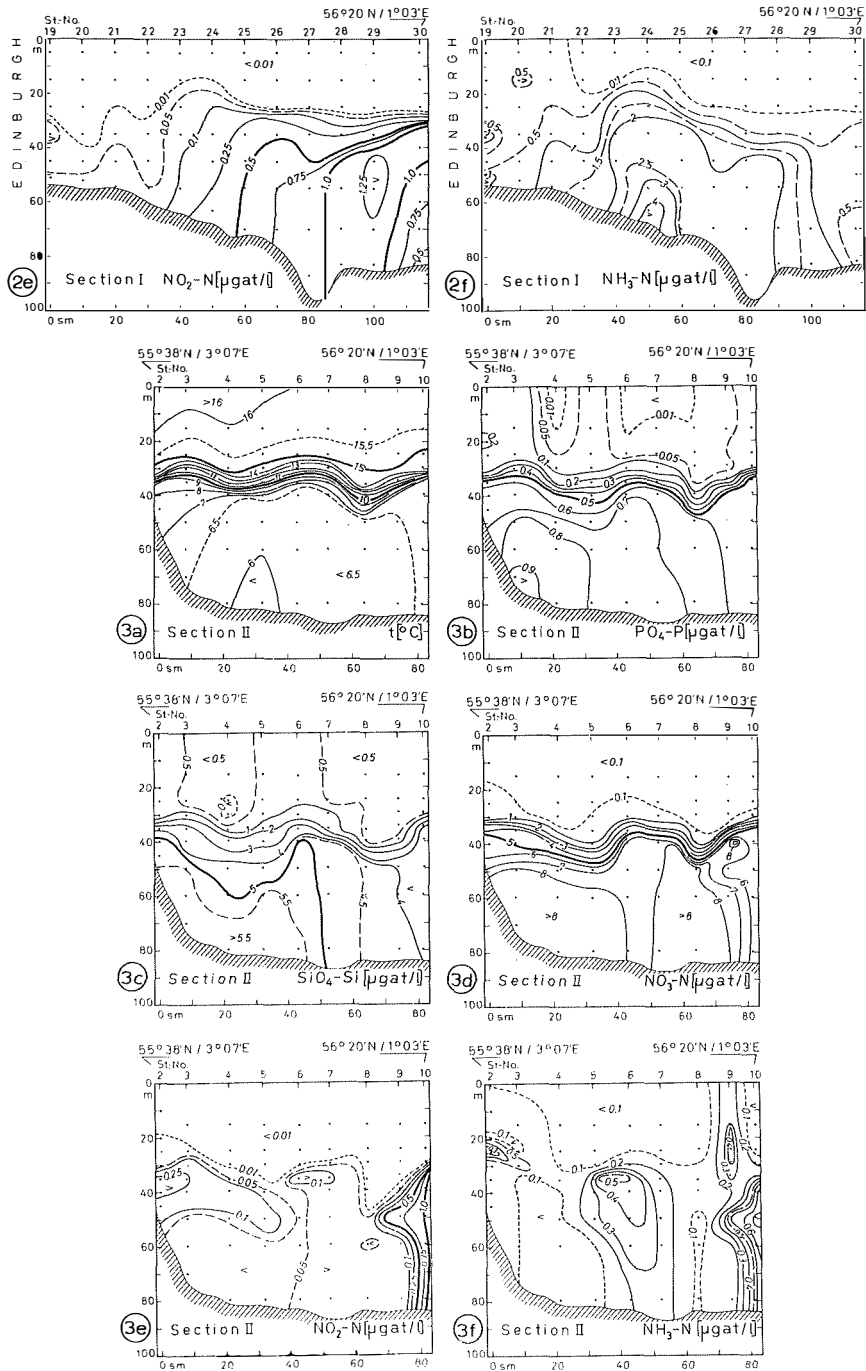
The data presented here were collected by R. V. "Alkor" during a cruise into the North Sea in September 1968. Near Devils Hole 4 current meter chains were moored in a triangle of 2 nm side length. Current speed, current direction, and temperatures were recorded with a sampling rate of 5 min. at 3 levels in each chain. Three sections were investigated (see fig. 1): between the Dogger Bank and the current meter chain, from this position to Edinburgh, and back from Aberdeen to the mooring array with

Fig. 1: Station map with courses of R. V. "Alkor", September 1968. Position of moored current meter array at intersection of the courses.

Fig. 2: Distribution at section I (Devils Hole — Edinburgh) of
a) temperature b) phosphate c) silicate d) nitrate



Tafel 1 (zu F. Schott u. M. Ehrhardt)



Tafel 2 (zu F. Schott u. M. Ehrhardt)

3. Fluctuations of chemical parameters

In those parts of the investigation areas where a thermocline was developed horizontal gradients in temperature and salinity were negligible. Quite apart from this fact rather strong horizontal gradients of nutrient concentrations could be observed. Section II was investigated 5 days later than section I. The drawings derived from the observations could not be combined into a single drawing, because at the intersection significant changes had occurred for some components during this time difference. The fact of horizontal chemical gradients is apparent especially for ammonia in figs. 2f and 3f and nitrite in fig. 3e.

Similar features are shown by the results of the permanent station at the current meter chains. The hydrographical factors changed but insignificantly as to be seen for the temperature in fig. 6a. In the same time the phosphate concentration changed for more than 30% (see fig. 6c), this fluctuation being high above the measuring accuracy of 0.01 $\mu\text{gat/l}$; similar changes occurred in the silicate concentration (fig. 6b). Ammonia showed the strongest fluctuations (fig. 6d). In spite of the small absolute values of the ammonia concentrations and the accuracy of 0.1 $\mu\text{gat/l}$ these rather regular changes seem to be real. The physical processes influencing the distribution of any property in the sea are eddy diffusion and advection. To get an idea about the horizontal extent of "clouds" or "patches" of chemical properties passing a permanent station and to get a time estimate of the biochemical processes, the advective terms have to be separated from those of eddy diffusivity. For this purpose the current measurements of the moored instruments can be used in the form of a progressive vector diagram (p. v. d.).

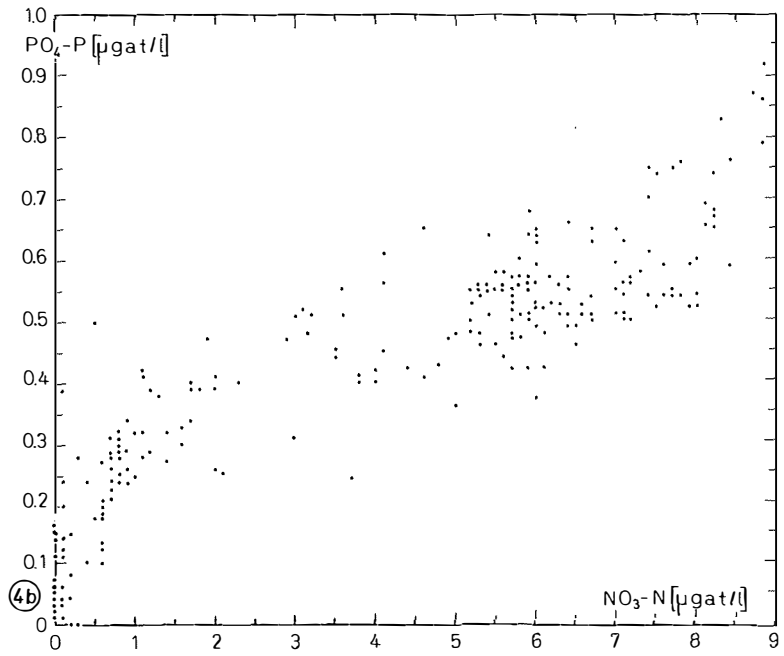
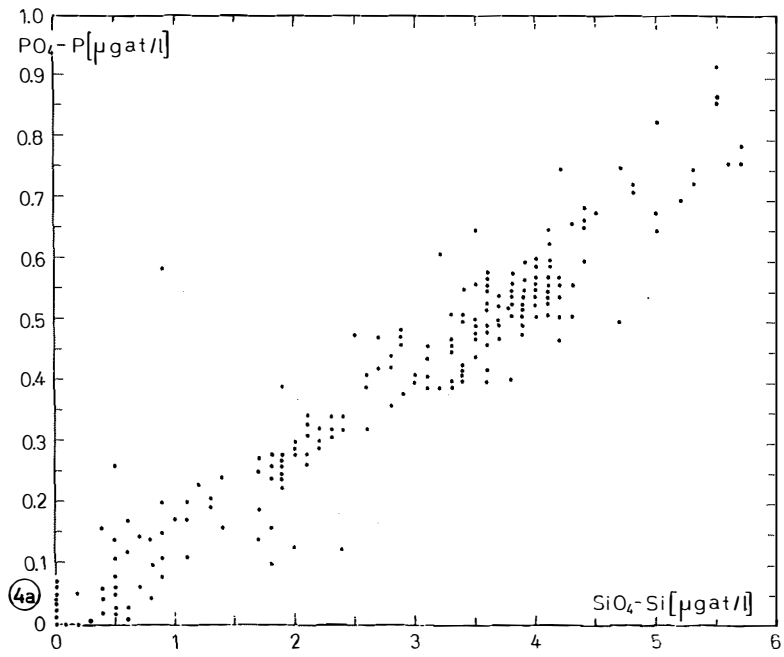
During the permanent station a north east going mean current was observed throughout the water column. The p.v.d.'s from hourly means for the positions "Ost", "West", and "Süd" from just within the thermocline are shown in fig. 7. Even at this depth of current shear the field motion around the station "Mitte" seemed to be rather homogeneous horizontally during the permanent station. If the assumption is made that in the lower layer the horizontal similarities are as sufficient, a p.v.d. may lead to useful values about the different positions of a water particle passing by "Mitte".

The p.v.d. for "Mitte" from 36 m depth shows considerably smaller distances for some water particle than those from the other stations 3 m higher up.

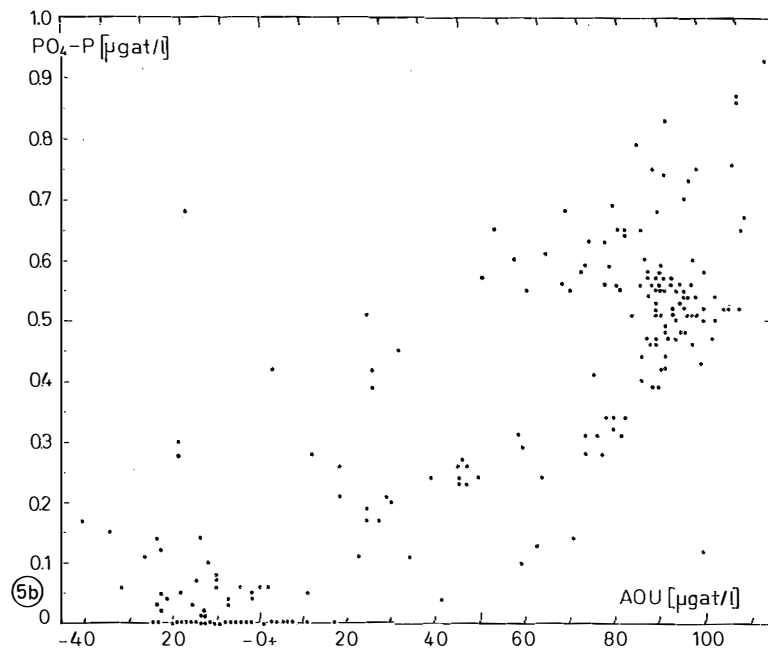
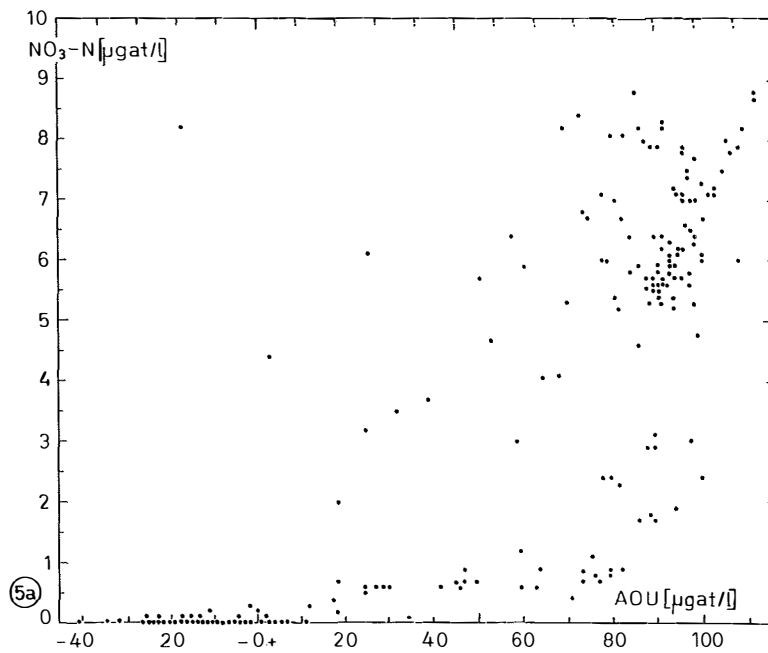
This vertical gradient in the mean currents can partly be explained by an internal wave. If in a two layered medium a current meter is positioned within the thermocline the current meter will for part of the wave period belong to the upper layer, and for part of it to the lower layer. The corresponding phase reversals result in the indication of a fictive mean current in the propagation direction of the internal wave. In fact an internal tidal wave with an amplitude of about 2 m was passing through the moorings towards North as shown by SCHOTT (loc. cit.). This wave might have contributed with a fictive mean current of up to 0.8 km per tidal period to the p.v.d.'s of stations "Ost", "West", "Süd". The 36 m current meter of "Mitte", however, was just at the lower end of the thermocline and so its p.v.d. does not show this additional fictive current component. Therefore the "rectifying effect" cannot be used to explain the current shear between the two records of "Mitte". In the following the 70 m record shall be taken as more representative for the lower water layer than the 36 m record. The latter may be influenced by other unexplained thermocline effects.

Fig. 4: Nutrient relationships:

a) phosphate/silicate b) phosphate/nitrate



Tafel 3 (zu F. Schott u. M. Ehrhardt)



Tafel 4 (zu F. Schott u. M. Ehrhardt)

From the p.v.d. at 70 m in "Mitte" the horizontal distances of points in the passing water column are calculated for every three hours, with which intervals samples were taken. These distances fall between 150 m (15—18 h at the 15th of September) and 840 m (0 to 3 h the 16. 9.). During one day a water particle had moved 1200 m towards east and 1500 m towards north from the station. Therefore the horizontal gradients of concentration are in the order of 50% per several 100 m.

In spite of the impossibility of making up statistics upon mean horizontal gradients from the few samples gathered at one location some conclusions can be drawn concerning the local time changes of concentrations.

We now suppose that concentration gradients derived from these measurements are common to the region (which will have to be subject to further investigations). It can be seen easily, that these "clouds" cannot be caused by the land drainage of the Firth of Forth. In this case, there would have to be a mean gradient from the shore to the station, but for all components — except NH³ which shows irregular distribution — the concentrations are rising offshore towards the measuring station (see fig. 2). The concentration gradients must therefore be created in the open sea. Some rough results concerning the approximate duration of the small scale biochemical processes can be obtained from the diffusion theory. Starting from the theory of a point source some concentrations which is vertically homogeneous shall be measured in a horizontal distance from some origin at time t¹).

The diffusion process will be described by

$$(1) \quad \frac{\partial s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(\mu(r) r \frac{\partial s}{\partial r} \right)$$

According to SVERDRUP (see STOMMEL, 1949) as well as JOSEPH and SENDNER (1958) the coefficient of eddy diffusivity is proportional to r:

$$\mu(r) = c \cdot r$$

The solution of the differential equation is then:

$$(2) \quad S(r, t) = \frac{S_0}{2 \pi c^2 t^2} e^{-\frac{r}{ct}}$$

The ratio of concentrations at r₁ and r₂ at time t is

$$K_t = e^{\frac{r_1 - r_2}{ct}}$$

For different time values t_a and t_b this relation yields

$$(3) \quad K_b = e^{\frac{\ln K_a}{1 - \ln K_a} \frac{c(t_a - t_b)}{r_1 - r_2}}$$

¹) The condition of vertical homogeneity is rather good approximated as shown from sections and isoplethes. This results from the rather low vertical stability resp. high vertical eddy diffusivity coefficient between bottom and thermocline.

(Plate 4)

Fig. 5: Oxidative relationships:

- a) nitrate/apparent oxygen utilization (AOU)
- b) phosphate/AOU

After MUNK, EWING and REVELLE (1949) — see BOWDEN (1966) — c takes values of about 1 cm/sec for values of r between 10^3 and 10^8 cm. For the scale up to 5 km in which we are interested here this value of c was proved by dye diffusion experiments carried out by JOSEPH, SENDNER and WEIDEMANN (1964) in the North Sea.

Suppose now $K_a = 50\%$ at $r_1 - r_2 = 500$ m. 24 hours later this difference will fall to 27%, after 4 days to 14% according to (3). This means that after about one week horizontal concentration differences of the observed small scale would have to be considerably diminished by turbulent diffusion. If a great many similar experiments would reveal horizontal gradients of the observed size the biochemical processes creating these clouds would apparently take not much longer than one week. The fastest reaction seems to take place with ammonia and seems to be responsible for its scattering appearance.

The extent of the clouds seems to differ considerably in scale. Besides the small scale variations observed at the permanent station larger clouds seem to be present with an extent of up to 10 nm. Their concentration gradients may cover more than one order of magnitude (see for ex. figs. 3e, 3f). According to the diffusion formula (3) an initial concentration gradient 1 : 10 per 20 km would have to fall to 1 : 4 after 6 days and after 12 days to 1 : 2. This estimate again indicates that in order to maintain the high horizontal gradients the biochemical processes ought to pass in a time scale of about one or two weeks. To get better estimates the diffusion velocity which has mostly been determined from near surface experiments will have to be known more accurately for the deeper layers.

4. Relations in the chemical parameters

a) Nutrient relationships:

Phosphate/silicate (see fig. 4a)

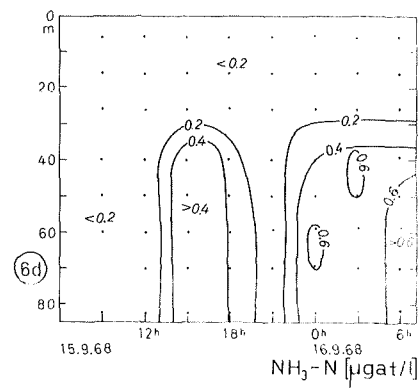
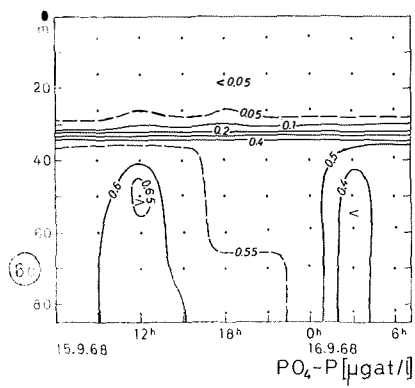
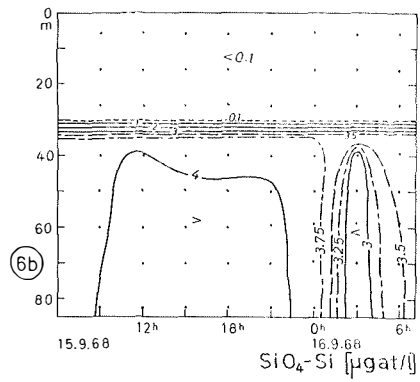
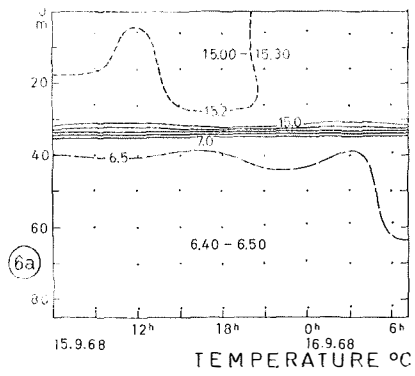
Phosphate and silicate show a positive linear correlation with a coefficient of correlation $r = 0.97$. The regression line which intersects the origin has a slope of $\Delta \text{Si} / \Delta \text{P} = 7.25$. These results are somewhat different from the findings of STEFANSSON (1968) who, in the northern Irminger Sea, found a non linear correlation between phosphate and silicate. Certainly, the silicate concentrations in the Irminger Sea are significantly higher than those in the sea area under investigation but, in a comparable concentration range, the agreement with our results is nevertheless a rather good one. For phosphate concentrations of 0.4—0.5 $\mu\text{gat/l}$ STEFANSSON (loc. cit.) found a $\Delta \text{Si} / \Delta \text{P}$ ratio of 6.9—8.1 covering the figure 7.3 that we found.

Nitrate/silicate: The nitrate/silicate relationship seems to be a non linear one the plot having more or less the appearance of a saturation function. In the upper nutrient deficient water layer silicate is still present while the nitrate concentration reaches zero. In the deep water, silicate concentrations are increasing faster than nitrate concentrations. Nevertheless, a linear regression line has been computed which intersects the abscissa at 0.25 $\mu\text{gat/l}$ $\text{SiO}_4\text{—Si}$. The slope is 1.57, the coefficient of correlation is $r = 0.91$.

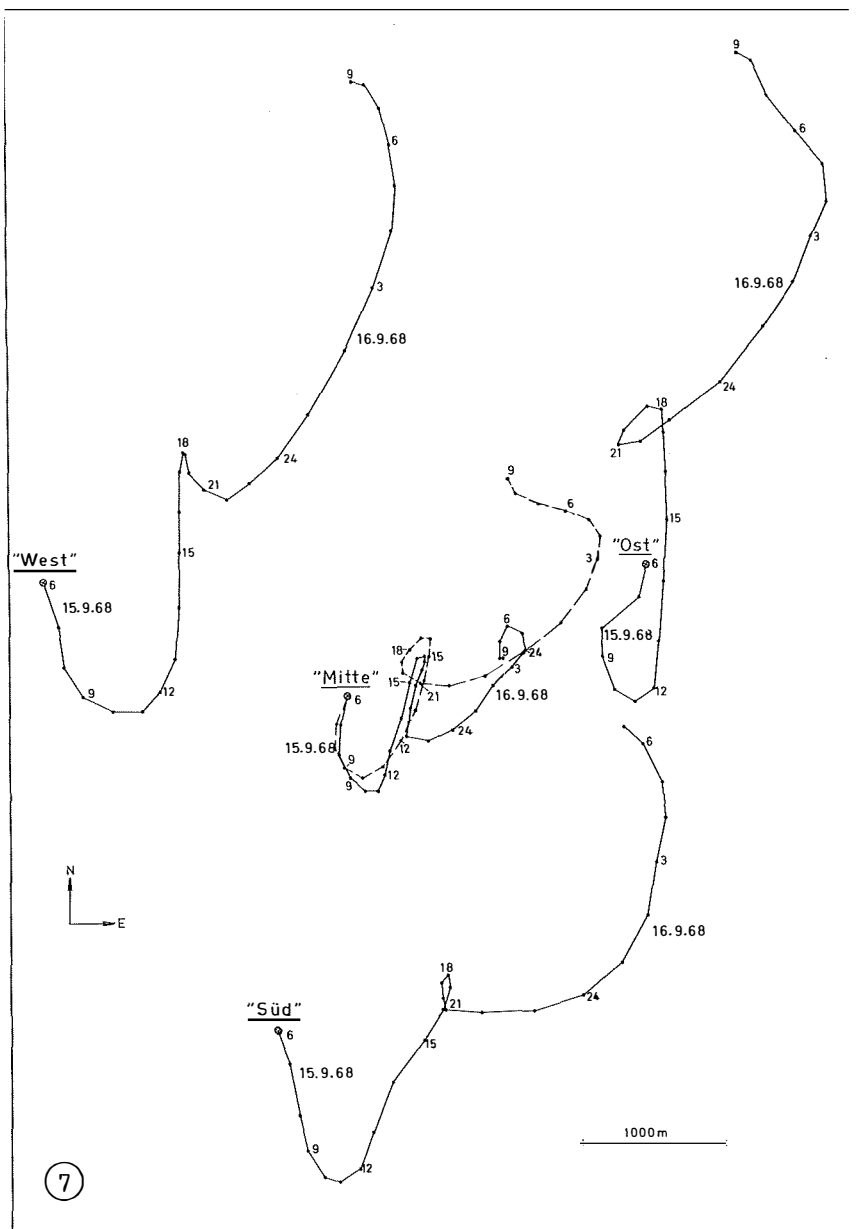
Nitrate/phosphate (see fig. 4b): Since the phosphate/silicate relationship is a linear one with a high coefficient of correlation and the nitrate/silicate relationship may be described by a sort of saturation function, the plot of nitrate vs phosphate should

Fig. 6: Isoplethes at a permanent station of R. V. "Alkor" at $\varphi = 56^{\circ}21.0'N$, $\lambda = 1^{\circ}0.3'E$ (water depth 83 m):

a) temperature b) silicate c) phosphate d) ammonia



Tafel 5 (zu F. Schott u. M. Ehrhardt)



Tafel 6 (zu F. Schott u. M. Ehrhardt)

have the same general appearance. The correlation coefficient of the linear correlation is $r = 0.90$. The regression line indicates, that phosphate is still present in a concentration of about $0.1 \mu\text{gat/l}$ while the nitrate concentration reaches zero. These observations strongly suggest that in the sea area under observation nitrate is the growth limiting factor. This conclusion is further supported by the nitrate/AOU relationship which indicates a preformed nitrate concentration close to zero.

Though the authors are quite aware of the fact that the computation of oxygen utilization values and oxidative ratios in this particular sea area is open to some criticism they nevertheless include the results in this paper. The difficulties encountered in the computation are due to the relative shallowness of the water and the peculiar weather and atmospheric conditions in this area causing surface oxygen saturation values which differ considerably from 100%. Even so, the results seem to justify their presentation.

b) The oxidative ratios

Nitrite/AOU (see fig. 5a): Though there is a wide scatter of points a regression line has been computed which indicates a very minor quantity of preformed nitrate. The coefficient of correlation is $r = 0.86$. In fact, considering the ratios in which the different nutrients are incorporated into planktonic organisms the concentration of preformed nitrate is the lowest one of all computed conservative nutrient concentrations.

Phosphate/AOU and silicate/AOU: The plot phosphate against the AOU (see fig. 5b) shows two aggregations of points corresponding to the well aired nutrient deficient upper water layer and the nutrient rich water below the chemocline. The coefficient of correlation is $r = 0.84$. The silicate/AOU relation has a similar appearance. The coefficient of correlation is 0.71.

The combination of oxidative ratios: From the linear least squares regressions the oxidative ratios have been computed which are not quite in agreement with theoretical expectations. This is especially true for the silicate/AOU relation. The reason for this discrepancy might be the composition of planktonic organisms in this particular sea area besides the influences which have been demonstrated amply by REDFIELD, KETCHUM and WILLIAMS (1963) and STEFANSSON (loc. cit.). Furthermore, the land drainage from the Edinburgh area will most probably also contribute to this phenomenon. The oxidative ratios as computed by the least squares regression method are the following:

$$\Delta \text{ AOU} : \Delta \text{ P} : \Delta \text{ N} : \Delta \text{ Si} = 276 : 1.2 : 14.7 : 7.2$$

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Fig. 7: Progressive vector diagrams at 4 stations (position "Mitte" $56^{\circ}21.0'N$, $1^{\circ}0.3'E$). Depth of current meter 31.8 m for position "West", 32.4 m for "Ost", 33.8 m for "Süd", 36 m for position "Mitte" (full line), and 70 m for "Mitte" (dashed line).

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