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Synthesis of research on nutrients in the Southern Bight of the North Sea

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Synthesis of research on nutrients in the Southern Bight of the North Sea[1]

J.P. MOMMAERTS[2], W. BAEYENS[2] and G. DECADT[3]

Introduction

When the "nutrients" group was set up in 1977, the problems had already been clearly set forth. Later on, they were regularly recalled, but progress is very slow. Such is the case of a fundamental question which concerns the dynamics of our coastal eco-system and which was raised for the first time six years ago (!) within the framework of the "Sea Project" : Is there a limiting element ? What is it ? How does it limit planktonic production ?

There is clearly a need here for some research which no-one has to date been disposed to fulfill.

It is however also in the biogeochemical cycle of an element such as nitrogen (rather than that of carbon) that the clear translocations between biological compartments are most apparent.

A major part of the problems is obviously due to the technical difficulties associated with measuring the uptake and excretion activities and the practical difficulties associated with measuring the inputs on the borders of the system.

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1. This paper is a part of the report "Synthesis of research on nutrients" OM/77-78/02 of the Belgian National Program, by the same authors.

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The research undertaken during the 1977-1978 period covered two main aspects :

1) *the regulation of phytoplanktonic activity* [based on work of A. Bertels, Excretie en primaire productiebepaling in de Noordzee, personal communication, 1978; J. Nijs et al., Bruto resultaten van de partikulaire en opgeloste primaire produktie voor Oostende - Calais - Hansweert, personal communication, 1978] with

a) examination of the seasonal curves observed in the three media in order to determine :
   1° the periods at which the concentrations of certain nutrients fall to a value such that one can reasonably estimate that they are limiting ("kinetic" limitation), G. Decadt et al., Seizoenvariatie en ruimtelijke verspreiding van de nutriënten in de Zuidelijke Noordzee, personal communication 1978.
   2° the periods at which the N/P ratio varies considerably from its mean value (~ 7 in weight) ("stoechiometric" limitation).
b) enrichment experiments (conducted at sea) to determine which nutrient (therefore limiting) can stimulate photosynthesis.
c) enrichment experiments conducted in a reactor to determine the nature of the limiting element and to define the nutrient-uptake speed relation.
d) dosages of nitrate-reductase in the phytoplankton to determine if a capacity for the use of NO_3^- exists, even in the presence of NH_4^+, M. Somville, Nitrification et dénitrification dans l'estuaire de l'Escaut, Dosage de la nitrate réductase en Mer du Nord et dans la partie aval de l'estuaire de l'Escaut, personal communication 1978.

2) *the search for coherence* (means of translocation)

If the direct (or calculated) measurements of the flows of consumption and regeneration by the biological compartments, plus the inputs and outputs at the borders of the system are correct, then the variations of nutrient concentrations observed in the medium must be coherent with the resulting flow. The following points are discussed :

a) method of analysis of nutrients,
b) seasonal variations (time and space) of nutrients in the Belgian coastal zone,
c) the flows implied by these variations.

Results

1.- REGULATION OF PHYTOPLANKTONIC ACTIVITY

1.1.- Recall of a few theoretical aspects

Just as light controls the intensity of primary production, the concentration of one or more nutritious elements (one generally thinks of NO_3^-, NH_4^+, PO_4^{---}, $Si(OH)_4$, but there may be others) influence the rate of biosynthesis and play a determinant role in the interspecific competition within the phytoplankton.

A mathematical model of the ecosystem must necessarily take into account the regulating effect which the limiting nutrient exercises on :

1°) the uptake speed U of this nutrient S : it is generally accepted that the relation has a hyperbolic form, described by Michaëlis and Menten :

$$U = U_{max} \times f(S)$$

with

$$f(S) = \frac{S}{K_s + S}$$

varying between 0 and 1 ;

2°) the uptake speed of other elements (nutrients or constitutive elements such as carbon) with two approaches :

a) *the simple approach* : the speeds are in the same ratio as the constituents of the living matter (phytoplankton) : 41 : 7.2 : 1 for C : N : P (in weight). The ratios C/N = 5.7 and its inverse

$$\frac{1}{\text{Yield}} = Q = 0.18$$

are particularly used.

b) *the complex approach* : several works indicate that a distinction should be made :

α) between the metabolism of *carbon* (photosynthesis, regulated primarily by light) and the *limiting nutrient* (uptake, regulated primarily by the ambient concentration);

β) between the *uptake* and *growth* mechanisms.

In actual fact, whatever Monod might have written, the equation which best describes the growth (cf. net particulate production) does not necessarily have the same Michaëlian form as that which describes the uptake : growth will be achieved rather by drawing from an internal reservoir which is constituted during a period of non-limitation. Droop (1973) proposed a new formula taking into account the very minute studies made in chemostats :

- uptake (e.g. in nitrogen) :

$$U = U_{max} \times \frac{S}{K_s + S}$$

- growth (e.g. in carbon) :

$$\mu = \mu_{max} \left(1 - \frac{Q_0}{Q}\right)$$

where $Q = \frac{S}{C}$ in the cell (quota)[1], with S is nitrogen for example and Q_0 is the minimum value of quota;

- evolution of intracellular quota :

$$\frac{dQ}{dt} = u - \mu Q$$

This formula, having been established for a system of constant light and based, as regard growth, on numbers of cells, cannot therefore be directly used in an ecosystem model.

Also taking into account the restriction referred to in § (α), Mommaerts (1978) proposed a model which incorporated these various elements in a logical manner :

- gross primary production (carbon) :

$$\frac{dC}{dt} \times \frac{1}{C} = U^C = U^C_{max} \times f_1(I) \times f(Q)$$

where U^C_{max} is the maximum speed of uptake of C (per unit of C), $f_1(I)$ is the function of light intensity, $f(Q)$ is the function of internal pool of nitrogen (ex.: $1 - \frac{Q_0}{Q}$) ;

1. The form in which the nutrient reserve is stored is not specified. What is important here is that there is an approach per model which takes into account the biochemical composition of the phytoplankton, cf. Nijs et al., personal communication, loc. cit.

- uptake of nitrogen (if limiting) :

$$\frac{dN}{dt} \times \frac{1}{C} = U^N = U^N_{max} \times f(N) \times f_2(I)$$

where U^N_{max} is the maximum speed of uptake of N (per unit of C), $f(N)$ is the function of the external concentration of nitrogen, $f_2(I)$ is the function (to be specified) of light intensity (perhaps, function of stock of ATP available);

- evolution of the intracellular quota of N :

$$\frac{dQ}{dt} = U^N - (U^C - r)\, Q$$

where r is the rate of respiration.

Comment

Since Q can vary only within certain limits, the models provides for excretion (nitrogen or carbon, depending on the case) of the excess assimilated. In this, it is coherent with the observations of Fogg (1971) who writes that the excretion is much more important in an oligotrophic medium, or other more recent observations, regarding the photoreduction of O_2 (with release of glycollate) which can be taken as a means of absorbing an excess reducing power brought about by photosynthesis, cf. Bertels, personal communication 1978, loc.cit.

1.2.- Research into the limiting element

1.2.1.- *Theoretical considerations*

It may be useful to recall that there are two fundamental approaches to this problem :

1°) *the stoechiometric approach* : the study of the N/P ratio (for example) in water makes it possible to forecast the nature of the limiting element or at least that which would be the first limiting at the end consumption.

2°) *the kinetic approach* : below a certain concentration saturating value (in practice, less than 10 times K_s), the negative retroaction on the assimilation flow can effectively exist. Since the most commonly cited values of K_s (different phytoplanktonic species and different biotopes) are grouped around 1 µg at/ℓ of N(14 mg/m^3) or P(31 mg/m^3), one can

see that these two nutrients can occasionally be limiting, taking into account that the ranges observed in the North Sea vary between 3 and 30 µg at/ℓ for N and 1.4 to 3 µg at/ℓ for P (see also § 1.2.2.).

1.2.2.- *Seasonal variations of the main nutrients in the three zones*

Calais and Hansweert

The table 1 contains a few pieces of information (in µM/ℓ) extracted from the data of the Belgian team and also from the data issued by P. Mangelsdorf of the Biologisch Anstalt Helgoland, personal communication, 1978.

Table 1

	$NO_3^- + NO_2^-$	NH_4^+	PO_4^{---}	SiO_2	Source
Calais					
04.04.78	5.45	3.18	0.50	2.2	OM/1978 : 15
07.04.78	4.40	3.75	0.73	1.0	"
11.04.78	19.33	3.76	0.88	3.2	"
17.04.78	8.48	0.40	0.40	3.5	"
18.04.78	11.08	2.81	0.51	3.0	"
Hansweert					
05.05.77	215	61	-	-	OM/1978 : 21
07.04.78	261	28.17	-	-	"
21.04.78	191-249	18.0-36.3	-	-	"

Belgian coastal region

The seasonal variations in the different nutrients are made known to us by internal reports, cf. Mommaerts et al., personal communication, 1977, Decadt et al., personal communication, 1978. One can see that the ranges of concentration are roughly as given in table 2.

These results are discussed more particularly in § 2.3 and 2.4 as regards the precautions to be taken for their interpretation, the spatial and temporal variations and the flows they imply.

Discussion

The few results collected here are insufficient to establish a final comparison of the three biotopes : let us say that the presumption of a greater wealth in Ostend than in Calais is not invalidated. The even greater

Table 2

	1977	1978	
$NO_3^- + NO_2^-$	0 - 850	100 - 2000	in µg N/ℓ
	(0 - 60)	(7 - 143)	in µM/ℓ
NH_4^+	0 - 600	25 - 175	in µg N/ℓ
	(0 - 43)	(1.8 - 12.5)	in µM/ℓ
PO_4^{---}	40 - 300	25 - 300	in µg P/ℓ
	(1.3 - 9.7)	0.8 - 9.7)	in µM/ℓ
SiO_2	300 - 3000	250 - 1000	in µg Si/ℓ
	(10.7 - 107)	(8.9 - 35.7)	in µM/ℓ

wealth of the Scheldt cannot of course be questioned. As regards Ostend and Calais, one can see that the nitrogen and phosphorous are likely to fall to levels where they are kinetically limiting (if one acknowledges that the K_s of the phytoplanktonic organisms of the eutrophic waters in general exceed the unit). This would also be the case of the silica in Calais. In Ostend, and outside the main nitrogen peaks, the N/P ratio is always less than 7, which indicates that, in the case of prolonged consumption, the nitrogen would be exhausted in first place.

In conclusion, one cannot define the exact nature of *the most probable* limiting element without help of a more direct approach : enrichment experiments conducted at sea, enrichment experiments conducted in a reactor, taking into account all the "management parameters" who make the establishment of the exact relationship possible between *in vivo* and *in vitro* experiences (use of chemostat, controlled light, discarding effects of non limiting elements, etc.).

1.2.3.- *Enrichment experiments conducted at sea*

Stimulation effects on the primary production by adding NO_3^- (presumed to be limiting) have been studied during two cruises :

- in October 1977, positive stimulation effects have been observed at Ostend and at Hansweert (Nijs et al., 1978, loc. cit.);
- in April 1978, no stimulation effects have been observed at the three places under study (Ostend, Calais, Hansweert) [cf. Nijs et al., 1978, loc. cit.].

Discussion

One must first take into account the fact that this type of experience is not at all perfect in his conceptual formulation : on the contrary of the speed of *uptake* of the tested nutrient, the speed of *synthesis* of living matter is only indirectly related to the concentration of the limiting substrate (see also § 1.1.). Falkowski et al. (1975) have more particularly shown that the absence of stimulation can result from the competition between carbon dioxide and nitrate in the production scheme of ATP during the cyclical photophosphorylation processes. The absence of stimulation by nitrate, observed in the spring-time, near Ostend and near Calais, can also be a consequence of the limiting effect on the primary production due to other nutrients (PO_4^{---} for instance) :

Table 3

Concentrations in µM/ℓ

	NH_4^+	NO_3^-	PO_4^{---}	SiO_2
Calais (4-4-78)	3.18	5.30	0.50	2.2
Ostend (5-4-78)	5.38	16.81	1.91	7.30

The stimulation effectively observed in autumn is not however understood since the concentrations of all nutrients were high. Furthermore, one observes that the curves observed are not at all of the Michaëlis-Menten type (see linear transformations in fig. 1).

These few results therefore leave us perplexed; it is to be regretted that these experiments were limited to a single type of nutrient.

1.2.4.- *Enrichment experience in a reactor*

This study which is currently under way and which forms the object of a research simultaneously conducted by the Analytical Department (V.U.B., Brussels) and the "Unité de Gestion des Modèles Mer et Escaut", sets out to determine the limiting element and establish kinetic curves which describe the overall substrate uptake regulation for natural populations in the North Sea. It is an experiment inspired in part by the experiment of Harrison and Davis (1977).

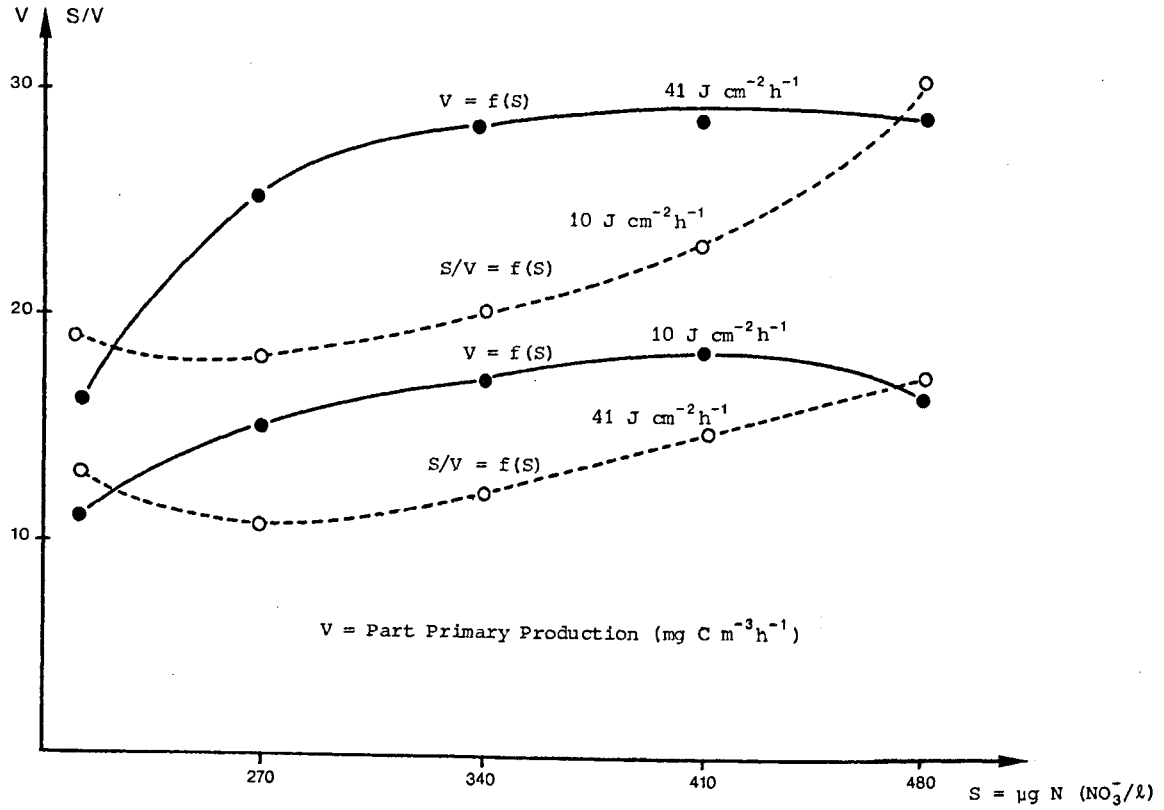

fig. 1.

Sampling point 33
(18-10-77)

1.3.- Ammonia-nitrate-reductase interaction

The phytoplankton can use the nitrate and ammonia as sources of nitrogen. This latter form would however be used preferentially since the cells thus dispense with a reduction.

To this must be added that, above a certain threshold of concentration (~ 1 µM NH_4^+/ℓ), the synthesis of the nitrate-reductase would be curbed. (e.g. Eppley et al., 1969). Since concentrations of NH_4^+ of more than 1 µM are currently observed, the assimilation of NO_3^- would in theory be virtually impossible in the three biotopes studied.

To check out this assumption, dosages of nitrate-reductase were regularly performed (Somville, personal communication, 1978, loc.cit.) by testing cellular extracts with a coenzyme in a reduced form (NADH in a non limiting concentration and in the presence of NO_3^-. The nitrite appearing in the extracts is a mesure of the degree of the enzymatic activity of the nitrate-reductase.

Results

In winter, the enzymatic activity cannot be determined except for a few offshore stations. This does indeed seem to be a question of detectability (very few phytoplankton) rather than a question of the presence or absence of enzyme.

In spring and in summer, nitrate-reductase is to be found virtually everywhere, particularly so the nearer one comes to the coast, whereas the NH_4^+ is generally present and sometimes very abundant (e.g. the greater enzymatic activities in the Scheldt).

In conclusion, the capacity for use of NO_3^-, even in the presence of NH_4^+ seems to have been established for our regions.

2.- THE SEARCH FOR COHERENCES

2.1.- Terms of the problem

By virtue of the principle of the conservation of matter, the net variations of concentrations of dissolved nutrients must be coherent with the direct measurements of the flows of consumption and regeneration (uptake by primary production and regeneration by microbiological processes

especially) as well as the input and output flows at the borders of the system.

As regards the latter, we have already seen for the South Bay of the North Sea (Nihoul et al., 1977) that the input and output flows are virtually equal (namely $\simeq 300.10^3$ tons N/year) and that the Scheldt and the coastal region contribute a quantity in the order of 10^4 tons N/year. Both this coastal input and the probable error on the "flows" balance sheet are small in the light of the circulation of matter exclusively due to biological processes. On the basis of a net primary production of some 200 g C/m^2 per annum, one calculates a consumption of some 200.10 tons N/year.

It is therefore very useful to compare the variations in biological activities with the variations in nutrients in the three zones (Calais, Ostend and Hansweert) studied by the "Organic Matter" group (cf. these proceedings).

Unfortunately, there are currently two problems being encountered :

a) with the exception of the Belgian coastal region which is regularly visited within the framework of the Monitoring national programme, the Channel and the Calais zone are known to us only through measurements fairly spaced out in time, and originating from various sources (problems of intercomparability, a.s.o., see § 1.2.2.). As regards the Scheldt, which though well followed up as regards nitrogen (Somville, personal communication, 1978, loc.cit.), the problems are obviously more complex because of the specific hydrodynamic mechanisms and the pelagic bacterial processes unknown at sea : nitrification and denitrification. The case of the Scheldt will therefore not be dealt with in this synthesis.

b) As regards the spatiotemporal variations in the concentrations of nutrients in the Belgian coastal zone, unexpected phenomena have been observed, phenomea never observed (or the significance of which was not realized) in the former network (1970-1975) which was also considerably more extensive, and as a result visited much less frequently. This double problem (significance of data originating from different sources, phenomena with no common measure with known biological mechanisms) has given rise to a great deal of thought and serious reconsideration.

The following paragraph in fact illustrates the need for great caution in the interpretation of nutrient analysis results when precise functional relations with biological compartments are studied. It is therefore not so much the reliability of the analyses which is questioned, but rather the need for a dynamic interaction between biologists and analysts.

2.2.- Discussion of analytical methods

2.2.1.- *Brief reminder of the techniques generally studied*

2.2.1.1.- *Conservation and pre-treatment techniques*

In all cases, the parameters are determined on samples which are neither filtered nor dialysed and conserved in plastic containers at - 20 °C , except in the case of PO_4^{---} (glass containers, addition of chloroform and cold storage).

2.2.1.2.- *Analytic methods*

a) Phosphorous

The analysis only concerns orthophosphate (dissolved and particulate). One induces the formation of a phosphomolybdic complex with a well defined pH (H_2SO_4 0.6 N), so as to prevent interference from the silica. This complex is reduced with ascorbic acid to obtain a blue colouring which absorbs particularly at 830 nm .

b) Ammonia

With Na phenolate and Na hypochlorite, the ammonia forms a blue complex of indophenol, the absorption of which depends on the pH and is measured at 625 nm . The precipitation of Ca and Mg hydroxides is prevented by the addition of EDTA on the one hand, and a mixture of Na and K tartrate and Na citrate on the other. A sample of aged seawater is used for checking.

c) Nitrate + nitrite

There are in fact two measurements :

1°) direct measurement of the NO_2^- using a classical diazoreaction with the sulfanilamide, coupled with a reaction with the N-naphtylethylene-diamine so as to induce a purple stained complex, the absorption of which is measured at 540 nm.

2°) measurement, using the same method, of the total ($NO_3^- + NO_2^-$) following

reduction to NO_2^- by passage on a column of cupro-cadmium. The pH of the sample does not play an essential role whilst it ranges between 5 and 9 .

d) Silica

One induces the formation of a yellow molybdic complex with a pH of approximately 1.6 so that there is little interference from the phosphates (furthermore the addition of oxalic acid considerably reduces the staining due to phosphorous which becomes negligible up to 5 parts for 1 part of silicium). This complex is reduced by amino-1 naphtol-2 sulphonic-4 acid or ascorbic acid so as to obtain a blue staining which is measured either at 815 nm or 765 nm .

2.2.2.- *Outline of the main problems raised by these methods*

In order to ensure correct *interpretation* of the analytical results and especially of their significance from the point of view of functional relations with the biological compartments, the following problem should be discussed : *Is the information obtained precisely that which is sought ?* In actual fact, the analytic methods described above provide the *total* concentrations of certain forms of nutrients whereas a more detailed speciation would be preferred.

Ex :

- the total orthophosphates measured concern the dissolved and particulate phases (adsorbed or solid). Moreover, neither the polyphosphates nor organic forms are measured although it would be interesting to know more about them.
- as regards the ammonia, there is no doubt that the easily degradable forms (ex. urea, amines) play a major role in the nitrogen cycle. To what extent can these forms interfere in the consumption patterns of the actual measured forms (NH_4^+, NO_2^- + NO_3^-) ? To what extent should a prior UV irradiation stage, before analysis - as recently introduced e.a. by UK teams - improve our knowledge in uptake mechanisms ?
- as regards the silica, one is faced with a fairly particular problem : considering the values of Si dissolved in the medium, one always finds values lower than those expected from the thermodynamic balances between the various solid forms (quartz, amorphous silica, carapaces of diatoms, etc.) and silica in solution. This situation results

either from the absence of some solids or from the biological activities which prevent the balance being struck. Furthermore, one can ask oneself if current analytic methods do not influence this balance in such a way as to provide incorrect results. Inversely, could the dialysis - which was already sometimes used and which is based on a completely different principle of analysis - not provide more information on this problem ?

2.3.- Spatial and temporal variations in the concentrations of NO_3^- , NO_2^- , NH_4^+ , PO_4^{---}, SiO_2 in the Belgian coastal zone

The data are drawn out from internal reports (Mommaerts et al., personal communication 1977, loc.cit.; Decadt et al., personal communication 1978, loc.cit.). These data give some idea of the major variations which occurred in the Belgian coastal zone in 1974, 1977 and 1978.

One can synthesize the information as follows :

- during the periods of (May-June) and/or (August-September) there sometimes occur very important peaks in concentration as regards the (NO_3^- + NO_2^-) and the NH_4^+. These peaks do not correspond to the overall summer consumption-winter regeneration plan which can be observed for the other nutrients.
- the variations (both spatial and temporal) in (NO_3^- + NO_2^-) and NH_4^+ are more or less associated. This applies also to those of the PO_4^{---} and SiO_2. The behaviour of these two couples is however radically different.
- regionally, the greatest values are always observed near the mouth of the estuary (Sector III) outside the peak periods. The map with the sectors is given in figure 2. The general trend is one of a decreasing coastal-offshore gradient (see figure 3). Inversely, when there is a seasonal maximum (peak) the highest values are observed offshore and to the west (Sector II). There is no longer a coast-offshore gradient, but high concentration nuclei situated rather more offshore than on the coast or in the estuary (see figure 4).

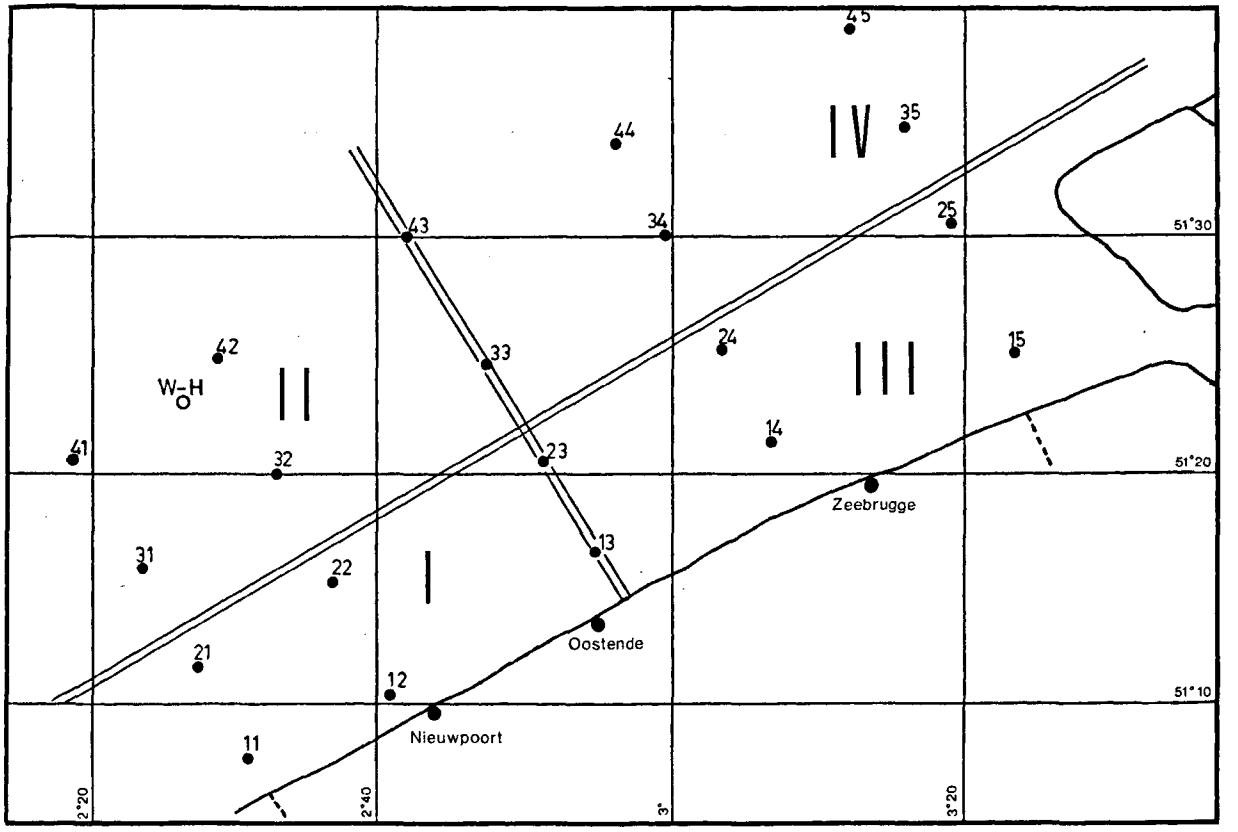

fig. 2.

Belgian coastal zone (sectors)

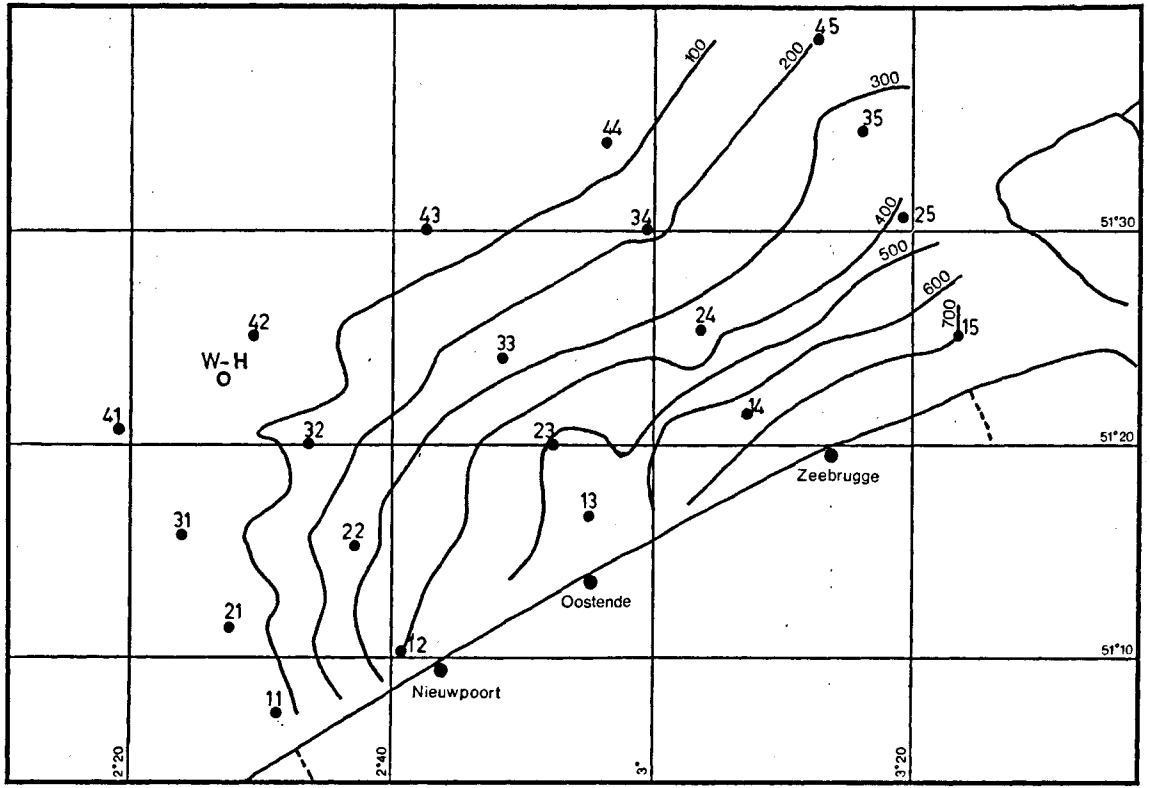

fig. 3.

Spatial distribution of $NO_2^- + NO_3^-$ (µg N/ℓ)
(April 1978)

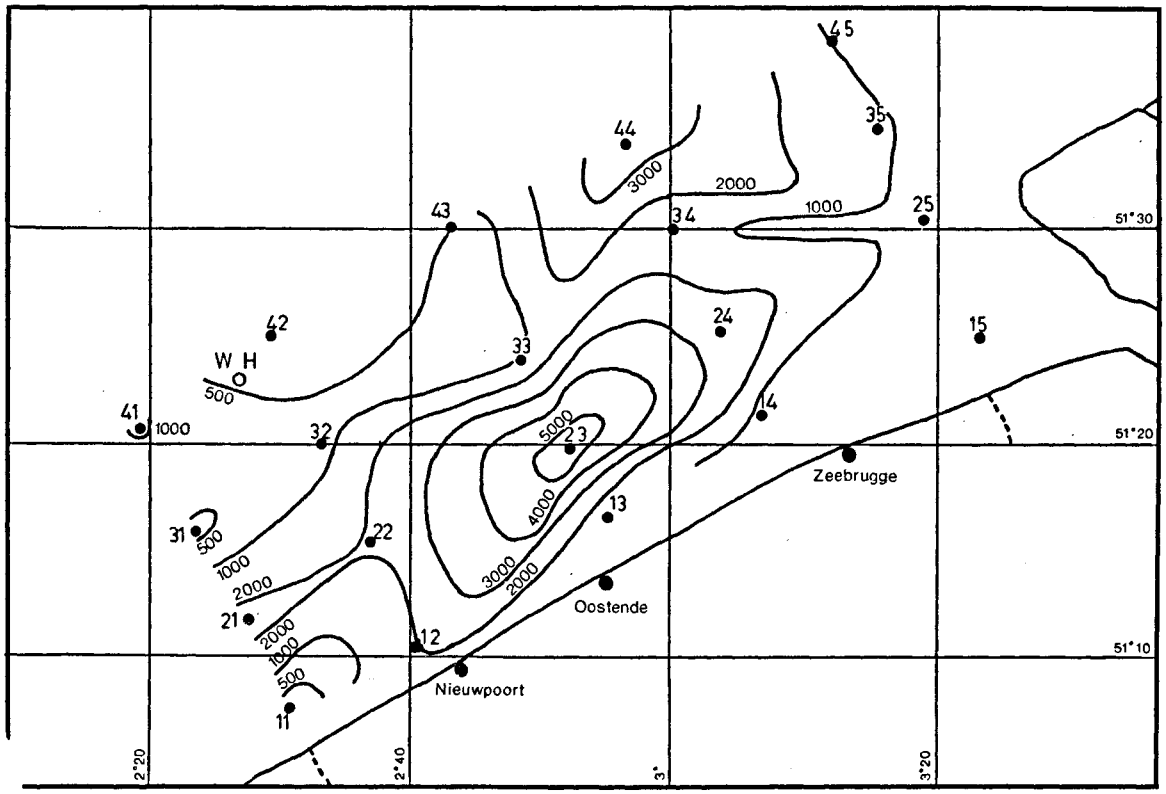

fig. 4.

Spatial distribution of $NO_2^- + NO_3^-$ (µg N/ℓ)
(June 1978)

2.4.- Flows of net consumption and net regeneration implied by the concentration variations observed

The figure 5 obtained by calculating the first derived function of the concentration curves show that the net consumption and regeneration of nitrogen observed *outside the springtime period* largely exceed the minimal primary productions they imply (especially in 1977).

On the other hand, the flows of consumption of N , P and Si observed in the spring period of 1978 imply perfectly normal primary productions and are in the N : P : Si proportions typical of living matter.

During the important nitrogen peaks, one observes nothing in the water column (turbidity, abnormal bacterial activity, chlorophyll) which could cast light on this problem.

Moreover, there is no question of the Scheldt being such an important source of nitrogen at certain times of the year, if only because of the major dilution brought about by the mixture with North Sea waters.

2.5.- Conclusion

One could conclude this paragraph by bringing to mind certain recommendations (this list is by no means exhaustive) :

- from the analytic point of view, it would be useful if current methods were to have more specificity
- it would also be interesting to cross-check the results measured using other methods in the dissolved and particulate phases. This is particularly true for nitrogen (methods currently developed).
- from the point of view of sampling strategy, there should be a way of reducing the analysis time so as to be able to adapt the sampling frequencies whenever a special phenomenon is observed.

References

DROOP, N.R., 1973. Some thoughts on nutrient limitation in algae, *J. Phycol.*, 9, 264-272.

EPPLEY, R.W., COATSWORTH, J.L. and SOLORZANO, L., 1969. Studies of nitrate reduction in marine phytoplankton, *Limnol. and Oceanogr.*, 14, 184-195.

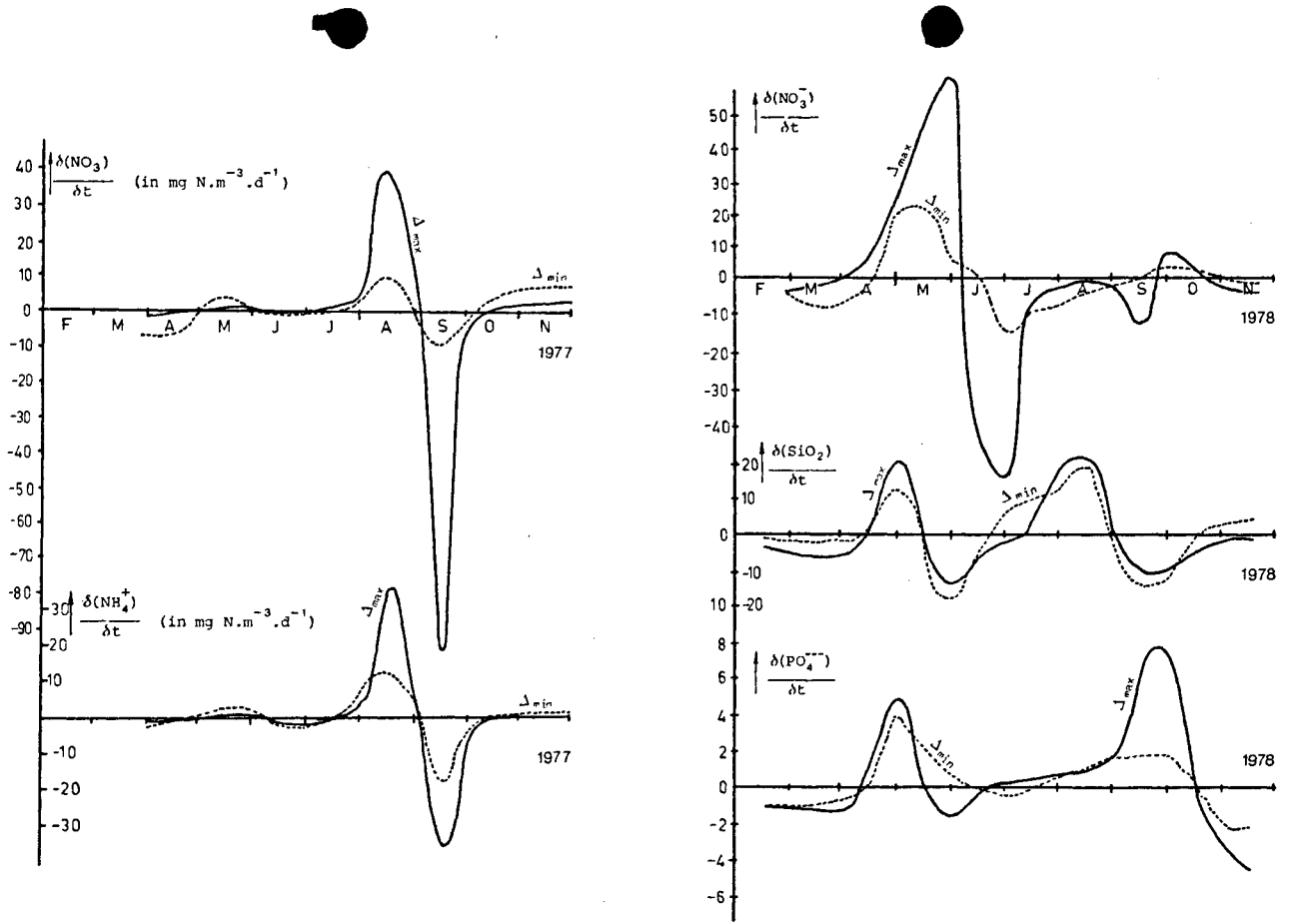

fig. 5.

Flows of net consumption and net regeneration of some nutrients

FALKOWSKI, P.G. and STONE, D.P., 1975. Nitrate uptake in marine phytoplankton : energy sources and the interaction with carbon fixation, *Marine Biology*, 32, 77-84.

FOGG, G.E., 1971. *Extra-cellular products of algae in freshwater, Ergebnisse der Limnologie*, V, Elster & Ohle (Ed.), Schweizerbart, Stuttgart.

HARRISON, P.J. and DAVIS, C.O., 1977. Use of the perturbation technique to measure nutrient uptake rates of natural phytoplankton populations, *Deepsea Research*, 24, 247-255.

MOMMAERTS, J.P., 1978. *Systeembenadering van een gesloten marien milieu, met de nadruk op de rol van het fytoplankton*, Thesis, V.U.B., Brussels.

NIHOUL, J.C.J. and POLK, P., 1977. *Chaînes trophiques et cycles des nutrients*, Rapport final du Projet Mer, vol. 8, Programmation de la Politique Scientifique, Bruxelles.