Chapter X

Some aspects of the dynamic behaviour of metallic and other pollutants

in the water column and the associated sectors

by

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Introduction

As global population, material standard of living and consequential industrialization continue to grow, specially around the Southern Bight of the North Sea, it becomes necessary to understand and if possible to manage the consequences of this situation within the context of *interactions* between the domestic and industrial wastes continuously transported and the finite and relatively small water mass of the southern bight of the North Sea.

Although the global impact of the Southern Bight on the whole North Sea seems to be unimportant at this time [ICES (1973)], one must take into account that at *local scale*, this situation implies very high stationary concentrations of pollutants and possible modifications in the system within a relatively short time scale.

Although the quantitative description of interactions and transfers, temporally and spatially integrated, gives a *"frozen" picture* of the real system, no other method is available to describe, in a global report and in a first approach, the dynamic distribution of the pollutants. In such a representation, the patch formation concepts, the seasonal influences, the irregularities due to sporadic dumpings and so many other influences are emasculated in such a way that the only perfect tool will be the mathematical one. Nevertheless, we will use the "frozen" picture in a first approach, but the sensitivity of the proposed figures, specially concerning the determination of the influence of the boundary conditions, and the magnitude of some chosen parameters will be given by simulation with the mathematical tool fully described elsewhere [Nihoul (1974a)].

For that purpose we surveyed our results (and also those from the literature) on the individual chemical and physical aspects of the movement of some pollutants through the ecosystem in the water column, taking into account exchanges with benthos and atmosphere.

The picture is incomplete and in places apparently contradictory but our purpose, at this stage, is to show how, after selection, the results of many individual studies may be assembled into a useful policy tool. There may be errors in the studies reviewed, but the sensitivity analyses mentioned above either suggest that their impact on our basic conclusions is small, or indicate where the need for further information appears, although our understanding of the real system will never be perfect.

1.- Nutrients

The nutrient content analysed in the water column (phosphorus, nitrogen, silicium) shall not be examined in this chapter, insofar as their

evolution in time and space is the subject of a detailed interpretation associated with the study of the *activities* of the different organisms (primary and secondary production, heterotrophic activity, etc.) already presented in chapter VI (Podamo).

In view of the conclusions of that important chapter, we will, at most, express a few comments which may have an impact on the discussion of the other chemical parameters under study.

In the last paragraph, dealing with the nitrogen transfers in the southern bight of the North Sea, it is mentioned that the data concerning the activity of phytoplankton, zooplankton and (pelagic and benthic) bacteria justify *a posteriori* the validity of the division of the network in three zones where significantly different types of biological mechanisms seem to be demonstrated. In fact, although our previous work [Elskens (1972)] had shown only a zone differentiation corresponding to different hydrodynamic regimes, we will in further discussions adopt the *three* subdivisions, fully aware that these different types of activity will play a specific role in the distribution of pollutants engaged in or circulated into the food web.

As stated in the conclusions of this same paragraph, the unbalanced ecological behaviour in *zone 1 north*, where the greatest part of the primary production occurs at the expense of exogenous nutrients without important recycling, is the consequence of *eutrophication* of this part of the North Sea. This statement, based on an annual balance of nitrogen transfers, may be supported by other techniques of approach [Anderson (1972)] and should be more finely detailed, simultaneously considering other nutrient budgets [Beckers (1973)] since a zone's trophic state is characterized not only by its nutrient content but also by the quantity and above all the *type of biota* it supports [Mommaerts (1973)].

The abnormal situation in zone 1 north (see fig. 6.42, chapter VI) partly confirmed by other investigators [Hagel (1973)] illustrates quite well that in developping a formal model for a system, one must begin by defining the system boundary not only in time but also in space. As a matter of fact, the boundary is chosen *in response* to the questions the model seeks to answer. The responses would be quite different if we were

thinking of a one day period or a twenty year period, if we were consi-
dering the global North Sea system or the local southern North Sea, or
even one part of the latter. This explains the formal discrepancy of
some conclusions [ICES (1974)] : "... however, although *no effects* have
been noted which might indicate a danger of eutrophication arising in
the North Sea, there is some evidence of increases in nutrient levels
in the waters of the southern North Sea in recent years ...". The first
statement is based on a global budget, taking into account the inputs
of nitrogen and phosphorus in sewage, and on the consequential oxygen
demand of the present organic matter, this load being *evenly* distri-
buted over the *total* surface of the North Sea.

As shown by Nihoul (1974a), the evolution of a marine constituent
results from advection, migration, dispersion and also from ecological
interactions. If pollution damage may theoretically be controlled in
two ways [Meadows (1972)], *i.e.* by decreasing the rate of pollution ge-
neration or by naturally or artificially removing the pollutant
from those areas where it causes harm, we may conclude that eutrophic-
ation is one pollution problem in which the second response is sponta-
neously effective for the total North Sea, at this stage at least, but
that for the zone 1 north (and probably very soon for the zone 1 south)
only the first response may be effective, considering the coupled hydro-
dynamical and ecological reasons.

2.- Metals

Regular surveys of the distribution of selected trace metals in
the waters of the North Sea have been conducted by laboratories in Bel-
gium, the Netherlands and the United Kingdom. A preliminary examination
of the results had shown differences in the *mean* level of "dissolved"
metals measured by the three groups. An international intercalibration
program was therefore established (under sponsorship of the ICES), to
investigate this problem. A working document [Elskens (1973a)] including
computations on the 1971-1973 data representative of the whole belgian
survey network was presented to an *ad hoc* working group in charge of the

preparation of the report concerning the distribution of trace metals in the waters of the North Sea.

The final document [ICES (1974)] presents a compilation of the available data produced by the three countries, completed with a critical study of the apparent anomalies. In those regions of the North Sea where surveys by the three groups coincided geographically, the mean levels of most metals recorded by the belgian investigators where higher than the U.K. figures, and the Netherlands data occupied an intermediate position. There is evidence, however, that these apparent anomalies may be attributed to variation in the fraction of metal passing the membrane filter after sample collection. Prior to analysis, seawater samples were filtered through membranes of pore size 0.22 , 0.45 and 0.8 µm by the U.K., Netherlands and belgian laboratories respectively.

Although this explanation will be satisfying in a first approach and for the determination of the overall spatial trends in the distribution of "dissolved" metals, we presume that other factors must play a role in some of the observed discrepancies. First one must take into account that any physical treatment (freezing, filtering, extraction, etc.) changes the "matrix" of the treated sample and very often not in a simple way.

Peptonization and flocculation processes may occur [Steen (1974)] and even the comparisons made by filtering natural water through membranes of different pore sizes can provide rather unexpected results [Jones (1974)]. This is an example where a coupling of the measured parameter with a series of other incompletely or not at all defined parameters appears and plays the major role. In the same field, one must indubitably consider the influence of speciation [Kamp-Nielsen (1972)], the indirect consequences of speciation [Gillain (1974)] and the heterogeneous nature of suspended or particulate phases; especially in some regions where the very fine material is definitely richer in adsorbed metals, as compared to the "mean" suspended material very similar in terms of composition to the "recent" sediments [Duinker (1973)].

In order to establish a more detailed geographical picture of
metal distribution and especially to define precisely the representa-
tive concentrations [1] of trace metals in water masses, well defined in
regards to the spatial boundaries, the same statistical treatment
[Elskens (1973)] was made for *each* zone (zone 2, zone 1 north, zone 1
south; see fig. 6.38, chapter VI) of the belgian sampling network.

Table 10.1 summarizes the mean values for cadmium, zinc, copper
and lead. The purpose is to define as closely as possible the specific
characteristics of each bulk. There is then no reason to exclude *a
priori* the very high values [2] observed in coastal zones (confirmed in
other respects by further intercalibration experiments, *cf.* cruse Clione,
Sept. 1973, samples K6 and J10), these values playing an outstanding
role in the calculation of the fluxes. Fully aware that some of those
high values appear sporadically, our problem is to integrate these va-
lues in an adequate time scale, in the same way one must average some
parameters over a certain number of tidal periods.

The first question arising from the examination of the results of
table 10.1 concerns the physical sense that one must or may give to
those "mean" concentrations in view of their practical use. Despite the
fact that these concentrations (relative to the water column alone) are
isolated from the other compartments, we know, as stated by Nihoul (1974b),
that the exploitation of this kind of result is not meaningless. When the
interaction processes are not yet entirely understood and cannot be for-
mulated with sufficient accuracy to use in a reliable simulation model,
it is then preferable to base the predictions on the estimates of a *pas-
sive* dispersion model, until new experimental and theoretical data are
available and the interaction forms can be determined with the required
precision. Such models always provide valuable estimates of the distri-
bution of *non passive* constituents by at least appraising their possible
transport by the overall motion of the Sea.

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1. Arithmetic weighted mean, in the sense of optimization of the number of samples
   with the effective volumes of the water masses.
2. Or to emphazise the low values, using the geometrical mean.

Table 10.1

Mean measured metal concentrations in the Belgian sampling network   ($\mu g/dm^3$)

Metals	Zone	Year	Mean	Nb	σ	Range	Med.	Distrib. 5 classes	Nb runs	Excl.	Methods
Cd	1N	1971	0.25	5	0.18	0.15-0.56	0.19	4- 0-0-0-1	1	0	ASV
Cd	1N	1972	0.38	16	0.24	0.16-1.0	0.28	9- 3-2-1-1	1	0	ASV
Cd	1S	1971	0.19	12	0.07	0.06-0.34	0.19	2- 3-2-4-1	2	1	ASV
Cd	1S	1972	0.37	24	0.21	0.10-0.84	0.31	9- 6-2-5-2	2	1	ASV
Cd	2	1971	0.18	21	0.09	0.05-0.42	0.19	7- 6-5-2-1	2	1	ASV
Cd	2	1972	0.30	37	0.23	0.09-1.01	0.21	23- 6-4-2-2	2	2	ASV
Zn	1N	1971	3.6	5	1.7	0.8 -5.0	4.0	1- 0-1-1-2	1	0	ASV
Zn	1N	1972	15.5	15	17.5	1.0-52.4	10.4	9- 2-1-1-2	2	1	ASV
Zn	1S	1971	9.0	12	6.6	1.2-21.8	8.5	5- 3-1-1-2	2	1	ASV
Zn	1S	1972	23.9	24	23.6	1.5-91.7	13.2	15- 4-3-0-2	2	1	ASV
Zn	2	1971	5.9	21	5.1	0.2-18.8	5.9	9- 7-3-0-2	2	1	ASV
Zn	2	1972	15.4	35	16.7	2.0-65.4	9.1	26- 2-2-2-3	2	3	ASV
Cu	1N	1971	4.8	5	3.1	1.5- 8.3	5.3	2- 0-1-0-2	1	0	ASV
Cu	1N	1972	9.8	16	3.9	3.2-17.6	10.0	2- 5-5-3-1	1	0	ASV
Cu	1N	1972	7.1	4	5.9	1.9-14.8	5.9	2- 0-1-0-1	1	0	AAS (0.22 μm)
Cu	1S	1971	4.7	6	4.4	0.8-12.7	3.5	3- 1-1-0-1	1	0	ASV
Cu	1S	1972	12.0	24	12.2	3.2-56.5	7.6	19- 1-3-0-1	2	1	ASV
Cu	1S	1972	5.3	6	4.5	0.4-11.6	4.5	2- 1-1-0-2	2	1	AAS (0.22 μm)
Cu	2	1971	3.9	14	2.6	0.6-10.4	4.1	5- 4-4-0-1	2	1	ASV
Cu	2	1972	7.9	38	3.5	2.6-15.2	7.6	10-10-8-6-4	2	1	ASV
Cu	2	1972	4.4	10	4.4	1.0-15.2	2.3	6- 2-1-0-1	2	1	AAS (0.22 μm)
Pb	1N	1971	2.0	6	1.8	0.6- 5.6	1.4	4- 1-0-0-1	1	0	ASV
Pb	1N	1972	4.1	14	2.9	1.0-10.8	3.1	6- 5-1-0-2	2	1	ASV
Pb	1S	1971	3.1	12	1.8	1.1- 7.5	2.7	5- 5-0-1-1	2	1	ASV
Pb	1S	1972	7.2	24	5.3	0.5-17.6	6.4	10- 3-5-3-3	2	1	ASV
Pb	2	1971	2.3	20	1.8	0.6- 6.2	1.8	9- 6-1-2-2	2	2	ASV
Pb	2	1972	5.0	36	3.4	1.2-14.5	4.1	16-10-5-3-2	2	3	ASV
Pb	2	1972	3.2	10	1.9	0.2- 6.5	2.3	1- 5-0-3-1	2	1	AAS (0.22 μm)
Pb	2	1972	10.1	10	4.3	4.1-18.2	10.1	2- 3-3-1-1	2	1	AAS (0.8 μm)

In fact, this first approach can be used to describe the general features of the space and time variations for *active constituents* as long as some *conditions* are satisfied. When one considers the relatively short residence times of the water masses in each zone : 20 , 23 and

34 days[1] for zone 1 south, zone 1 north and zone 2 respectively, it seems evident that the most important part of the transfers must be the transport by the sea motions. The calculation of the residence times is based on the estimates of the hydrodynamicians [Ronday (1973)]. Considering in a second step the transfer mechanisms in the food web presented elsewhere by the biologists [Podamo (1974)], computing the mean productivity value and the grazing coefficient (respectively 140 g carbon/m^2/year and 46.2 g carbon/m^2/year , for zone 2 for example) with the mean cadmium content of zooplankton (20 mg Cd/kg carbon, for the same zone, see table 10.2), it can be calculated that the maximum quantity of cadmium involved (engaged in and circulated into) in the plankton box of zone 2 is about 4.25 tons/year [Jacob (1974)]. Compared with the several hundred tons of the same material transported through the water mass of zone 2, this leads to the same conclusion as above.
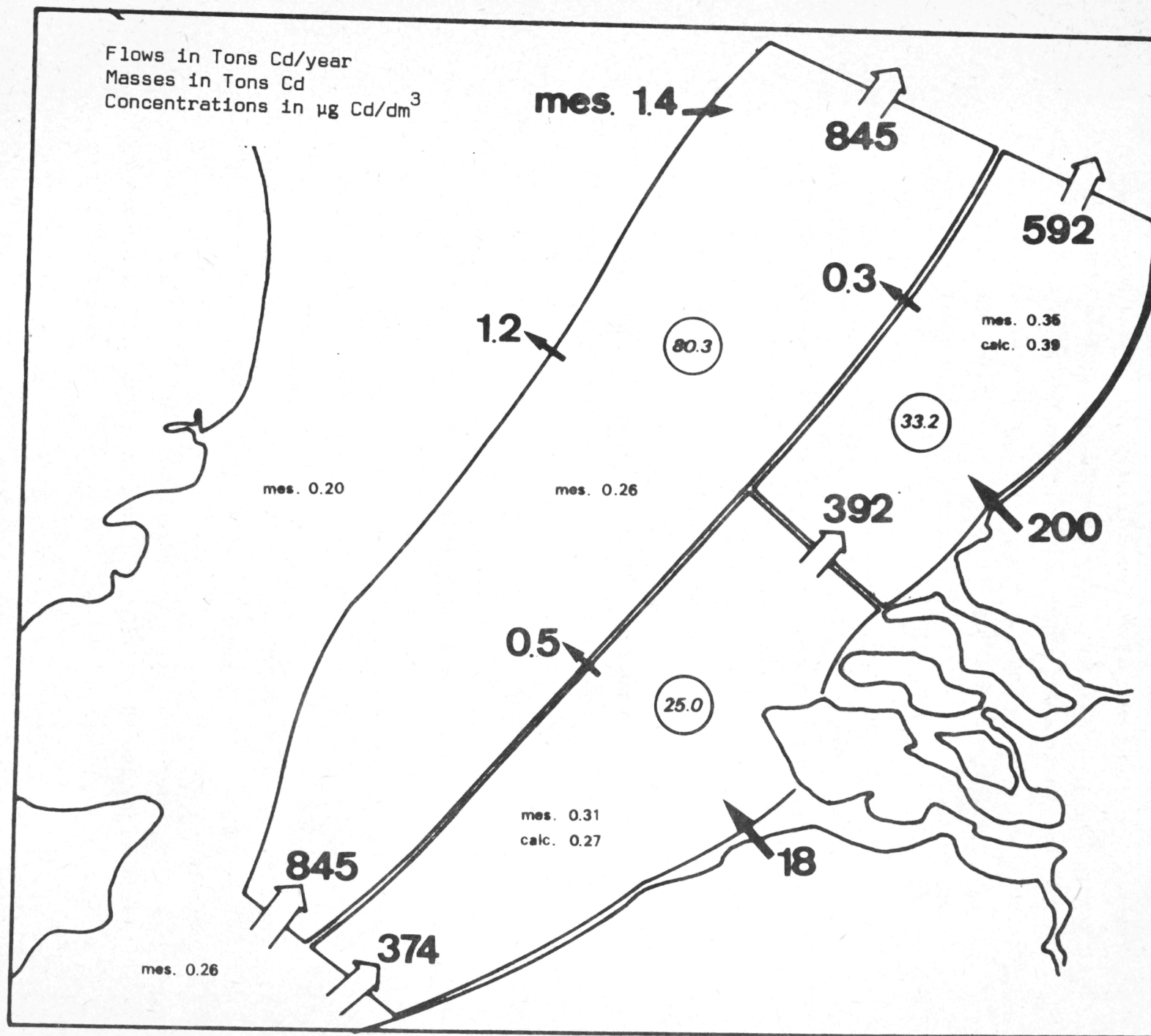
To come back to the above mentioned example, this does not at all mean that, in these conditions, cadmium never plays an outstanding role in the food chain and that one should minimize or even neglect the cadmium pollution problems. In another paragraph, a rough estimate of a circulation model inside the food chain will be discussed, with some comments on interactions, translocations and the consequential influences on a passive dispersion model.

In any case, if the interactions play a significant role (recycling in the food chain as a modification of the reservoirs, sedimentation processes, etc.), they can be taken into account in a passive dispersion model if one assumes that their net result is a production or destruction of the considered constituent, which can often be expressed as a function of the concentration of that constituent alone [Nihoul (1974b)].

The criteria presented above, applied for example to the cadmium budget, led to figure 10.1 where the fluxes are expressed in tons/year,

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1. We simultaneously ascertain a given value for the future time scale of the samplings, in order to improve the "mean" values presented here.

Flows in Tons Cd/year
Masses in Tons Cd
Concentrations in µg Cd/dm^3

mes. 1.4

845

592

0.3

1.2

80.3

mes. 0.35
calc. 0.39

33.2

mes. 0.20

mes. 0.26

392

200

0.5

25.0

mes. 0.31
calc. 0.27

845

374

18

mes. 0.26

fig. 10.1.– Passive dispersion patterns for cadmium.

the engaged masses in tons, the concentrations in micrograms per liter [Steen (1974)]. The calculated concentration values were derived from the hydrodynamical data and a proper choice of inputs and boundary concentrations. The measured concentration values are those derived[1] from the weighted means taking into account the results collected during 1971 and 1972, since a monthly survey is not an acceptable time scale, as regards the residence times, for a convenient integration. Here again appears the superiority of the mathematical tool.

Figure 10.1 suggests a few comments.

The tremendous sensitivity of such a circulation model to the choice of the boundary conditions implies that one must give more information about the chosen values. The input figures, Rhine (200 T/y , for an outflow of 75×10^9 m^3/year) and Scheldt (18 T/y , for an outflow of 3.3×10^9 m^3/year) are respectively extracted from the literature [Weichart (1973)] and from our own previous results [Elskens (1972)]. The direct inputs of cadmium along the belgian [IHE, IRC (1973)] and probably also the dutch coast can be neglected as compared with the adopted values for the Rhine and the Scheldt. The concentration at the border between the belgian network and the Channel (0.26 µg Cd/dm^3) equalized to the mean concentration of zone 2, is in agreement with the *overall mean* value of our observations (1971-1973) in this region (0.28 µg Cd/dm^3), although very important fluctuations[2] have been observed (range 0.10 - 1.01) or reported; the values cited in the literature range from 0.06 µg Cd/dm^3 [Preston (1973)] to 1.6 µg Cd/dm^3 [Dutton (1973)].

Finally the border concentration along the belgian network and the U.K. coast (0.20 µg Cd/dm^3) is derived from the ICES figures [Jones (1973)].

The difference between the calculated value (0.27 µg Cd/dm^3) and the measured value (0.31 µg Cd/dm^3) in zone 1 south, is in agreement

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1. Restricting our attention to mean vertical concentrations, the profiles are discussed elsewere [Steen (1974)].
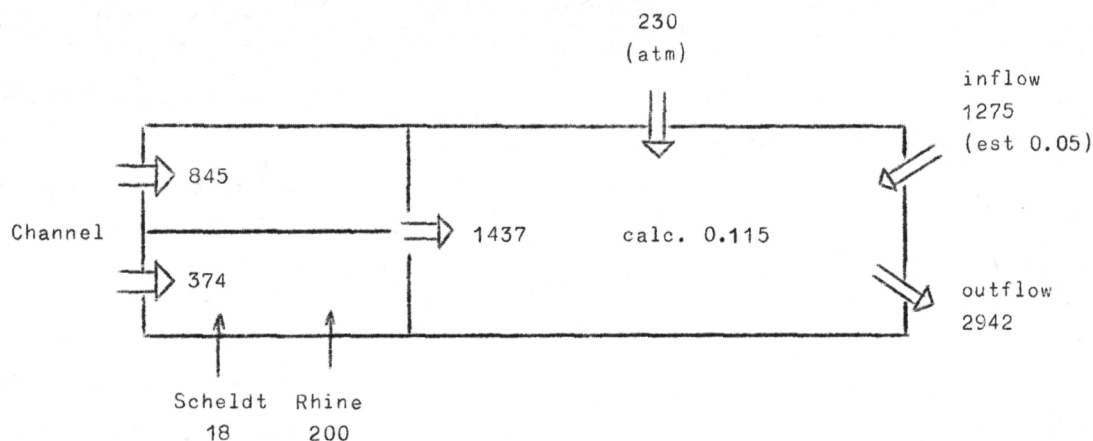
2. In an other paragraph we will discuss the sporadic influence of the dredging products dumped in this region.

with the same kind of discrepancy observed between estimation and measurement for the salinity (see fig. 6.38, chapter VI). The final answer to this problem probably lies in the influence of the "tidal stress" on the residual circulation [Nihoul (1974c)]. Apparently the real residence time in this zone must be a little longer than the value obtained by formal calculation; this also concurs with the silt accumulation in the same zone (see this chapter, § 4). As a result, the net flux between zone 1 south and zone 1 north must be somewhat deflated; and moreover, taking into account the fact that the mean concentration associated to the zone 1 north is probably overly influenced by the number of samples located under the Rhine estuary, one may consider that the agreement between the estimated and the experimental values is fairly good.

Introducing the fluxes due to dispersion will improve the figure. These values are mentioned at each border-line between zones, averaged all along the border for the mean values of the dispersion coefficients [Nihoul (1974d)] and oriented in the direction of the concentration gradient. One exception appears to the north of the outside border-line; the great axis of the iso-concentration ellipse is oriented at $72° - 05$ referred to the geographical north and the concentration gradient may be reversed during some periods. This explains why, on that line, some spots of high concentrations are detected, as shown by our own results and simultaneously in some U.K. surveys [Jones (1973), fig. 1a, Corella cruises 1971]. The feeding element is probably a combination of the Straits of Dover and the Thames.

Last, the figure 10.2 schematically presents the global influence of the part of the southern bight under study on the global North Sea system [Steen (1974)] simultaneously considering the atmospheric input [ICES (1974b)]. The induced concentration gradient Δc equals $0.07 \ \mu g \ \ Cd/dm^3$.

The same figures may be constructed for zinc and copper but at this stage of our knowledge no further information on the possibilities of the passive dispersion models will be gathered, with the possible exception of direct information on the sensitivity of such a model as

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                              230
                             (atm)                        inflow
                                                          1275
                                                          (est 0.05)
         ⇒ 845
                                   ⇓

Channel          ⇒ 1437        calc. 0.115

         ⇒ 374                                            outflow
                                                          2942
            ↑       ↑

         Scheldt  Rhine
           18     200
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Note : same units as for fig. 10.1.

fig. 10.2.- Contribution to the North Sea.

concerns the inputs. The only excluded value in the copper survey (AAS
determination, table 10.1, p. 421) concerns a sampling point located
in the Straits of Dover, precisely where dredging products were dumped
a few days before the sampling. The recorded value (about 64 µg Cu/dm^3)
was used to simulate the influence on the nearby sampling points and to
determine the time constant of the induced perturbation [Jacobs (1973)].

The lead budget also suggests a few specific comments. Although
admitting that many previously published lead concentrations in sea
water are probably too high, we cannot agree with all the conclusions
of the workshop sponsored by the IDOE Conference (May 1972) and espe-
cially with those concerning the AAS and the ASV analytical methods
[Patterson (1974)]. The "particulate" nature of most of the lead in
the sea water samples has been confirmed by systematic ultrafiltration
processes on the same sample. A regression analysis on the contents of
the corresponding filtrates shows that for a theoretical porosity zero,
one obtains concentrations of lead "in solution" ranging from 50 to
250 nannograms/dm^3 , values concurring with the theoretical definition
of a "true" solution in sea water [Goeyens (1973)].

Therefore, in considering a global lead budget in a passive dis-
persion model, one must consider the important fraction of lead trans-
portation under particulate form, assuming that a minute portion of
that fraction is collected by sediments (see § 4). Simultaneously,

one must incorporate into the model the non negligible atmospheric input [ICES (1974b)].

Due to some important gaps in our information in its actual state, it seems untimely to present even a rough estimate of the lead budget in the several zones of the network under study. Nevertheless, some information dealing with the inputs may be of interest.

The mean concentration of lead in the rainwater we surveyed from March 1972 to March 1973, $i.e.$ 27 micrograms Pb per liter (range 3-160 µg Pb/ℓ) concurs with the figure presented by the UKAEA Research Group, $i.e.$ 34 micrograms Pb per liter [Pattenden (1974)], and also with the estimate of the annual fall out on the North Sea published by the ICES [Jefferies (1973)]. The enhanced washout factors observed at the sea-based stations in respect to the land stations is probably due to reextraction processes in the upper layer of the sea [Nihoul (1972)].

Assuming that 27 µg Pb/dm^3 represents the true amount of fall-out through rain on the sea surface and for an average rainfall of 80 cm/year , the net annual contribution is 216 t/year , 113 t/year and 100 t/year for zone 2, zone 1 south and zone 1 north, respectively. In these conditions, the ratio — atmospheric contribution/estuaries contribution — in the belgian network is completely different from that of the whole North Sea, since the contribution of the Rhine alone is 2000 t lead/year [Weichart (1973)]. This is in accordance with the existence of a negative concentration gradient along the on shore — off shore profiles in the water column and in the sediment distribution (see § 4).

From another point of view, the relatively small contribution of fresh waters in the lead budget (in the absence of direct injection of wastes) is due to the fact that lead does not seem to $move$ after it has come in contact with soil and humus particles, $except$ when the soil particles themselves move. As regards the rainfall on land, this assumption is strengthened by the fact that leaves, the best receptacle for lead contained in rainwater [Impens (1973)], fall to the ground every year, carrying with them whatever lead is on their surface. The figure generally offered for the solution half-life of lead, that is, the time required to remove 50 percent of the lead in soils by suspension

of particles in rivers *only*, is in the order of 30 years. This value
is of course only a very rough estimate. However, all we need to know
is that this processes (mobilization on land) is very slow indeed,
compared to other direct transportation mechanisms (rainfall on sea).

The data given by the biologists [Podamo (1974)] concerning the
food chain pattern in zone 2, may be summarized in a flow diagram as
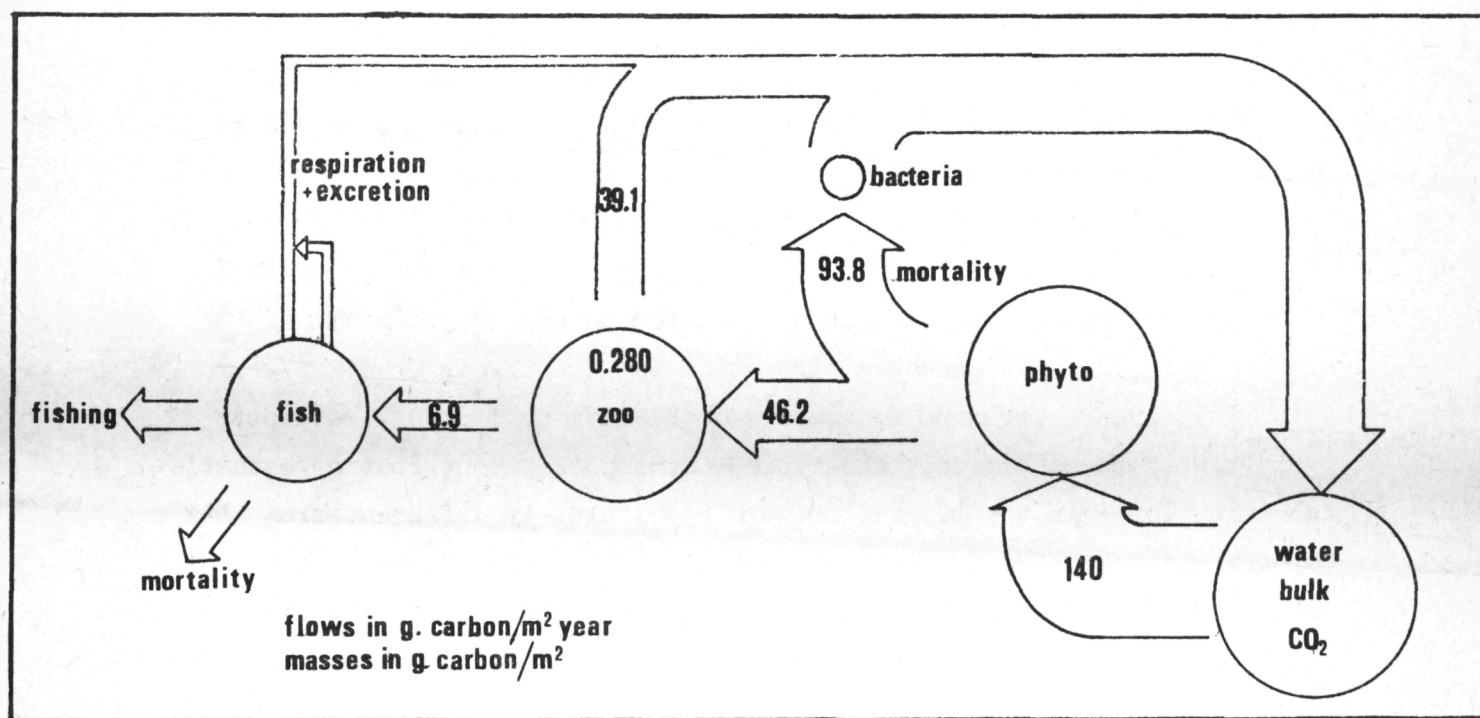shown in figure 10.3 where the biomasses are expressed in g carbon/m^2

fig. 10.3.- Food chain pattern, water column zone 2.

and the flows in g carbon/m^2.year . This figure is, of course, not
completely detailed; the unimportant flows, such as, for instance,
excretion by zooplankton, are neglected.

Taking into consideration the zooplankton mean mercury content
for zone 2 (see table 10.2), *i.e.* 20 mg Hg/kg carbon[1] , and assuming

1. Attention to the units chosen; in order to obtain the concentration on <u>wet</u> ma-
terial, the best figure is to multiply by a factor 0.08 for zooplankton.

Table 10.2

Concentration of heavy metals in lyophilisated plankton

Identification	Hg mg/kgC	Zn 10^3.mg/kgC	Cd mg/kgC	Pb 10^3.mg/kgC		Cu 10^3.mg/kgC	
	AAS	ASV	ASV	AAS	ASV	AAS	ASV
1S-M05	37.3	8.3	11.6	0.39	0.31	0.93	0.86
M06	28.4	5.9	17.8	0.51	0.63	0.60	0.64
M1343	11.4	8.9	12.1	0.42	0.45	0.73	0.71
M1450	7.6	14.6	32.9	0.25	0.40	0.67	0.57
M1452	25.6	24.5	30.4	0.21	0.24	2.44	1.01
M60	8.8	3.3	21.1	0.89	0.39	0.91	0.23
M1097	12.0	-	-	0.29	-	0.29	-
M1101	19.3	6.8	6.8	0.35	0.44	0.37	0.43
M02	15.4	7.1	28.9	0.27	0.35	1.12	1.61
M07	16.9	7.7	11.6	0.097	0.15	0.62	0.46
M52	17.9	11.3	15.5	0.24	0.61	0.19	0.43
Mean	18.2	9.8	18.9	0.36	0.40	0.80	0.70
1N-M59	16.0	5.0	1.9	0.10	0.24	0.17	0.35
M2689	39.2	19.0	95.1	1.03	1.92	1.11	2.41
M21	13.2	15.7	11.9	0.29	0.24	0.40	0.60
M1989	27.2	48.7	646	0.69	0.41	0.44	0.38
M1695	8.9	102	-	0.33	0.23	0.44	0.27
M64	44.8	48.5	-	0.24	0.31	4.42	2.60
M17	10.5	4.6	70.6	0.12	0.15	0.32	0.36
M63	58.6	37.4	-	1.15	0.031	13.7	8.0
M1993	134.-	20.6	2.0	0.24	0.054	2.42	0.95
Mean	39.2	33.5	36-138	0.47	0.40	2.60	1.80
2 - M14	46.3	6.0	-	0.23	0.029	0.94	1.84
M23	5.6	12.4	46.1	0.077	0.146	0.15	0.19
M22	6.3	4.4	1.4	0.14	0.09	0.20	0.17
M18	18.0	1.2	12.2	0.008	0.048	0.78	0.68
M65	32.7	93.6 *	44.7	0.11	0.74	0.45	0.98
M1995	11.3	20.1	5.1	0.15	0.073	0.54	0.16
Mean	20.0	8.8	21.9	0.12	0.19	0.51	0.67

AAS : Atomic absorption spectroscopy.

ASV : Anodic stripping voltametry.

* Some values were excluded, because they are located at the frontier of the zone and under direct influence of another zone, or because the observed ratios C/N and C/P are not consistent with the composition of zooplankton.

quasi stationarity, at least on a short time scale, the consequential
flows for the mercury budget *inside* the food chain can be calculated
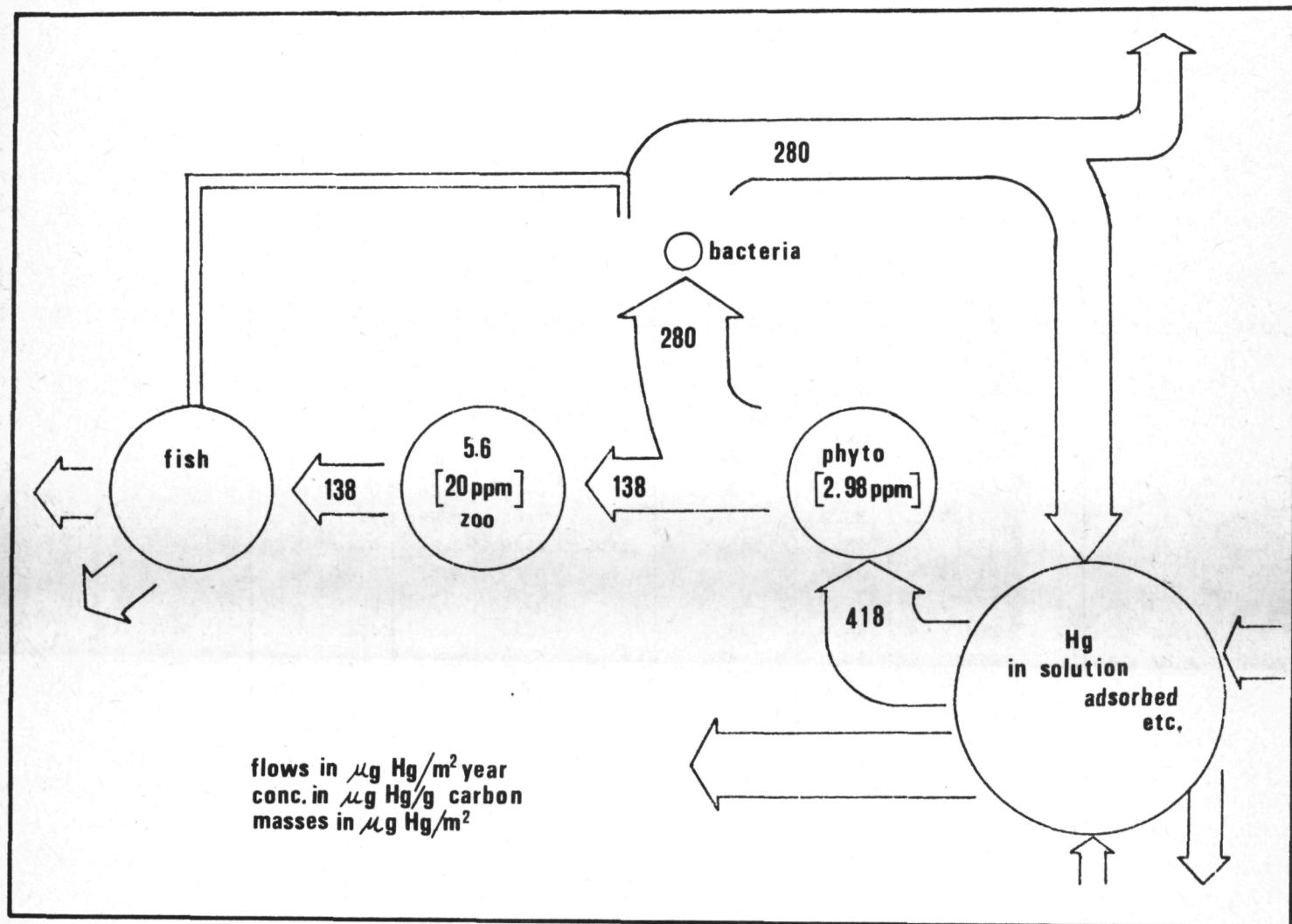(figure 10.4). The theoretical mercury content in phytoplankton derived

fig. 10.4.- Mercury pattern inside zone 2.

from this calculation is 2.98 mg Hg/kg carbon ; this means a concen-
tration factor of about 6.7 , in agreement with the value obtained by
tracer techniques. It is noticeable that the *practical* concentration
of mercury *in* phytoplankton is almost impossible to determine experi-
mentally with accuracy, considering the tremendous adsorption properties
of mercury as regards organic and suspended matter [Cranston (1972)].

Finally, combining these data with those given by a passive dispersion model, one may present a rough estimate of mercury circulation in zone 2 (figure 10.5). This figure may be completed with a few considerations relative to interactions at the border-line of the water column [Jacob (1974)].
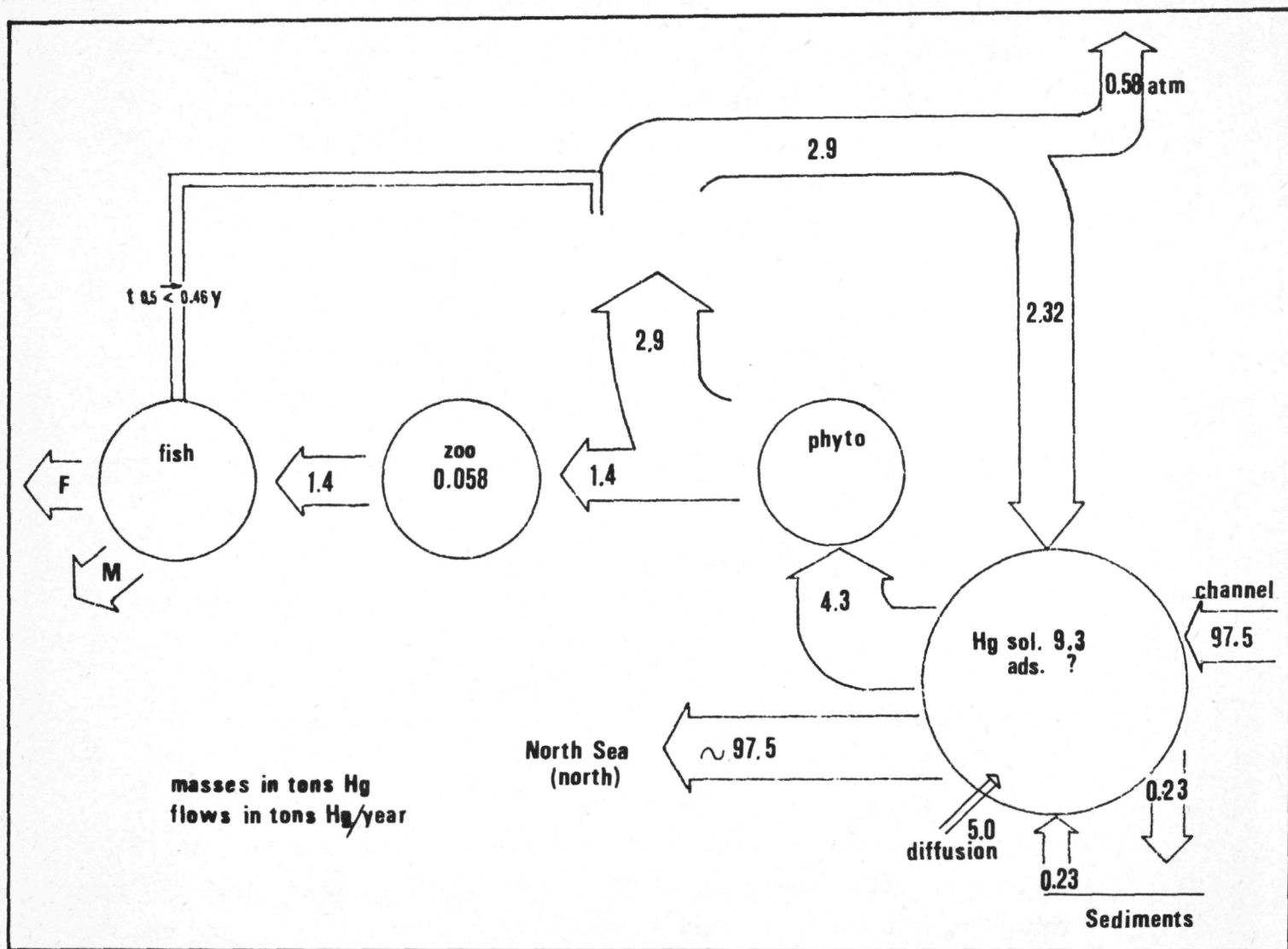
fig. 10.5.- Mercury pattern zone 2 global.

In a tentative model for the present *global* cycle of mercury [Wollast (1974)] the authors point out pathways between atmosphere and water column where the fallout of mercury by rain on ocean exceeds

the evaporation by about 20 % . Considering the residual stationary
concentration of *dissolved* mercury in the North Sea [ICES (1974)], we
observe a deflation by a factor of 3 as regards the "equilibrium"
concentrations generally admitted for the water column in global models
[Anderson (1973)]. This fact may not be completely supported by the
"promotion of productivity" observed in coastal regions, considering
that the fraction of mercury engaged in the food chain is only 4 %
of the total circulation (*cf.* fig. 10.5). In these conditions, one must
admit that, somewhere, mercury escapes from the water column. We admit,
in a first approach, that in zones like those under study, the water
column feeds the atmosphere (so that the net balance is reversed as
regards to the global cycle). As a consequence, figure 10.5 gives an
output to the atmosphere of about 20 % of the flow provided by treat-
ment of dead cells by bacteria. This flow represents, of course, the
net balance between fallout by rain and evaporation of mercury. It is
a rough approximation for a problem still under study, knowing that
other mechanisms such as transportation by suspended matter may also
support the depleted residual concentration observed in "dissolved"
mercury.

As most of the mercury from phytoplankton is recycled in the
water column, the dynamic behaviour of the two sectors (food web and
hydrodynamic circulation) is determined in the final analysis by the
uptake of mercury by fish, the excretion of mercury by fish, the death
of the fish and the fishing activities. Fish have a typical feeding
rate equal to 1,5 percent of body weight per day, *i.e.* 10 times a
fish's body weight per year [Randers (1973)]. Since in zone 2 the total
amount of plankton available and grazed per year is given by figure 10.3,
the total mass of fish corresponding to zone 2 amounts to about 7100 t
of carbon. The quantity of mercury in fish (see chapter IX) is but a
small fraction of the total involved in the model; therefore, errors in
the assumptions just made can have *little effect* on the behaviour in the
other sectors of the model. But, as concerns the fish box, considering
the yearly uptake of mercury, the average life time of fish, *i.e.* about
three years [Randers (1973)] and supposing no overfishing problems
occurs, one must admit, in order to explain both the relatively low mean

content of mercury in fish and the increment of that mercury content in time, that the half-life of mercury in the excretion processes of fish is a little shorter than the value generally admitted in the literature, *i.e.* 0.46 year [Montague (1971)].

Finally, as concerns the border-line water column-sediments, we assume that the *net* balance is zero, since, except for some coastal regions where silt deposit occurs, no accumulation of mercury was detectable. The relative values of the flows returning to the water column and the fraction attaining the bottom is given by comparison to a similar figure for the silicium budget in the North Sea [McCave (1973)], still considering that the relatively short residence time of the water masses in the zones under study, rendered negligible the direct contribution of mercury in solution, when compared with the mercury transported by the detrital material.

In another field, and in order to complete our knowledge of the interactive part of the pollutant's dispersion models, a complete survey of trace metals in plankton material was prepared. The samples were lyophilisated, after collection on a decreased mesh size net. Intercalibration experiments for low temperature dry ashing technique and wet digestion of the residues (EPA methods) were conducted [Gillain (1973)]. For practical reasons, the results (see table 10.2) are given in milligram of metal per kilogram of carbon in the considered samples (mostly zooplankton) and corrected for the presence of phytoplankton and other impurities, considering the simultaneously determined content of silicium, the carbon-nitrogen and the carbon-phosphorus ratio's [Jacob (1974)].

This list requires no further comment, since the values presented were directly used in some of the above described budgets. Nevertheless, the figures 10.6 to 10.10 show the spatial distribution of zinc, cadmium, copper, mercury and lead respectively, in the considered plankton compartment.
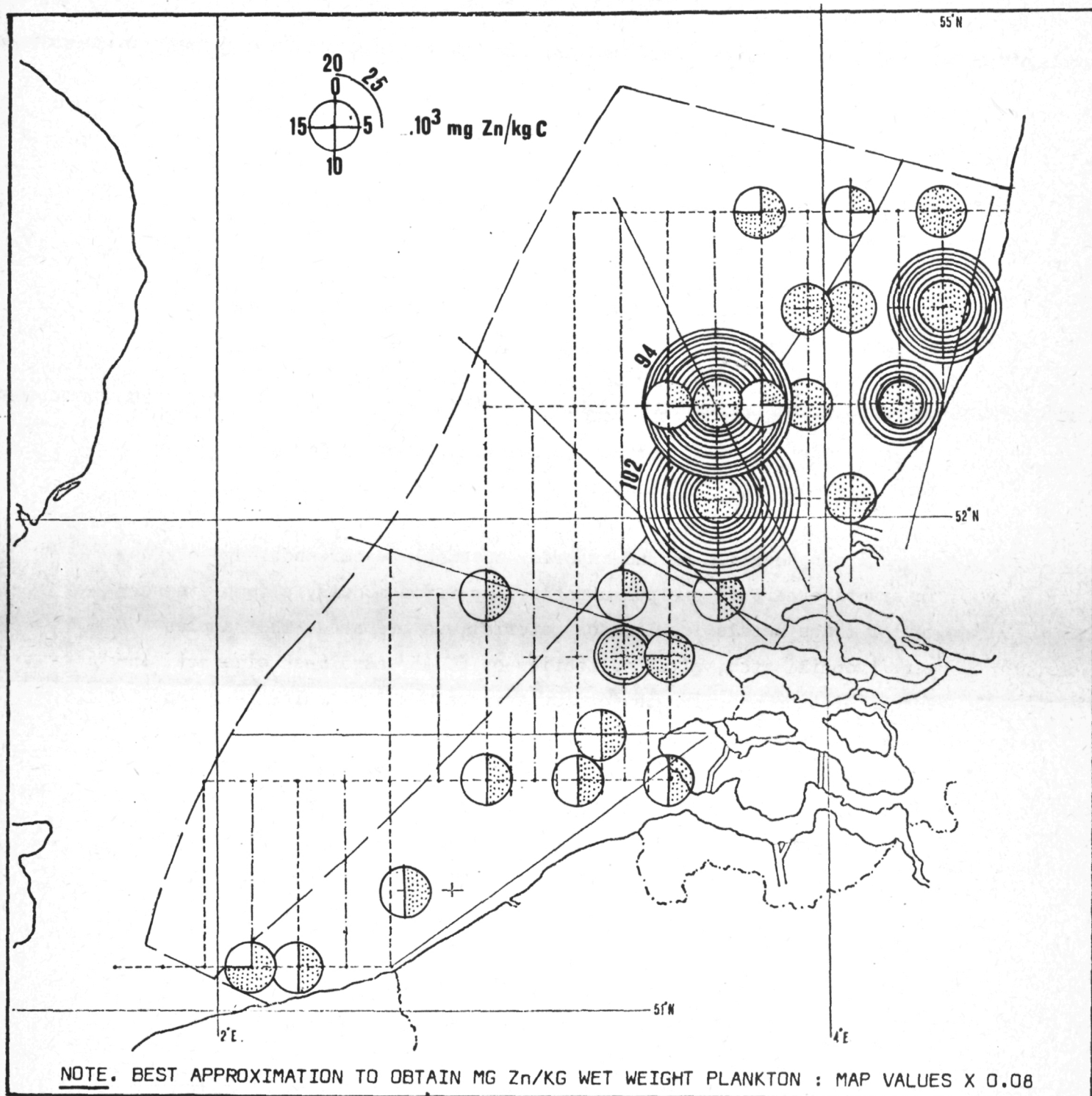
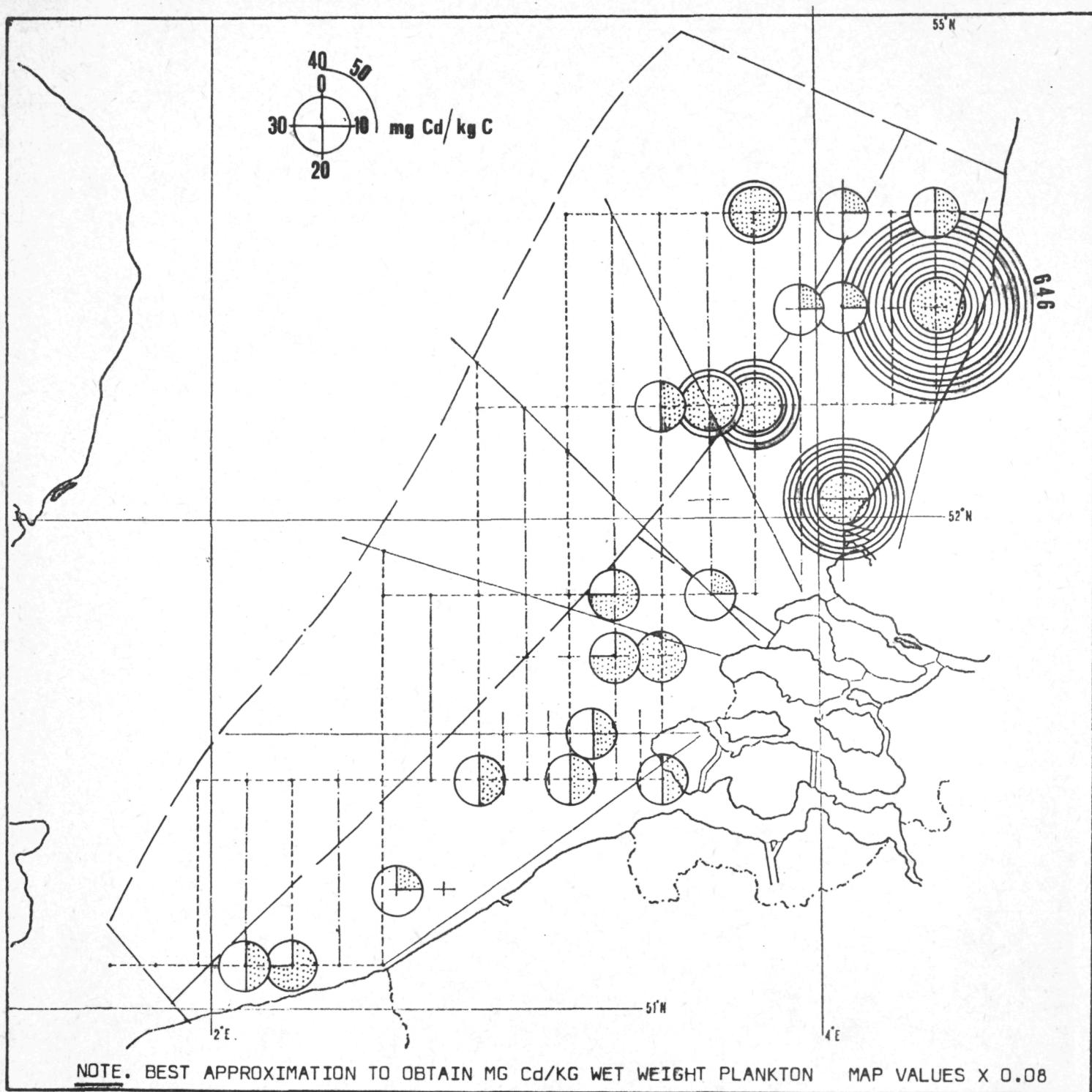fig. 10.6.- Zinc content of lyophilisated plankton samples.

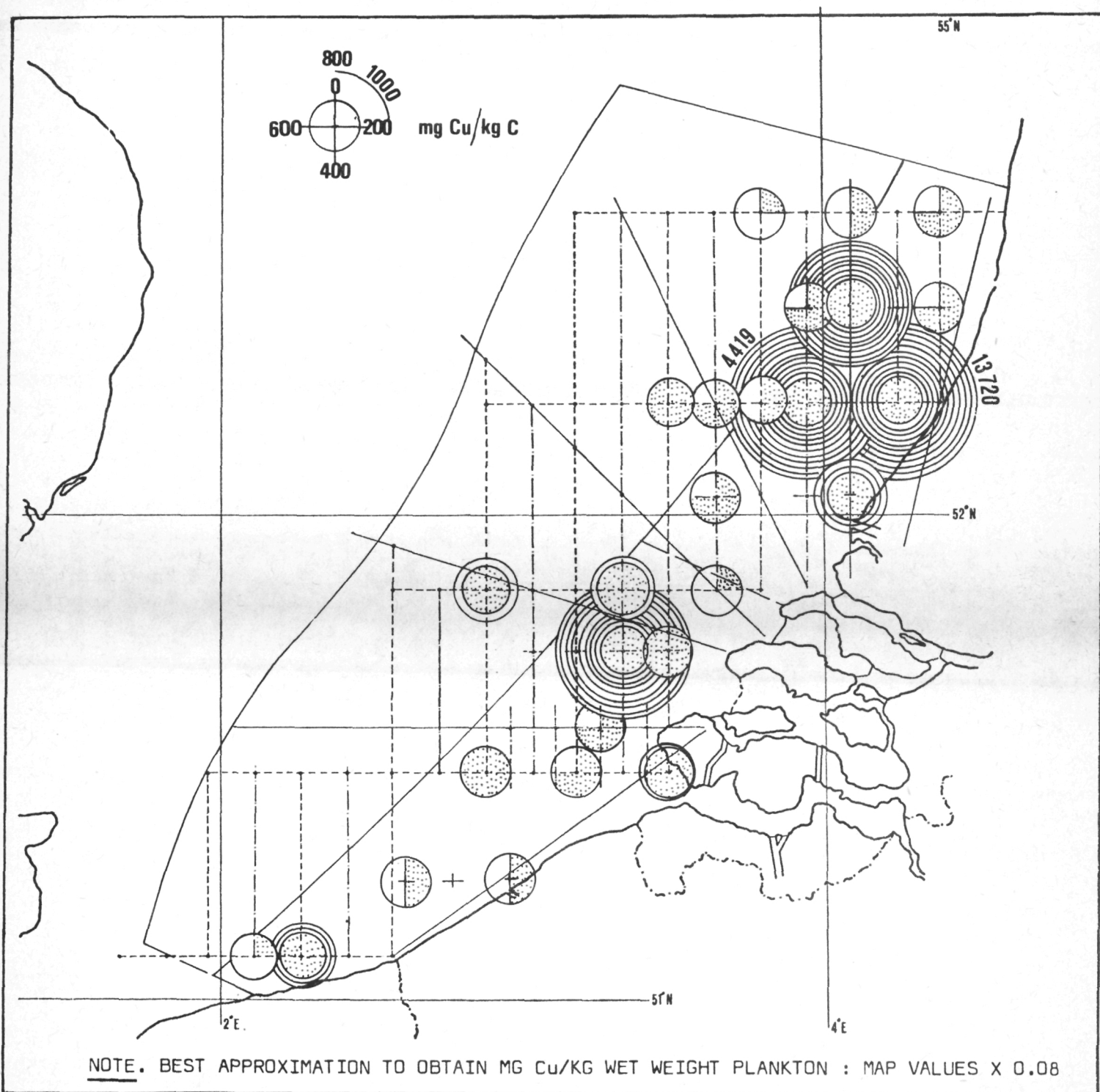fig. 10.7.- Cadmium content of lyophilisated plankton samples.

NOTE. BEST APPROXIMATION TO OBTAIN MG Cu/KG WET WEIGHT PLANKTON : MAP VALUES X 0.08

fig. 10.8.- Copper content of lyophilisated plankton samples.

NOTE. BEST APPROXIMATION TO OBTAIN MG Hg/KG WET WEIGHT PLANKTON : MAP VALUES X 0.08
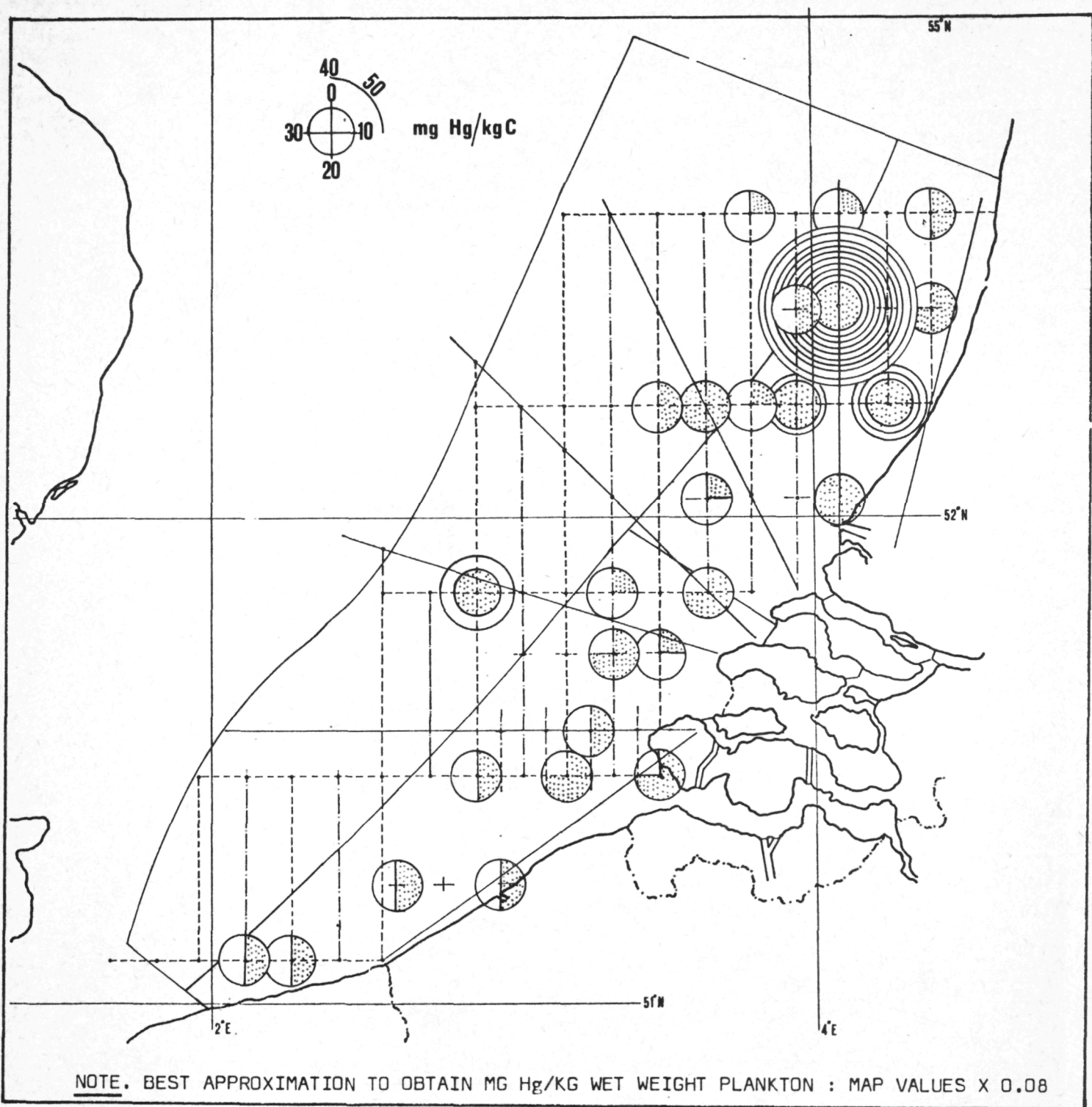
fig. 10.9.- Mercury content of lyophilisated plankton samples.
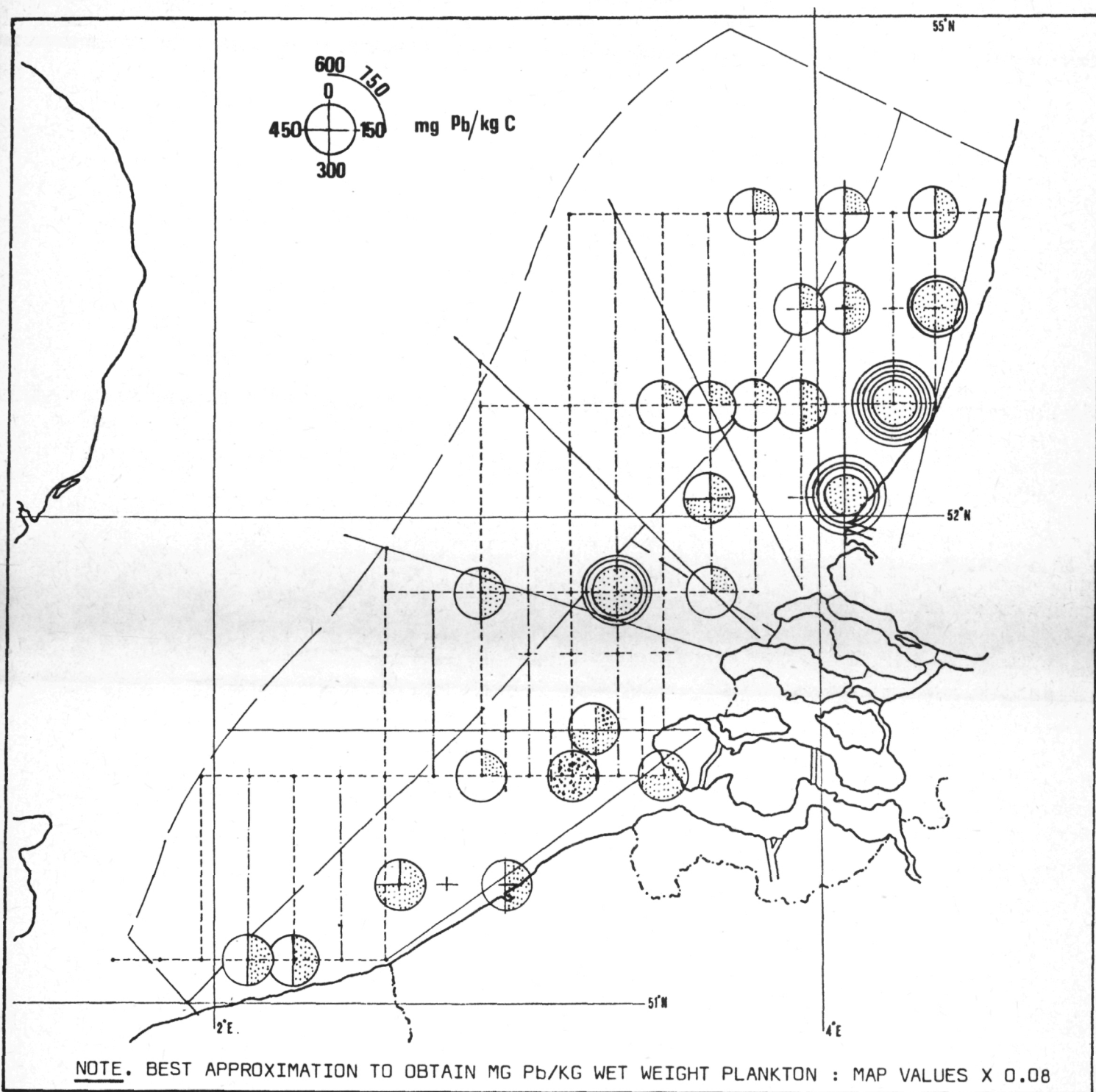
fig. 10.10.- Lead content of lyophilisated plankton samples.

3.- Chlorinated pesticides and PCB's

A complete inventory of chlorinated pesticides and PCB's in the water column, sediments and plankton was made between November of 1970 and December of 1973, but, in view of the considerable task which is the inventory alone, the dynamics study of the distribution has not yet been undertaken. Indeed, the technical problems arising in the application of the traditional methods of analysis : extraction, followed by gas-chromatographic determination, are well known.

The figures 10.11, 10.12 and 10.13 give a global outlook of the distribution of these pollutants in the three sections under study[1].

A preliminary report [Salsmans (1973)] exposes the working philosophy used in the dynamics study of the chlorinated pesticides distribution, mainly as regards the definition of interaction coefficients and the flow of materials within the food web. Mass spectrometry and its possibilities in this field of investigation are the subjects of a complementary paper [Van Binst (1974)].

4.- Sediments

The chemical study of the sediments in the network is, as we know, based upon a sampling net of 1000 points [Wollast (1973)]. The collected samples of sediments taken in this network were analyzed by ashing between 550° and 1000° . Moreover, the heavy metal contents (Zn, Pb, Cu, Mn and Fe) were determined by atomic absorption on some 180 samples.

As has been previously shown [Wollast (1972)], weight loss at 550° is directly related to the presence of silt[2]. The corresponding chart (fig. 10.14) shows the belgian coast to be a privileged zone of silt accumulation in relation to the whole of the network studied. The

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1. The "fish box" is treated separately, see chapter IX.
2. As proposed by McCave (1973) the term "mud" is taken to comprise all material of quartz-equivalent sedimentation diameter < 63 μm , i.e. silt and clay sizes.
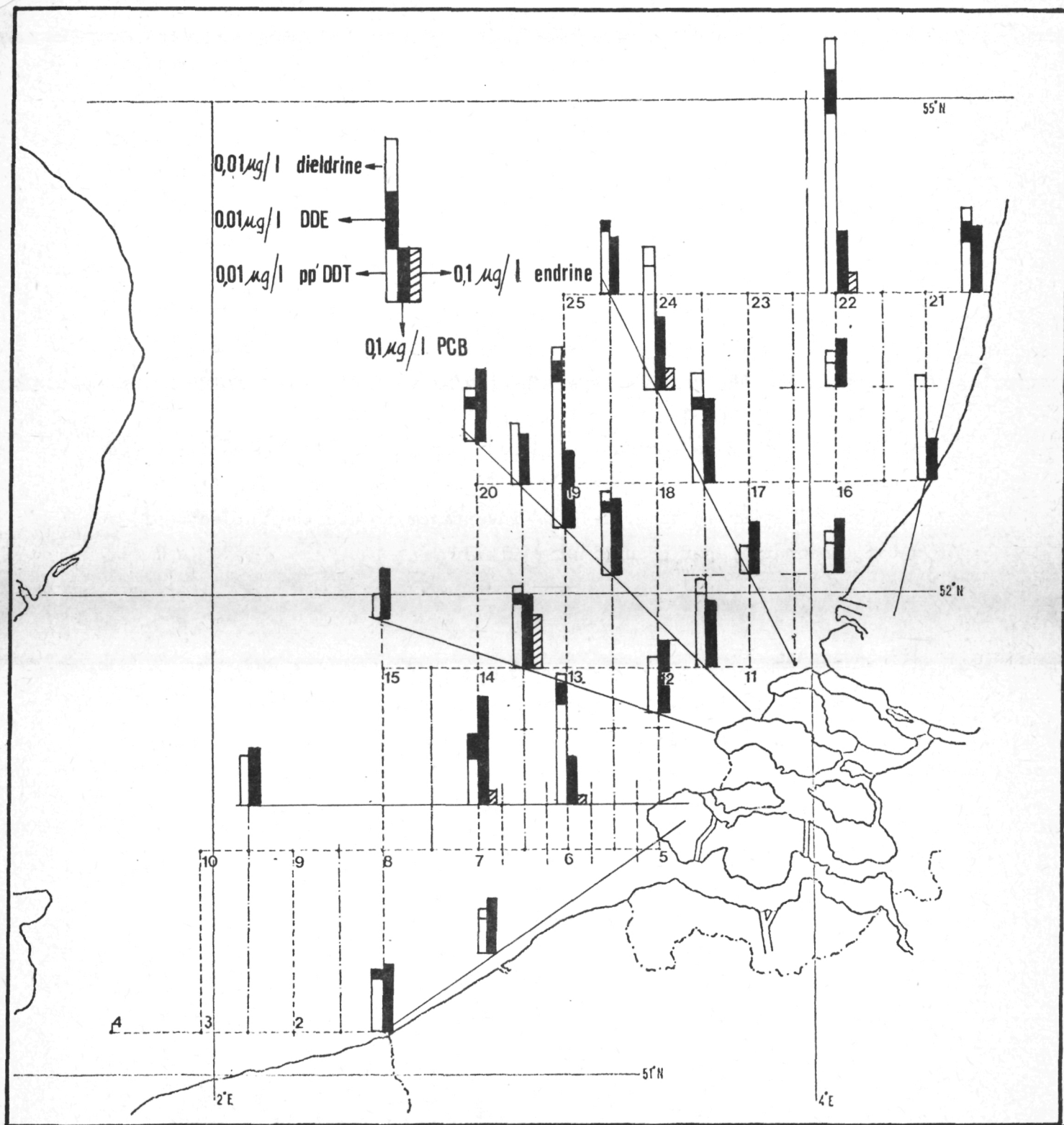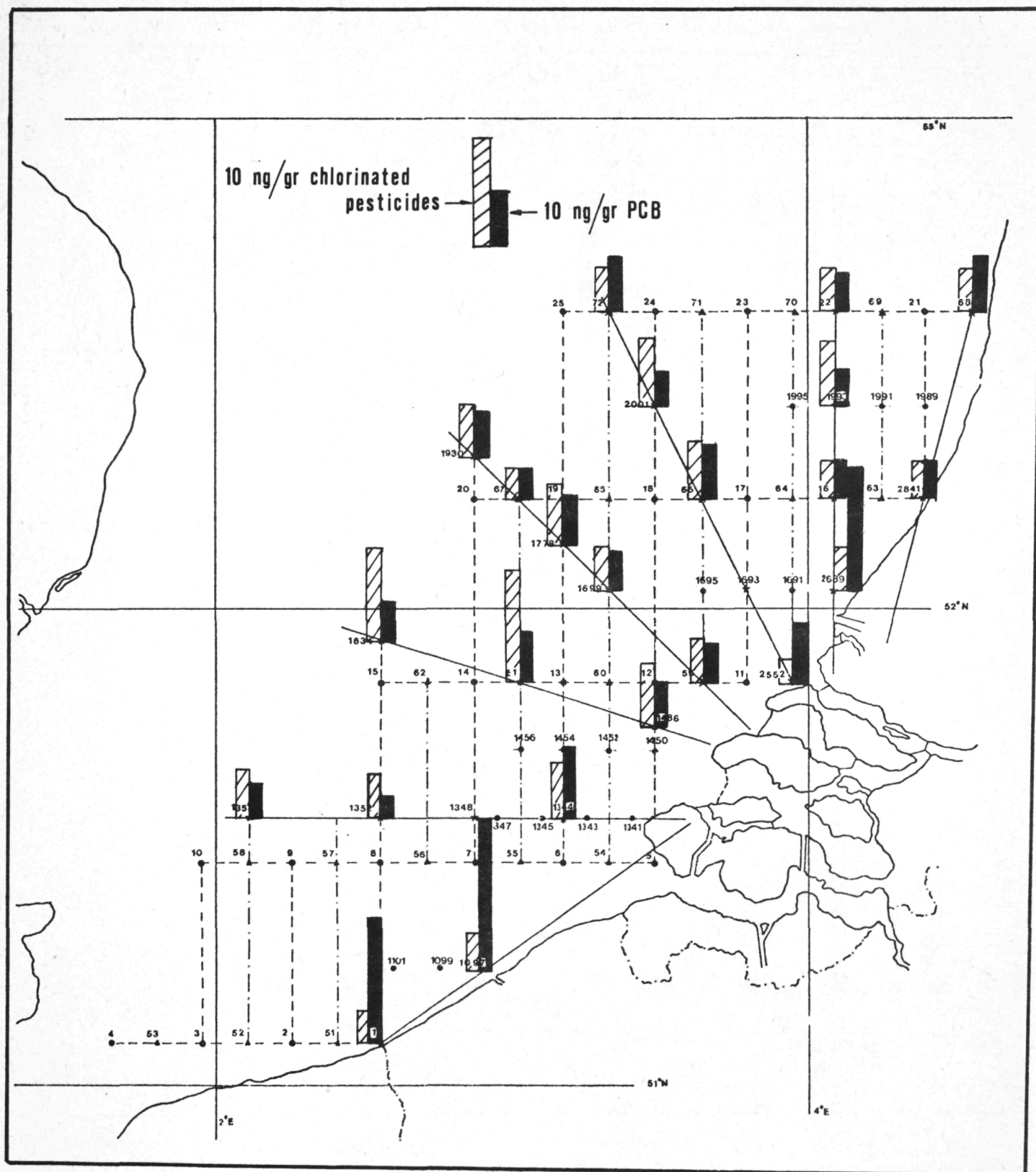
fig. 10.11.- Pesticides in seawater (cruise september 1972).

fig. 10.12.- Pesticides in sediments (cruise september 1972).
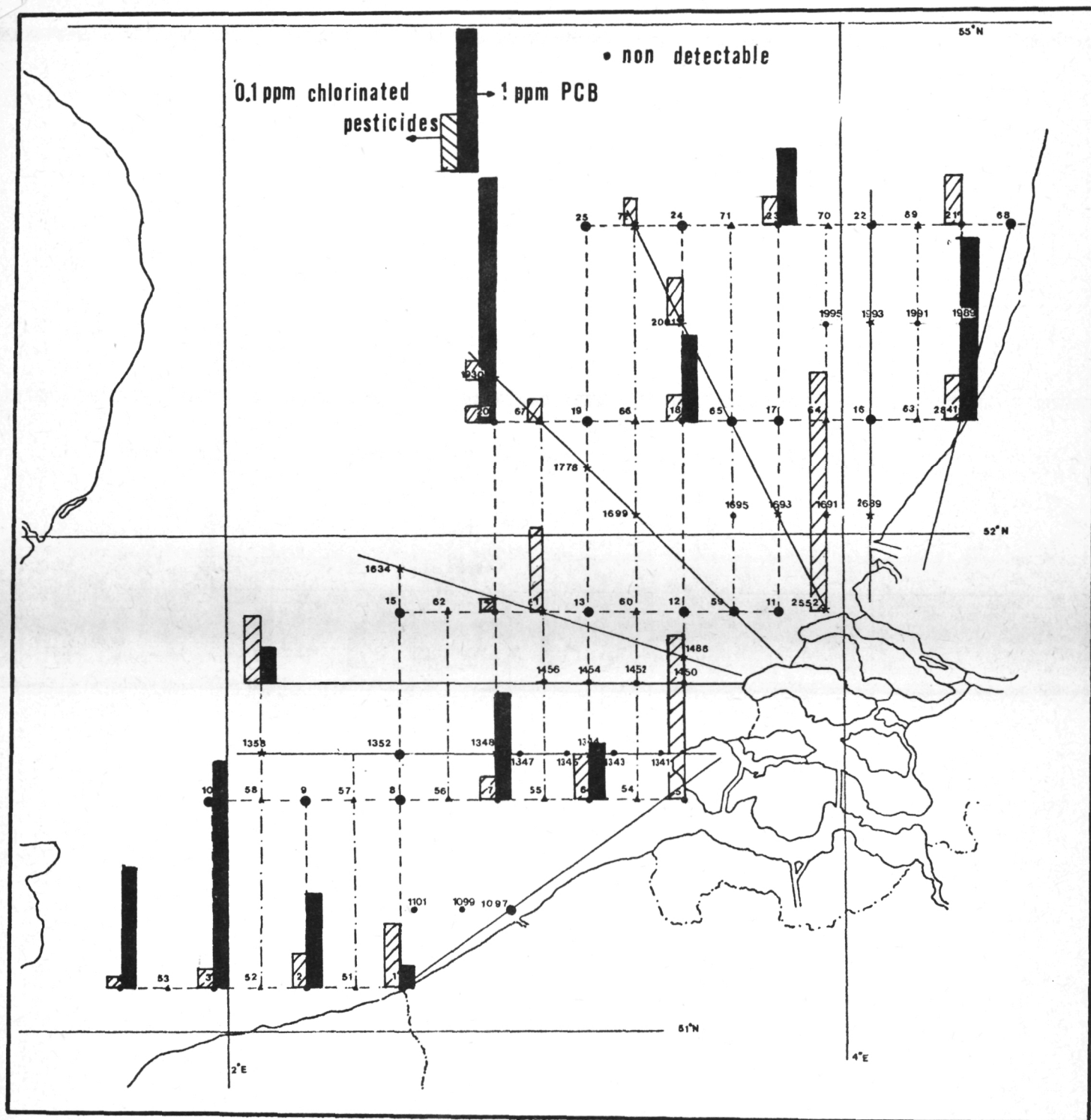
fig. 10.13.- Pesticides in plankton (samples taken during 1972 and 1973).

Weightloss at 550 °C
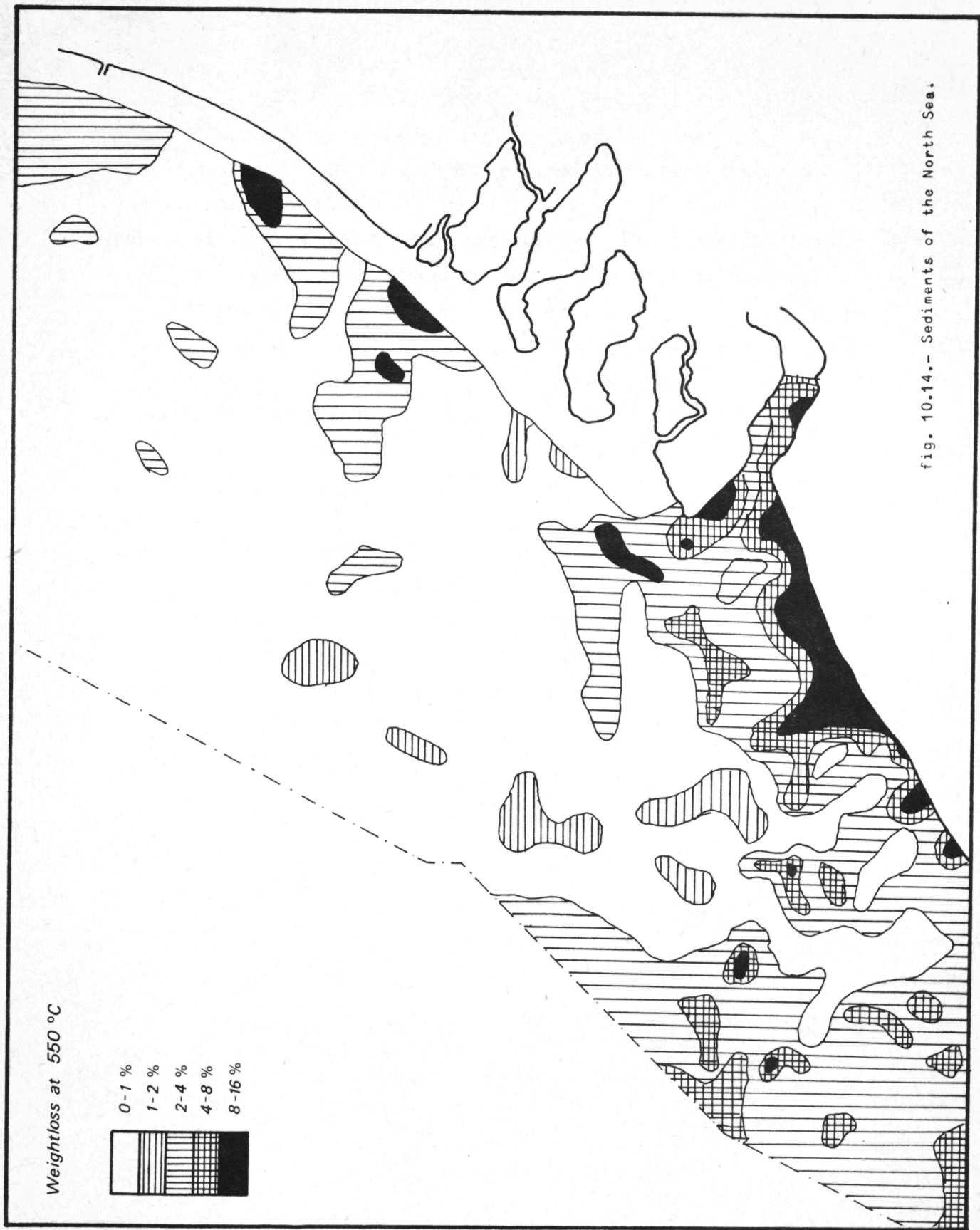
0-1 %
1-2 %
2-4 %
4-8 %
8-16 %

fig. 10.14.-- Sediments of the North Sea.

same situation likely occurs at the exit of the Rhine estuary and along the dutch coast between "Hoek van Holland" and Katwijk.

The weight loss chart between 550° and 1000° corresponding to the CaCO$_3$ contents (fig. 10.15) shows the carbonate-rich sediments to be mainly within the southern part of the network. In these sediments, a large part of the carbonates consists of shell-fish debris. In the south-western part of the network, one must moreover consider a contribution of chalk sediments erosion from the Pas de Calais.

As for the heavy metals[1], iron (fig. 10.16), manganese (fig. 10.17), copper (fig. 10.18) and zinc (fig. 10.19), the distributions follow those of the silts, in accord with the previously established relations [Wollast (1972)].

Lead, on the other hand (fig. 10.20), is distributed as previously, erratically, asides from the dutch and belgian coastal zone where one finds a systematically higher lead content. There are other spots, distributed on the whole network area, where the concentrations are abnormaly high. It must, however, be noted that lead content is never very high, contrarily to that of the other heavy metals.

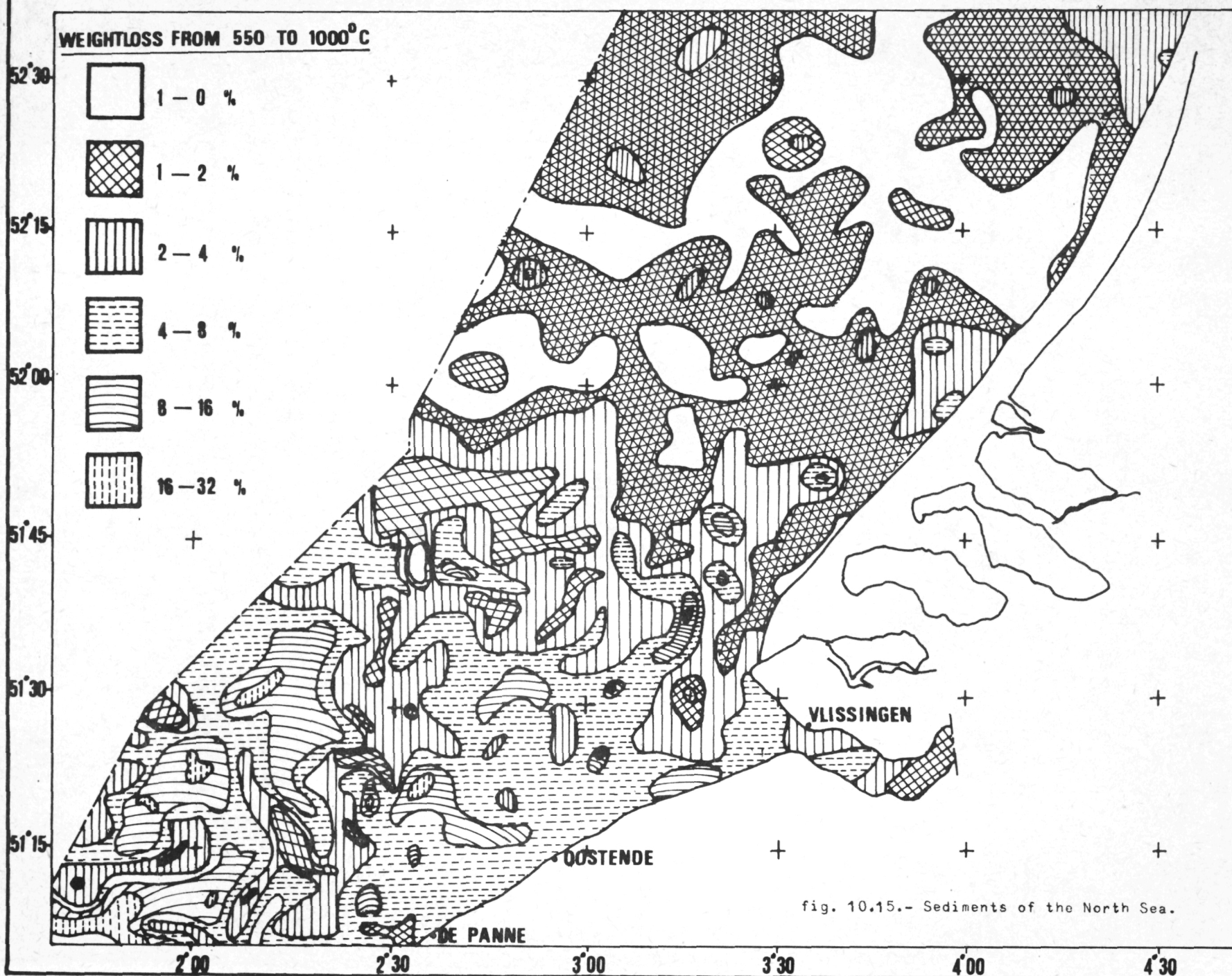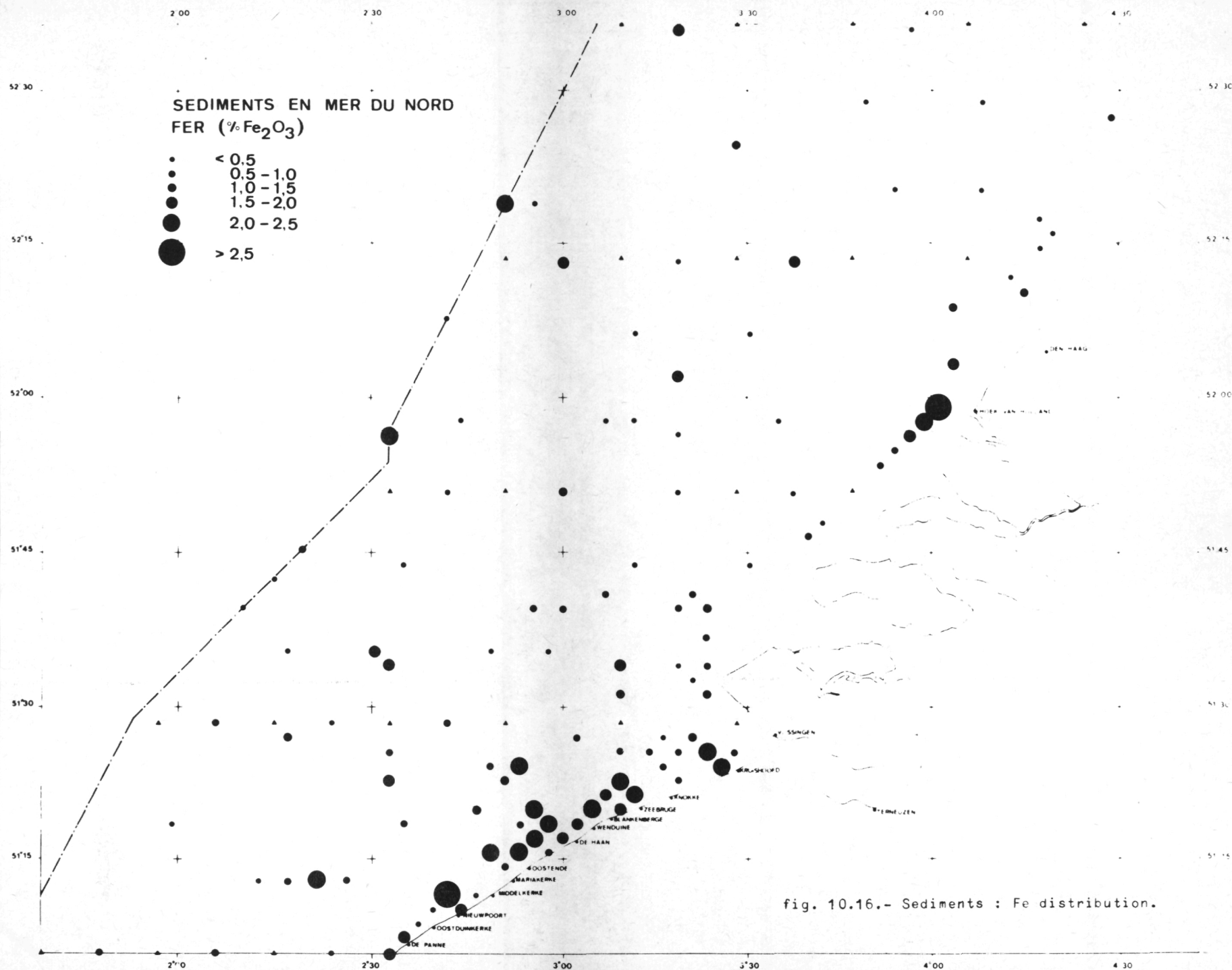1. Chlorinated pesticides and P.C.B. 's are specifically discussed in § 3.

WEIGHTLOSS FROM 550 TO 1000°C
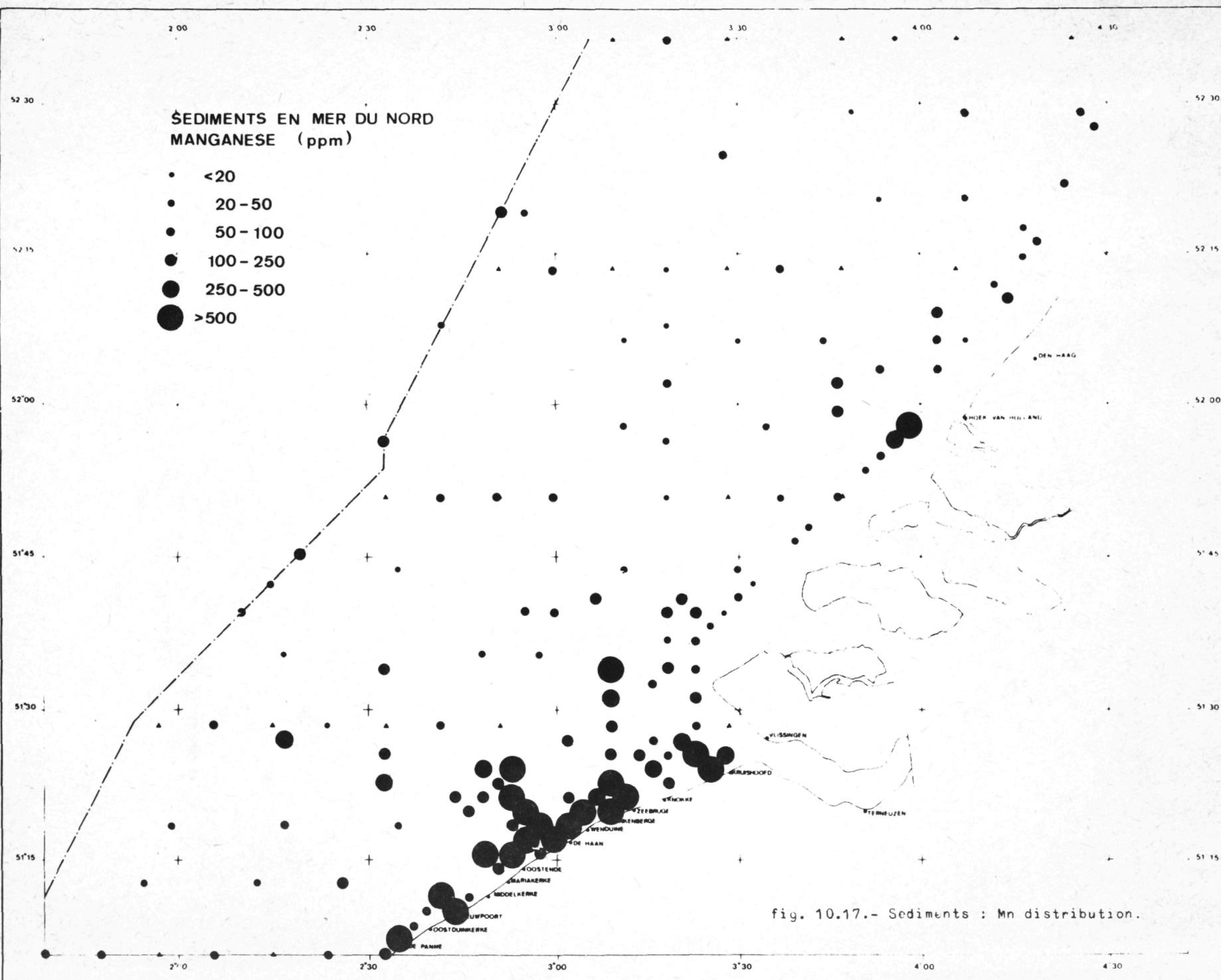
- 1 — 0 %
- 1 — 2 %
- 2 — 4 %
- 4 — 8 %
- 8 — 16 %
- 16 — 32 %

52°30

52°15

52°00

51°45

51°30

51°15

VLISSINGEN

OOSTENDE

DE PANNE

fig. 10.15.- Sediments of the North Sea.

2°00   2°30   3°00   3°30   4°00   4°30

SEDIMENTS EN MER DU NORD
FER (% Fe$_2$O$_3$)

- ·   < 0,5
- ·   0,5 – 1,0
- •   1,0 – 1,5
- ●   1,5 – 2,0
- ⬤   2,0 – 2,5
- ⬤   > 2,5

fig. 10.16.- Sediments : Fe distribution.

SEDIMENTS EN MER DU NORD
MANGANESE (ppm)

- . <20
- • 20 – 50
- • 50 – 100
- ● 100 – 250
- ● 250 – 500
- ● >500

fig. 10.17.- Sediments : Mn distribution.

SEDIMENTS EN MER DU NORD
CUIVRE (ppm)

- · < 5
- · 5 - 10
- ● 10 - 15
- ● 15 - 20
- ● 20 - 30
- ● > 30

fig. 10.18.- Sediments : Cu distribution.

SEDIMENTS EN MER DU NORD
ZINC   (ppm)

- • < 20
- • 20 – 50
- • 50 – 100
- ● 100 – 200
- ● > 200

fig. 10.19.- Sediments : Zn distribution.

SEDIMENTS EN MER DU NORD
PLOMB (ppm)

- ·   < 10
- ·   10 - 15
- ·   15 - 20
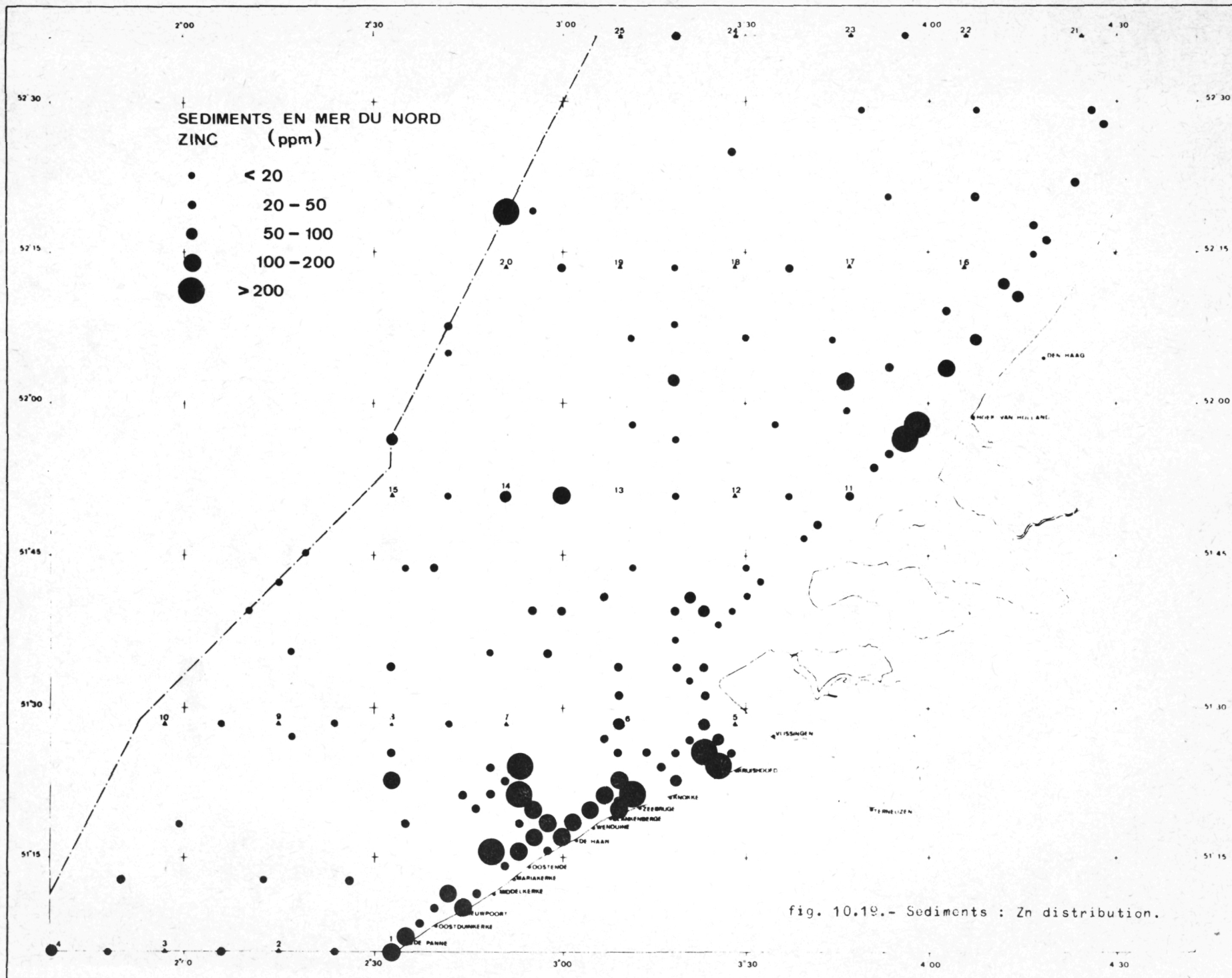- ●   20 - 25
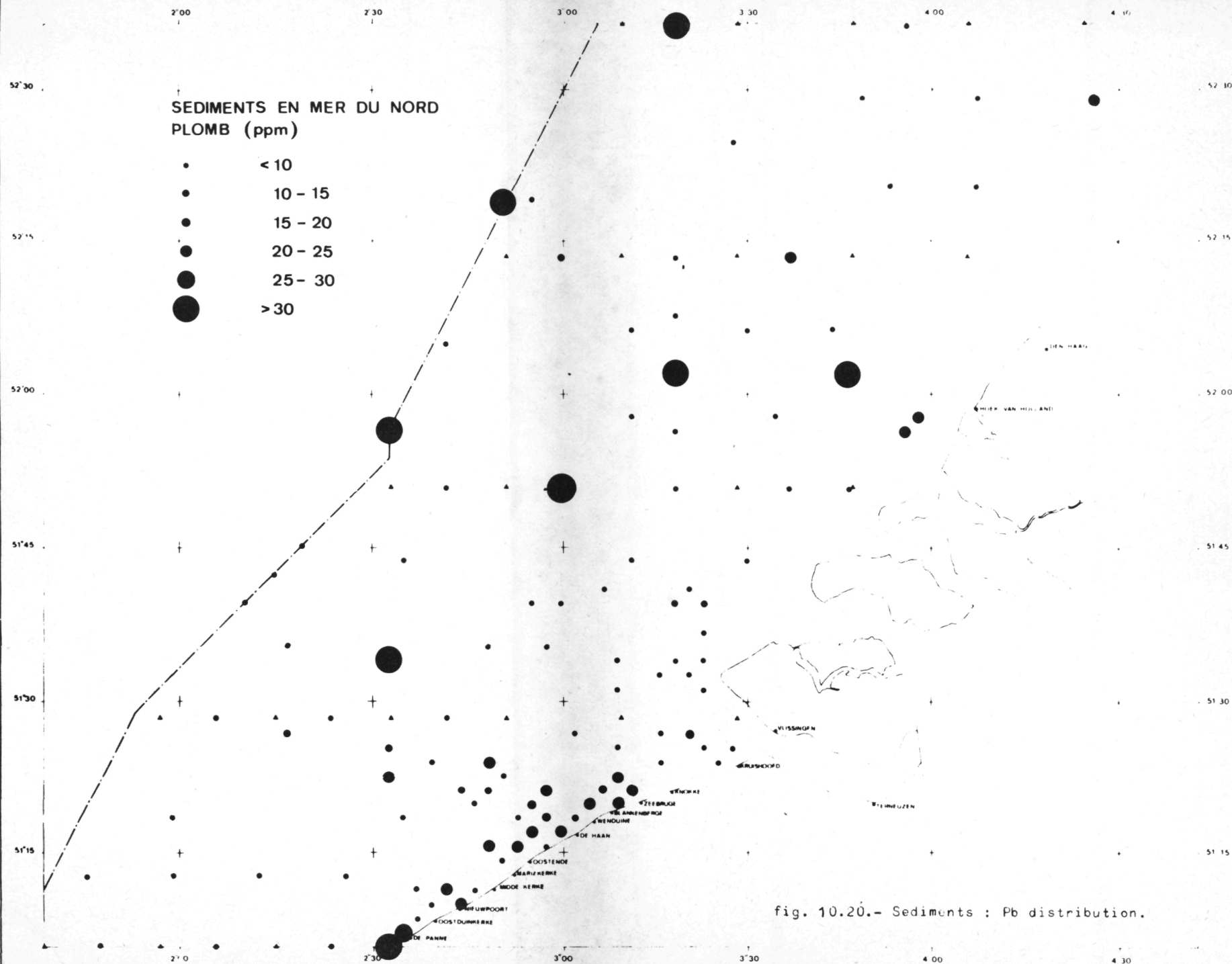- ●   25 - 30
- ●   > 30

fig. 10.20.- Sediments : Pb distribution.

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