EFFECTS OF THE CONSTRUCTION OF IRRIGATION RESERVOIRS ON THE DISTRIBUTION OF POLLUTANTS IN ESTUARINE ZONES OF SMALL MEDITERRANEAN RIVERS. THE CASE OF SPERCHIOS RIVER, GREECE

EFFETS DE LA CONSTRUCTION DE RÉSERVOIRS D' IRRIGATION SUR LA DISTRIBUTION DES POLLUANTS DANS LES ZONES ESTUARIENNES DE PETITES RIVIÈRES MÉDITERRANÉENNES. LE CAS DE LA RIVIÈRE SPERCHIOS, GRÈCE

GLI EFFETTI DELLA COSTRUZIONE DI INVASI IRRIGUI SULLA DISTRIBUZIONE DI INQUINANTI IN ZONE DI ESTUARIO DI PICCOLI CORSI D'ACQUA DEL MEDITERRANEO. IL CASO DEL FIUME SPERCHIOS, GRECIA.

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Abstract

Sperchios is a small river in central Greece and although its estuary has been characterised as an Important Bird Area and is included in the European network "NATURA 2000", it is very poorly managed from an environmental point of view. The Sperchios basin is one of the most important agricultural regions in Greece but it is influenced also by industrial and urban pollution. An earthen dyke is erected b every summer about 2km upstream from the river mouth in order to collect the river water for irrigation purposes. The change in the site of the intermixing zone due to this fact affects the salinity of the water and the amount of suspended matter as well as the chemical behaviour and partitioning of both heavy metals and nutrients. The suspended matter was found to be the major carrier for most metals e.g. lead, zinc, copper whereas phosphorus was the limiting factor for the phytoplankton growth.
Keywords: *Sperchios river*; water pollution; heavy metals; salinity; phytoplankton.

Résumé

Le Sperchios est une petite rivière en Grèce centrale dont l'estuaire a été reconnu comme un territoire important pour les oiseaux et inclus dans le réseau européen "NATURA 2000". Néanmoins, d'un point de vue environnemental la rivière est mal administrée. Le bassin versant du Sperchios est une des régions agricoles des plus importantes en Grèce, mais il est aussi influencé par la pollution industrielle et urbaine. Une digue de terre est édifiée chaque été à approximativement 2 km en amont de l'embouchure de la rivière afin de collecter l'eau de la rivière pour l' irrigation. Le déplacement de la zone de mélange à cause de cet événement modifie

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la salinité de l'eau, la quantité de matière en suspension, le comportement chimique et la concentration en métaux lourds et en composants nutritifs.
La phase en suspension a été trouvée être le transporteur principal pour la plupart des métaux, comme le plomb, le zinc, le cuivre, mais le phosphore était le facteur limitant du development du développment de phytoplancton.
Mots-clés: Rivière Sperchios; métaux lourds; pollution de l'eau; salinité; phytoplancton.

Riassunto

Sperchios è un piccolo corso d'acqua della Gracia centrale il cui estuario presenta un territorio d'importanza comunitaria per gli uccelli incluso nella rete europea "NATURA 2000". Al contrario, da un punto di vista ambientale il corso d'acqua è male amministrato. Il bacino di raccolta dello Sperchio ricade in una delle regioni agricfole più importanti della Grecia, ma è anche interessato da inquinamento di origine industriele e urbana. A circa 2 km dal suo sbocco in mare il corso è stato sbarrato con una diga in terra per la creazione di un invaso per scopi irrigui. A causa di tale intervento è cambiata la regimazione delle acque che risente della salinità, della quantità del materiale in sospensione, della concentrazione di metalli pesanti e di sostanze nutritienti. La fase in sospensione costituisce il principale apporto di metalli, ed in particolare di piombo, zinco e rame, ma il fosforo rappresenta il fattore limitante per lo sviluppo del fitoplancton.
Parole chiave: *Fiume Sperchios;* inquinamento dell'acqua; metalli pesanti; salinità, fitoplancton.

Introduction

Estuarine zones are usually sites of major agricultural, urban and industrial activities that influence their environmental quality. The study of processes related to chemical behaviour, transport and accumulation of pollutants in estuarine environments is particularly important in order of providing a more appropriate scientific framework for the sustainable management of such critical areas. In most Mediterranean countries there is not systematic monitoring of the water quality although a lot of pollution problems have been observed. There is not also adequate management of water resources under scientific guidance. A common practice in the Mediterranean countries is the creation of small bunds along the rivers for irrigation purposes during summer when there is generally lack of water . These small dams have usually significant effects in the river and estuarine ecosystems as the marine water enter into the river mouth changing the physicochemical characteristics of the area. Changes in these parameters can be significant in small rivers that are systems in danger of environmental deterioration or ecological degradation, without the appropriate management towards sustainability. (Dassenakis et al., 1997, Waldman and Shevah, 1993; GESAMP/UNESCO, 1994). (GESAMP/UNESCO 1987, Greek Oceanographers Association 1994).

Sperchios is a small river in Central Greece. Its catchment area is 1,640Km^2, its length is about 80Km and the width up to 20m. The river flow ranges during the year mainly between 5 and 50 m^3/sec but in some cases it has caused dangerous floods (Kallidromitou, 1995)

The Sperchios estuary area has been characterised as an Important Bird Area (IBA) and also has been proposed as a Special Protected Area (SPA). It is also included in the European network "NATURA 2000" according to 92/43 E.U.directive (Pergantis 1995)

The Sperchios basin is one of the most important agricultural regions in Greece. The agricultural land is about 400km^2 which supports a highly competitive agricultural sector with dynamic growth. The irrigated area is about 200km^2. The main cultures are cotton cereals, olives, and pistachio trees, since large areas near the delta are planted with rice, irrigated with water brought by canals from the river. Agricultural activities enrich the water of Sperchios river with nitrogen, phosphorous and pesticides. About 23,000tn of fertilizers and 300tn of pesticides, insecticides, herbicides etc are used annually in the area. The results of this enrichment are increased phytoplankton populations, green blurred waters and the observation of some pollution episodes that led to massive deaths of fishes. In the area there is also industrial pollution by olive oil refineries, wheat mills, abattoirs, dying works etc. The illegal disposal of liquid wastes and sludge into the river is quite common. A bund is created every summer about 2km up the river mouth in order to collect the river water for irrigation purposes (Dassenakis et al 2000).

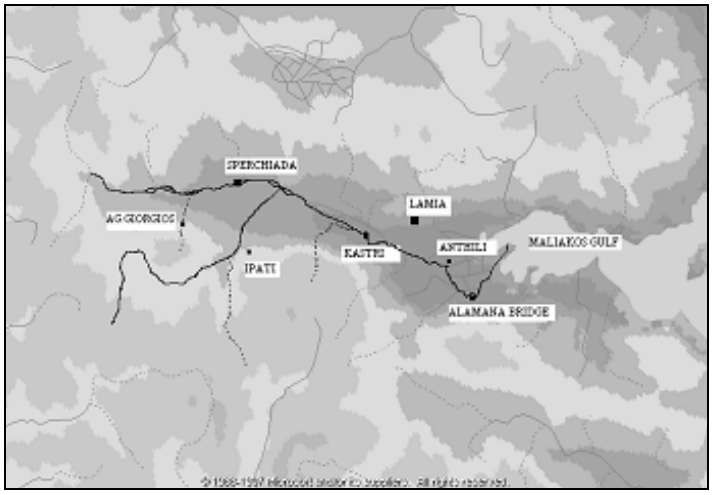

Figure 1

The studied area

Materials and methods

For the purposes of the study, two samplings took place during July and December 2005, along the intermixing zone of the estuary. The sampling stations were recorded by the use of a GPS and the portable YSI 63 and YSI 550A equipments were used for temperature, salinity, conductivity and dissolved oxygen measurements, During summer the samples were collected from the riverbed of

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Sperchios whereas in December, the intermixing zone, was outside of the river mouth, due to increased winter flow of the river. The samples were collected by a hydro-bios sampling bottle and were filtered in succession through pre-weighed Millipore 8 μm and 0,45 μm membrane filters. The filters were treated with concentrated HNO_3 in Teflon beakers. Dissolved metals were determined after preconcentration with Chelex-100 resin columns (Scoullos and Dassenakis, 1984, Rapti 2000). Metal concentrations were determined by flame or flameless atomic absorption spectrometry. Ammonia, nitrites, nitrates and phosphates were measured spectrophotometrically (Grasshoff et al 1999, APHA 1985). The quality of the measurements was reassured by repeatability and standard addition tests.

Results and discussion

The main hydrological characteristics of the river were rather typical for small Mediterranean rivers. The concentrations of dissolved O_2 were very close to the saturation values and the pH was 7.2-7.8 in freshwater and about 8.1 in seawater. The salinities of the samples are presented at Table 1.

Table 1

Salinity of the collected samples

Sample	Salinity (psu)
J1 (July)	15,1
J2	21,3
J3	29,4
J4	31,7
J5	35,5
D1 (December)	0,8
D2	6,8
D3	28,3
D4	33,3
D5	35,5

Two fractions of the Suspended Matter (SPM) were determined: the material with diameter between 0.45 μm and 8 μm and those with diameter larger than 8 μm. During both sampling periods, particles with diameter > 8 μm were most abundant, (percentage 70%). The concentrations of SPM were higher in December due to increased river flow but the most of the particles precipitated near the river mouth and only a small part came down to the Maliakos gulf. (Meybeck M.1982, Van Bennekom A.J. and W.Salomons 1981).

Nutrient behaviour. The chemical behaviour of nutrients was in general non conservative as it is clear fro figures 2-5. There were observed seasonal variations in the behaviour of nutrients as well as different trends between nitrogen and phosphorus. The dissolved organic nitrogen was removed from the estuarine system during winter, probably due to adsorption to sediments or consumption from the aquatic flora, whereas it is added to the estuarine water during summer probably due to the increased decomposition of organic matter. (fig. 2, 3, 4).

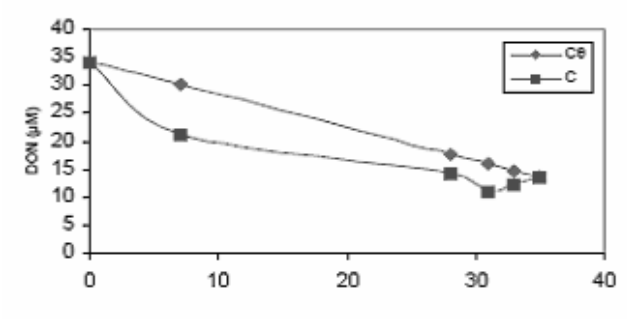

Figure 2

Non conservative behaviour of Dissolved Organic Nitrogen during winter.
[Cθ : theoretical dilution line]

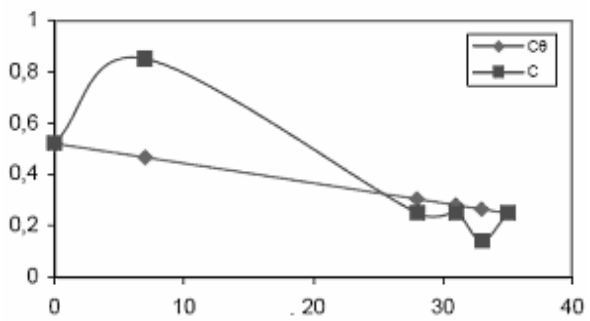

Figure 3

Non conservative behaviour of phosphates (in nmol/l) during winter.
[Cθ : theoretical dilution line]

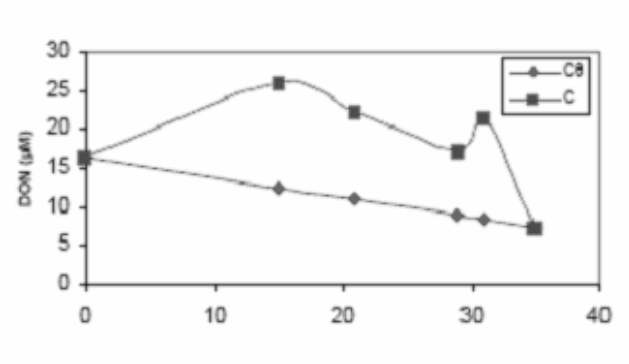

Figure 4

Non conservative behaviour of Dissolved Organic Nitrogen during summer.
[Cθ : theoretical dilution line]

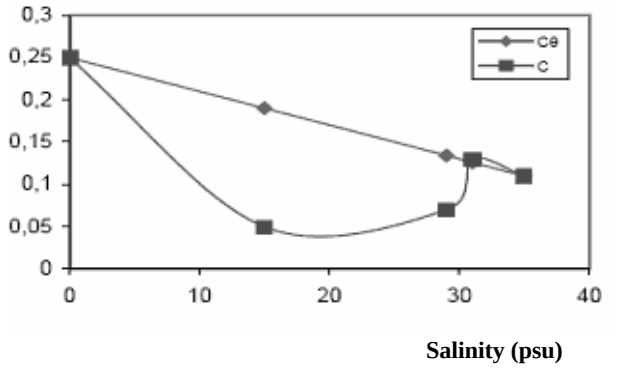

Figure 5

Non conservative behaviour of phosphates (in nmol/l) during summer.
[Cθ : theoretical dilution line]

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The dissolved organic nitrogen was removed from the estuarine system during winter, probably due to adsorption to sediments or consumption from the aquatic flora, whereas it is added to the estuarine water during summer probably due to the increased decomposition of organic matter. (fig. 2, 3, 4).
On the contrary the significantly lower concentrations of phosphates, have the opposite behaviour probably because there is addition during winter from agricultural activities (fertilizers), whereas during summer the very low phosphates concentrations are consumed by the aquatic flora. (fig. 3,5)

Metals behaviour during summer. The chemical behaviour of metals was affected by variations of salinity, pH and SPM. (McKee et al 2004). In general cadmium was transferred from the river in dissolved form, while zinc, copper, lead and manganese in particulate forms. The concentrations of zinc in the dissolved phase increased seawards whereas the concentrations of particulate metal were reduced from the estuary to the sea (Figure 6). Cadmium followed the same trend.

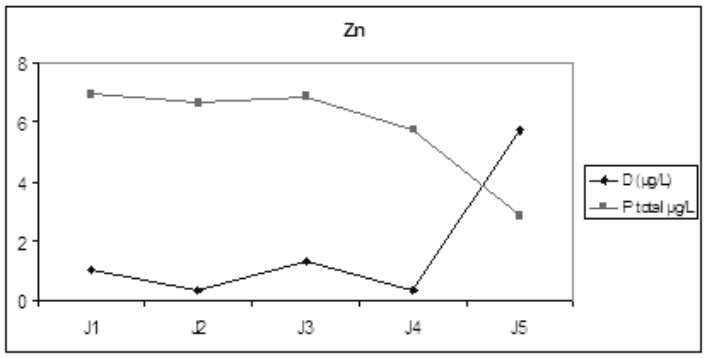


Figure 6

Zinc concentrations during July.

(D: dissolved, P: particulate)

The concentrations of both dissolved and particulate copper increased from the estuary to the sea (Figure 7). Lead followed the same trend as copper, implying that metal load was transferred from sediments to water column because of the bund construction.

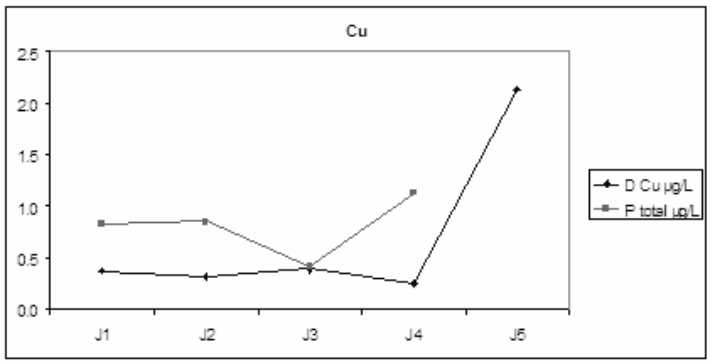


Figure 7

Copper concentrations during July,

(D: dissolved, P: particulate)

Both dissolved and suspended manganese concentrations were reduced as salinity raised (Figure 5). The same trend was observed in Mn content of particles (mg/g), suggesting transfer of manganese from the water column to the sediments.

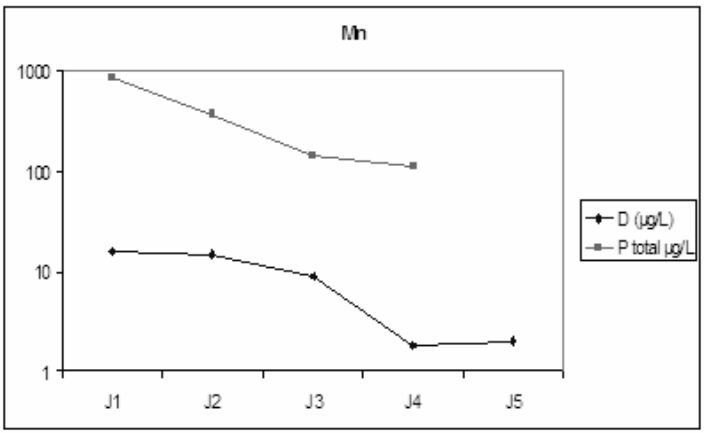


Figure 8

Manganese concentrations during July.

(D: dissolved, P: particulate)

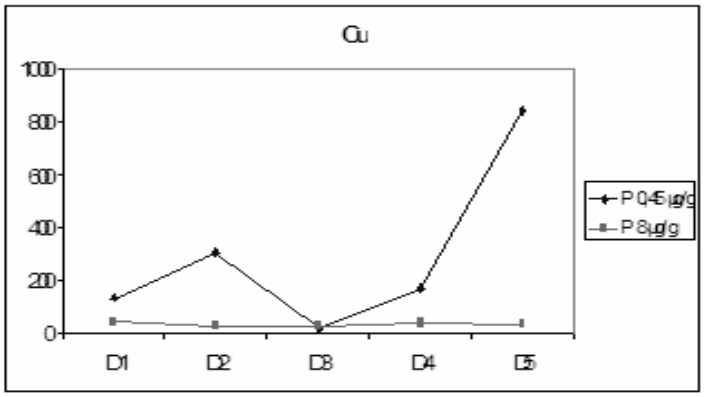
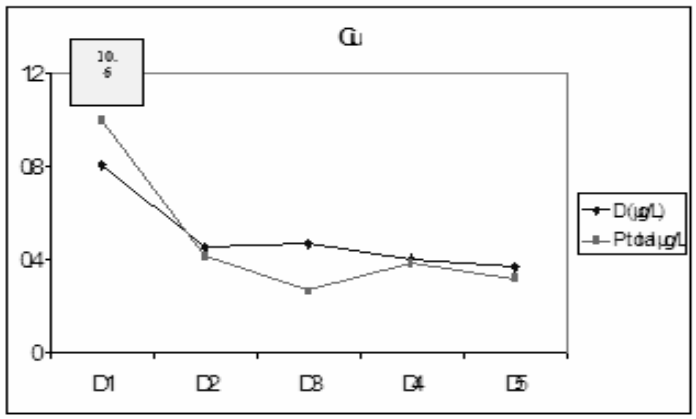


Figure 9

Copper concentrations during December.



The concentrations of copper in the dissolved phase were reduced as salinity increased, implying metal transfer from the water column to particles, which in combination with the reduction of particulate matter from the estuary to the sea, led to reduction in copper concentrations.

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Furthermore, the metal load of particles with diameter > 8 μm was almost stable while in particles with diameter 0.45 <d< 8 μm which are more active in adsorption procedures it was increased.
As far as zinc is concerned, the suspended load increased with salinity, especially in particles with diameters <0.45 μm. Probably, there is transfer of dissolved metal to particles or impact of polluted particles which enter the river from Maliakos Gulf. The concentrations in the dissolved phase were reduced in high salinities.
The cadmium was mainly in the dissolved phase and its concentrations were increased with salinity. The concentrations of particulate Cd were reduced as salinity increased possibly due to relevant reduction of SPM or due to adsorption of metal from particles.

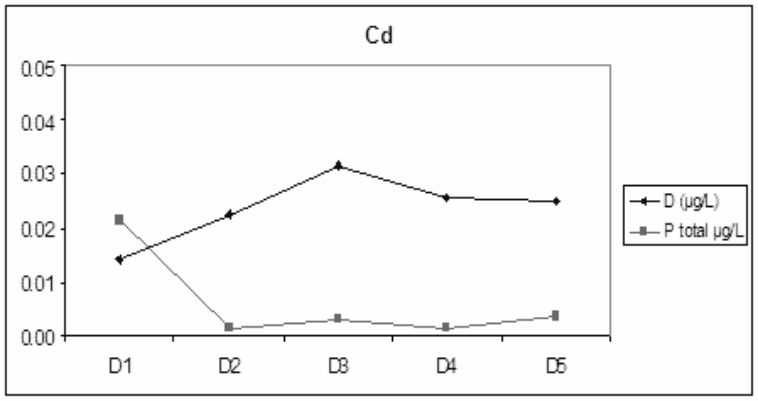

Figure 10

Cadmium concentrations during December.

(D: dissolved, P: particulate)

Lead was mainly transferred by particles, although the concentrations presented reduction as salinity increased, while dissolved phase presented a small raise. The reduction of suspended metal near the 'mouth' of the river is custom as adsorption occurs. (Dassenakis et al., 1997). Suspended particles were also the major carriers for manganese. Dissolved metal presented reduction from the river to the sea.

Conclusions

- The samples from the two periods had different concentrations in suspended matter due to the change of the river flow and the land wash out. Suspended matter presented reduction from the river to the sea due to its precipitation in the riverbed.
- The spatial and seasonal variation in chemical behaviour of nutrients affects significantly the ecosystems of the estuary.
- Phosphorus is the limiting factor for the phytoplankton growth and its release from sediments that occur during winter is probably to favour eutrophication phenomena.
- The dissolved phase was the major carrier for some metals e.g. cadmium, while the suspended phase was for the most metals e.g. lead, zinc, copper.

- The change of the site of the intermixing zone, due to human activities, affects the chemical behaviour of both metals and nutrients as well as the salinity of the water and the amount of suspended matter and have important role in metals partitioning.
- The study indicates the importance of scientifically guided environmental management in order to achieve sustainable development.

References

APHA-American Public Health Association, American Water Works Association, Water Pollution Control Federation (1985) Standard Methods for the examination of water and waste water, 16th edition, pp373-404, 437-463, 556-590.

DASSENAKIS M., THEODOROPOULOU A., SIANNOU V., PAPADIMITRIOU D. (2000) Water pollution problems in Sperchios river and estuary, Greece 1st World Wide Congress of International Water Association – Paris, July 2000, Abstract L219.

DASSENAKIS M., SCOULLOS M., GAITIS A. (1997) Trace Metals Transport and Behaviour in the Mediterranean Estuary of Acheloos River, Marine Pollution Bulletin, 34. 2:103 -111.

GESAMP/UNESCO (1987) Land/Sea Boundary Flux of contaminants: Contributions from rivers. Reports and Studies, 32:67-81.

GESAMP/UNESCO (1994) Anthropogenic influences on sediment discharge to the coastal zone and Environmental Consequences. Reports and Studies 52:4-30.

GRASSHOF K., KREMLING K. (1997) Methods of Seawater Analysis, WILEY-VCH 3rd Edition.

GREEK OCEANOGRAPHERS ASSOCIATION (1994) The water pollution monitoring in Greece. Mesopelaga, Athens, 3:1-8.

KALLIDROMITOU D. (1995) Satellite Telematics of Sperchios Basin Procedings of Conference ''Sperchios 2000'', Lamia, pp 58-68

MEYBECK M. (1982) Carbon, Nitrogen and Phosphorus transport by the world rivers. Am.J.Sci. 282:401-450

MCKEE B.A., ALLER R.C., ALLISON M.A., BIANCHI T.S., KINEKE G.C. (2004) Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: Benthic boundary layer and seabed processes Continental shelf research 24:899-926.

PERGANTIS F. (1995) The biotic environment in the Sperchios river basin, Procedings of Conference ''Sperchios 2000'', Lamia, pp 122-129

RAPTI K. (2000), Research for the conditions of the use of the resin Chelex-100 for the recovery and measurement of the trace metals Mn, Zn and Cu in seawater. National and Kapodestrian University of Athens, Department of Chemistry, Athens.

SCOULLOS M., DASSENAKIS M. (1984) Determination of dissolved metals in seawater, using the resin Chelex-100. In Proceedings of the first Greek symposium on Oceanography and Fisheries, National Centre for Marine Research, Athens, pp. 302-309.

VAN BENNEKOM A.J., SALOMONS W. (1981) Pathways of organic nutrients and organic matter from land to ocean through rivers. In : River input to the Ocean System, J.D.Burton, D.Eisma and J.M.Martin, Eds, UNESCO/UNEP/SCOR Workshop, Rome 1979, pp 33-51.

VAN DAMME S., STRUYF E., MARIS T., YSEBAERT T., DEHAIRS F., TACKX M., HEIP C., MEIRE P. (2005) Spatial and temporal patterns of water quality along the

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estuarine salinity gradient of the Scheldt estuary (Belgium and The Netherlands): results of an integrated monitoring approach, Hydrobiologia, 540:29–45.