

DISTRIBUTION AND SPECIATION OF Co AND Ni IN THE SCHELDT ESTUARY

by

H. Zhang and R. Wollast

Laboratory of Chemical Oceanography, University of Brussels, Belgium.

ABSTRACT

An analytical method for the determination of cobalt and nickel based on cathodic stripping voltammetry has been developed and applied to the study of the distribution of these two elements in the Scheldt estuary. The method based on the adsorptive collection of the dimethylglyoxime complexes of Co and Ni allows the determination of these metals at the low levels encountered in natural water samples with a satisfactory sensitivity and a good reproducibility. Various pretreatments (acidic hydrolysis and UV-irradiation) of the filtered and unfiltered samples allow a better description of the speciation of these elements.

Six cruises covering the entire Scheldt estuary were performed between August 1987 and August 1988. The longitudinal profile exhibits a similar trend independent of the seasonal fluctuations with a maximum in the region situated at about 60 km from the mouth, or at a salinity around 7 to 8 o/oo. Most of the cobalt is present as dissolved inorganic species while nickel is especially present as inorganic species and adsorbed Ni on the particulate matter. A strong linear relationship between total Co and Ni as well as dissolved concentrations actually is observed in the Scheldt estuary in spite of the possible large anthropogenic perturbations of the system for these two elements.

DISTRIBUTION AND SPECIATION OF Co AND Ni IN THE SCHELDT ESTUARY

H. ZHANG and R. WOLLAST

Laboratory of Chemical Oceanography, University of Brussels, Belgium.

ABSTRACT

An analytical method for the determination of cobalt and nickel based on cathodic stripping voltammetry has been developed and applied to the study of the distribution of these two elements in the Scheldt estuary. The method based on the adsorptive collection of the dimethylglyoxime complexes of Co and Ni allows the determination of these metals at the low levels encountered in natural water samples with a satisfactory sensitivity and a good reproducibility. Various pretreatments (acidic hydrolysis and UV-irradiation) of the filtered and unfiltered samples allow a better description of the speciation of these elements.

Six cruises covering the entire Scheldt estuary were performed between August 1987 and August 1988. The longitudinal profile exhibits a similar trend independent of the seasonal fluctuations with a maximum in the region situated at about 60 km from the mouth, or at a salinity around 7 to 8 o/oo. Most of the cobalt is present as dissolved inorganic species while nickel is especially present as inorganic species and adsorbed Ni on the particulate matter. A strong linear relationship between total Co and Ni as well as between the concentrations of the two dissolved metals is observed in the Scheldt estuary in spite of the possible large anthropogenic perturbations of the system for these two elements.

INTRODUCTION

The biogeochemical cycles of Co and Ni are still poorly known although these elements are of great importance in aquatic ecosystems because they are relatively accessible and may become toxic at high levels of concentration (Förstner, 1981, Friberg, 1979). Cobalt is a typical example of an element known to be essential for many aquatic organisms but it may turn into an insidious pollutant since it tends to accumulate in vital organs of planktons and acts progressively as a toxicant over long time periods (Venugopal, 1978). Furthermore both elements are strongly enriched in marine sediments either due to organic uptake or chemical coprecipitation in marine manganese nodules (Kauner et al., 1982, Bruland, 1983).

Studies on the distribution of Co and Ni in the Scheldt estuary are of particular importance and interest because high accumulation of persistent pollutants and intense modifications of chemically or biologically active substances have been found in this region (Wollast, 1988).

Our main interest is however related to the behaviour and ultimate sink of the radioactive Co released by nuclear power stations. The gamma emitting radionuclides of this element are the major radioactive isotopes injected in the aquatic ecosystems by nuclear power stations. This is the case for the nuclear power station of Doel on the Scheldt estuary. Since nickel has similar properties to cobalt, and has a

potentially strong toxic action, this element has been included in the present research.

Laboratory studies indicate that Co exists in seawater primarily as the Co^{2+} ion and as the carbonate complex. Organic complexes are not considered important (Mantoura et al., 1978). However, very little information is available on the distribution and speciation of Co and Ni (especially Co) and the processes controlling their geochemical behaviour in natural waters. It is therefore necessary to gain further knowledge concerning the distribution, behaviour and fate of Co and Ni by direct investigations of natural and perturbed environments. However, the low level of concentration of Co in aquatic ecosystems create significant analytical problems. An electrochemical approach based on advanced polarographic techniques which were shown to be highly specific and sensitive (Nürnberg et al., 1976, Nürnberg, 1977) was chosen here.

A direct method for the determination of Co and Ni using differential pulse adsorptive cathodic stripping voltammetry has been developed in our laboratory and applied to the study of the distribution and speciation of these two elements in the Scheldt estuary.

1 ANALYTICAL PROCEDURES

1.1 Sampling

Surface water samples were collected seasonally from the Scheldt estuary between 1987 and 1988. The sampling locations were selected to cover geographically the mixing zone of fresh and seawater through the entire estuary. Unfiltered surface samples were obtained directly from a polyethylene bucket sampler, acidified to pH2 with 10M Merck suprapure HCl. Filtered samples were obtained by vacuum of direct pressure filtration from sampler through 0.45 μm Sartorius filters. All containers and sample bottles were decontaminated by soaking in HCl bath for a few days and rinsing with Milli-Q water and then wrapped in polyethylene bags. All samples were stored in a refrigerator at approximately 5°C until analysis.

1.2 Reagents

All reagents used were Suprapure Merck or Merck analytical reagent grade. Stock standard solutions of Co and Ni were prepared separately by dissolving respectively their nitrate and sulphate salts into 0.1M hydrochloric acid. The required standards were prepared daily by appropriate dilution of the stock solutions. Dimethylglyoxime solution (0.1M) was prepared by dissolving the compound into ethanol or 0.05M NaOH solution daily. Milli-Q water was used in all the analyses.

1.3 Instruments

A PAR174 Polarographic Analyzer in connection with a PAR Model 303 stand (SMDE) and a PAR Model 305 Stirrer was used for voltammograms measurement. They were recorded on a PAR RE 0074 X-Y recorder. A three electrode system consisting of a hanging mercury drop electrode (HMDE) as working electrode, a coiled Pt-wire as counter electrode and an Ag/AgCl/KCl(s) electrode as reference electrode was adopted. Polarographic cells were soaked in a HCl bath until the time of use.

1.4 Methods

The analytical method used in this study for determining Co and Ni is differential pulse cathodic stripping voltammetry based on the adsorptive collection of the dimethylglyoxime (DMG) complexes of Co and Ni in the presence of an ammonium chloride (NH_4Cl) and triethanolamine (TEA) buffered supporting electrolyte (Zhang et al., 1988). It offers a satisfactory sensitivity and a good reproducibility. The detection limits for Co and Ni are about 3 ng/L and 20 ng/L respectively. The optimal experimental conditions used are as follows : the concentration of complexing reagent DMG is $1 \times 10^{-3}\text{M}$. The concentration of buffered supporting electrolyte is 0.1M NH_4Cl and 0.05M TEA. The pH is adjusted to around 8.7 using ammonia solution. The adsorption potential is adjusted to -0.8V vs an Ag/AgCl/KCl(s) electrode and the adsorption time used is 1 to 3 minutes depending on the content of Co and Ni in the sample. A scanning rate of $5\text{mv}\cdot\text{s}^{-1}$ is used for recording the voltammogram. Preparation steps and the detailed analytical procedures are the same as reported earlier (Zhang et al., 1988). The concentration of Co and Ni present in the samples are determined by the standard addition method using the differential pulse cathodic stripping peaks observed at about -1.15v and -0.98v respectively. The quality assessment of the analytical procedure was obtained by analyzing three certified water samples, respectively riverine water, nearshore sea water and Atlantic open sea water collected at 1300 m, provided by the National Research Council of Canada. The results of our determinations are compared with the certified values in table 1.

1.5 Speciation

Various pretreatments of the samples were adopted in order to get a better description of the speciation of cobalt and nickel. Four types of water samples were analyzed :

(a) filtered sample. The result from (a) is regarded as "dissolved inorganic" fraction. Strictly speaking this is an operational definition, but is usually a rather good approximation (Florence, 1980).

TABLE 1. Determination of Co and Ni in the Standard Reference Materials

Sample	Element	Found Values (ng/l)	Certified Values (ng/l)
Seawater NASS-2 (n = 8)	Co	4.8 ± 0.4	4 ± 1
	Ni	274 ± 12	257 ± 27
Nearshore Seawater CASS-2 (n = 6)	Co	22.6 ± 0.4	25 ± 6
	Ni	302 ± 11	298 ± 36
Riverine water SLRS-1 (n = 6)	Co	39.5 ± 0.3	43 ± 10
	Ni	1106 ± 17	1070 ± 60

n = number of independent determinations

(b) filtered sample, UV-irradiated with a Hanovia mercury vapor lamp (1KW) for three hours in the presence of 0.01M hydrochloric acid. The data obtained from (b) is considered as "total dissolved" which includes the dissolved inorganic fraction plus dissolved organic metal complexes decomposable by UV treatment.

(c) unfiltered sample, acidified with 10M HCl solution to pH about 2. The results obtained with this sample treatment include the truly dissolved fraction plus the metal ions leached from particulate matter during storage at pH 2 which may represent the weakly bound and easily available particulate fraction of the metal. It will be referred here as total inorganic fraction.

(d) unfiltered, acidified sample, UV-irradiated for three hours. This treatment allows a further release of the organic complexed fraction of the metals either dissolved or particulate by UV photo oxidation. We will designate this fraction as total concentration.

The difference obtained between the sample treatment (b) and (a) gives an estimation of the dissolved organic fraction. Similarly the difference between treatment (d) and (b) allows to evaluate the weakly bound fraction.

2 RESULTS AND DISCUSSION

2.1 Distribution of Co and Ni

Six cruises covering the entire salinity range of the Scheldt estuary were conducted between August 1987 and October 1988. Longitudinal profiles of the concen-

tration of Co and Ni were recorded as well as the evolution of these elements at a few fixed stations during one tidal period.

Figure 1 shows the longitudinal distribution of total Co in the zone of mixing of fresh water and seawater of the Scheldt. In most cases, Co exhibits a maximum concentration close to km 60 in the vicinity of Doel. The concentration of Co is however very sensitive to the fresh water discharge as shown in figure 2 where the concentration of total cobalt have been plotted as a function of salinity. The concentration of total cobalt in the fresh water part varies strongly on a seasonal basis which suggests that there may be a constant input flux of cobalt in the river system, diluted proportionally to the river discharge.

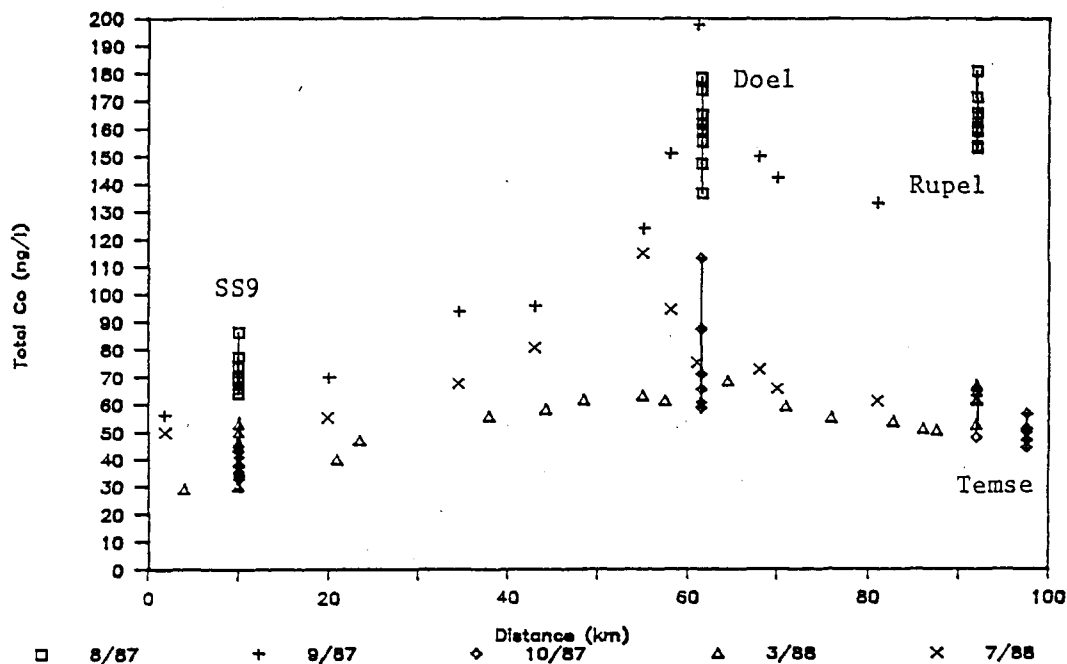


Fig. 1. Longitudinal distribution of total concentration of Co obtained during the various 87-88 cruises. The horizontal axis represents the distance to the sea (Vlissingen = km 0). Measurements carried out at fixed stations during one tidal period are connected with a vertical bar.

On the other hand, since there is no important tributaries in the mixing zone of the Scheldt estuary, it is possible to evaluate the conservative or non-conservative behaviour of the elements by examining the deviations of the distribution of the elements as a function of salinity from the ideal dilution line (Boyle et al., 1974, Mantoura, 1983).

Except under very high river discharge conditions (March 88), there is obviously a significant positive departure from the ideal mixing line corresponding to a conservative behaviour of Co in the estuary. We think thus that there must be a significant input of Co in the estuarine zone, probably in the vicinity of Doel.

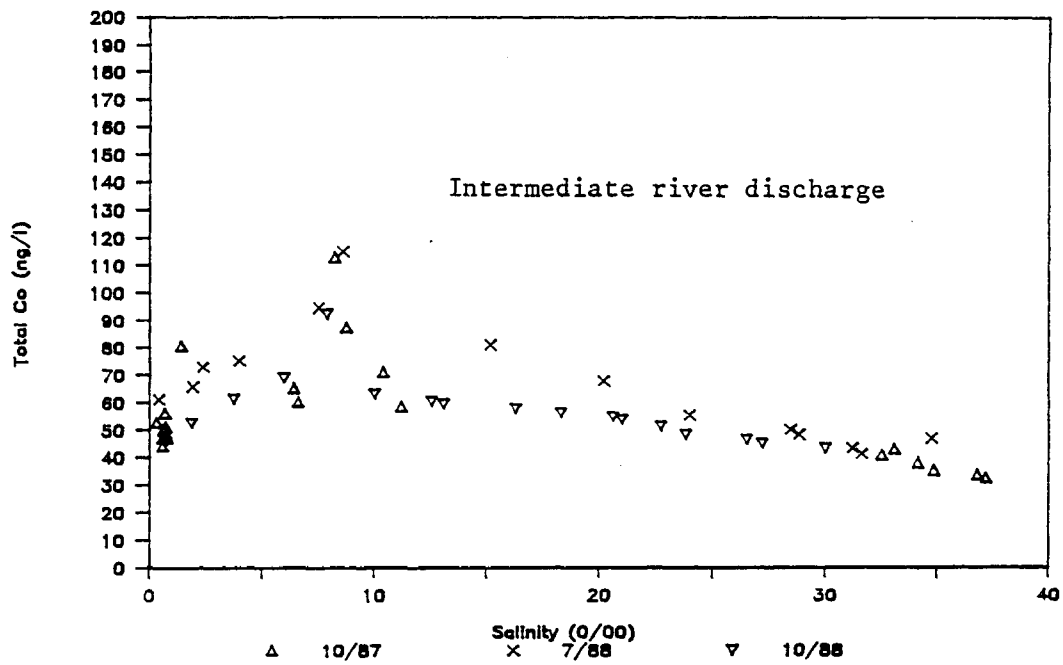
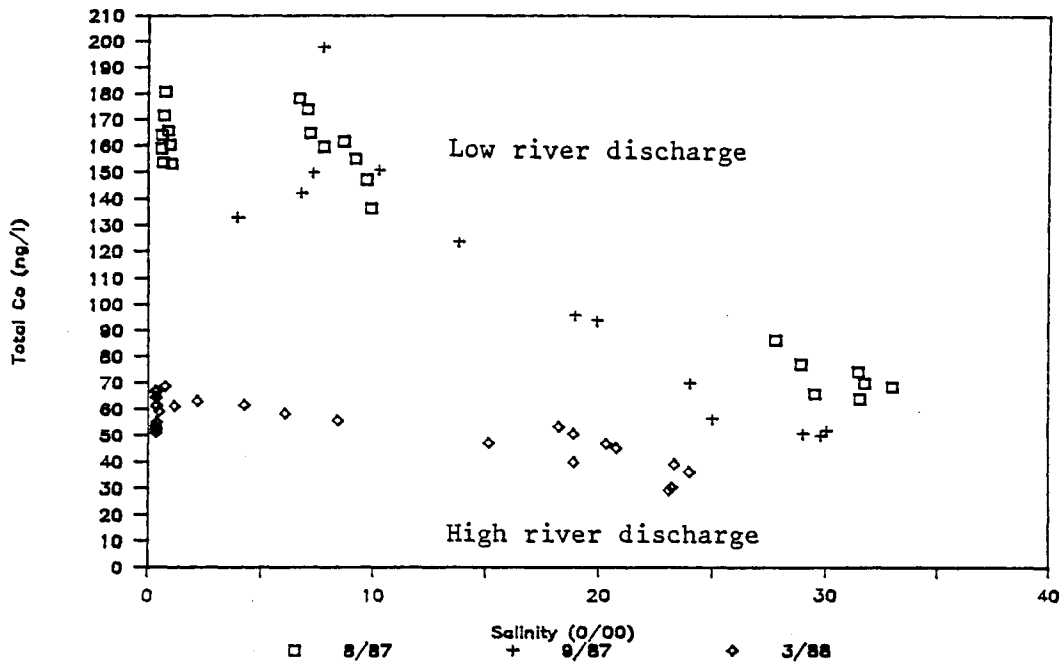


Fig. 2. Evolution of the concentration of total Co as a function of salinity for various fresh water discharge regimes.

Note also that the variations of Co concentration with tidal fluctuations in Doel are more pronounced than in other fixed sampling stations such as Schaar, Rupel and Temse.

Duursma *et al.* (1984) have found a similar trend for the longitudinal profile of ^{60}Co in suspended matter and sediments of the Scheldt (Fig. 3). The ^{60}Co distribution in recent sediments of the Scheldt estuary shows a very significant peak near 60 km (in Doel) whose concentration reaches 12000pCi/kgAl. The ^{60}Co concentration decreases in both landward and seaward directions. The conclusions of these authors indicate that the high concentration of ^{60}Co near 60 km can essentially be attributed to the discharge of the Doel nuclear power plants. In summary, the Scheldt estuary waters contain enhanced amounts of Co which suggests an anthropogenic input from the polluted industrial zone of the harbour of Antwerp and also very likely from the upstream part of the river Scheldt.

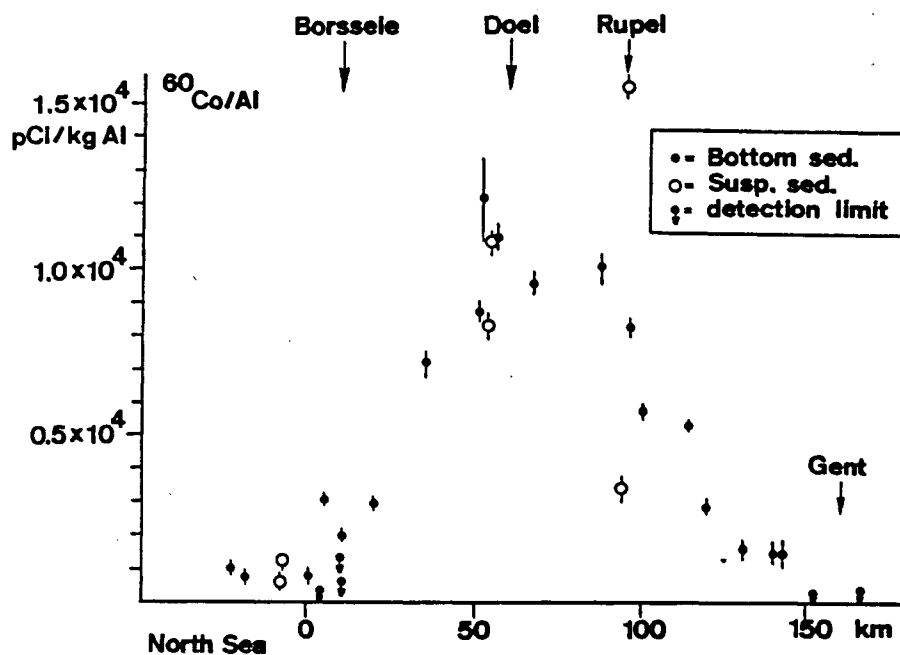


Fig. 3. Normalized ^{60}Co concentration with respect to Al in recent sediments of Western Scheldt estuary (1979-1984).

The results of our study show that the estuarine distribution of total Ni in water is similar to that of Co (Fig. 4), although Ni concentrations are about 50 times higher. Similar distribution curves for Ni and Mn in the Scheldt estuary were found by Kerdijk and Salomons (1981). A positive deviation from the ideal dilution line and the maximum Ni concentration in Doel are observed for all the distribution curves.

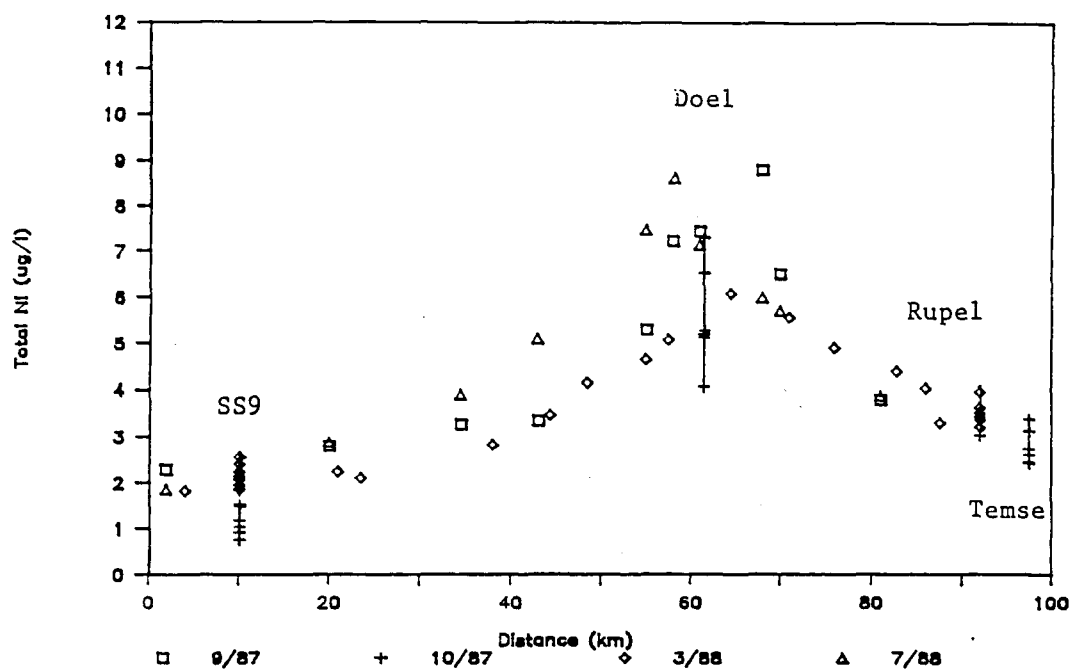


Fig. 4. Longitudinal distribution of total concentration of Ni as a function of the distance to the sea (cruises 87-88).

Similarly to cobalt, there is thus an additional source of Ni in the vicinity of Doel probably of industrial origin.

It must also be underlined that seasonal fluctuations of the concentration of Ni in the fresh water zone are by far less pronounced than those of Co. This less dependent trend suggests a relatively lower anthropogenic flux with respect to the natural flux in the case of Ni (Stumm, 1981).

2.2 Speciation of Co and Ni

The speciation of Co and Ni in the Scheldt, as obtained according to the analytical procedure described earlier, will be discussed in order to gain a better understanding of the biogeochemical behaviour of these two elements in the estuarine zone. As shown in figure 5, taken as an example, the total concentration of Co is largely dominated by that of dissolved Co, and in both dissolved and particulate fractions the contribution of the organic bound Co is small. The concentration of dissolved organic Co is rather constant and never exceeds 20 ng/l.

The relationship between total dissolved Co and cobalt weakly bound to the particulate phase is shown in figure 6. The curve is typical of an adsorption isotherm with a linear relationship in the lower concentration range and a saturation limit securing approximately above 50 ng/l.

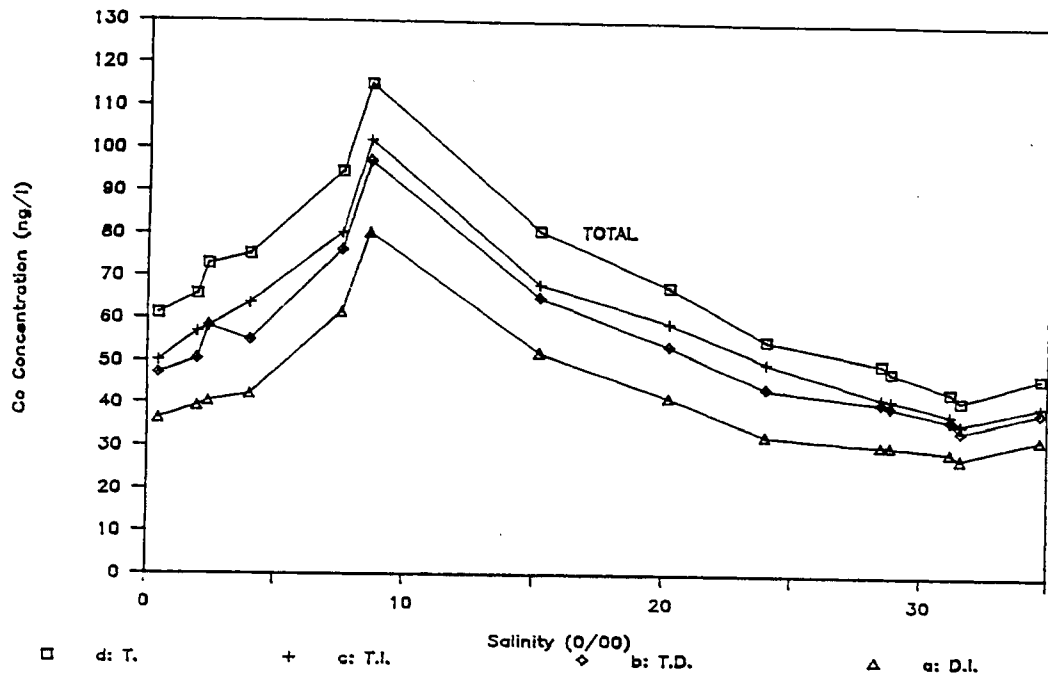


Fig. 5. Speciation of Co in the Scheldt estuary as a function of salinity for July 88 cruise. The definition of each fraction is conventionally defined in the text.

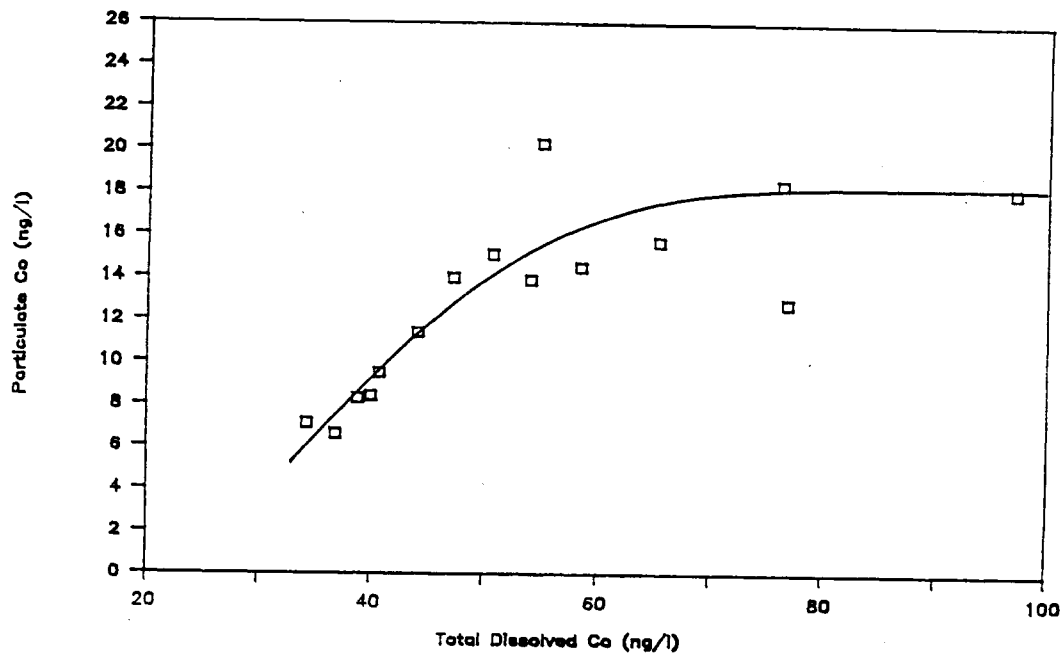


Fig. 6. Weakly bound particulate Co concentration as a function of total dissolved Co (cruise July 1988).

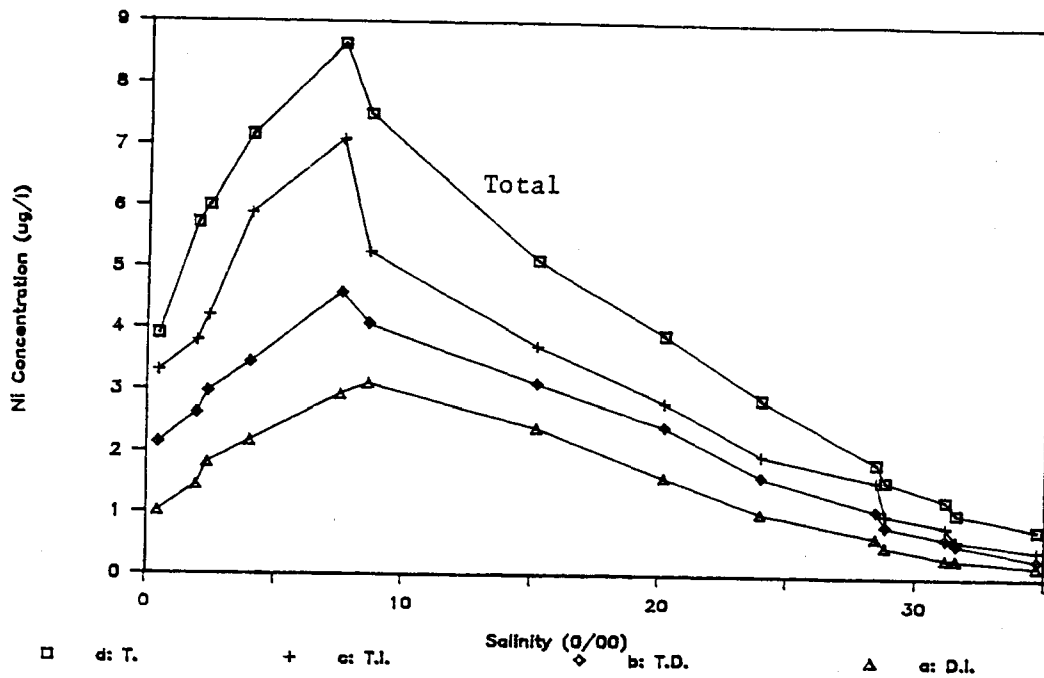


Fig. 7. Speciation of Ni in the Scheldt estuary as a function of salinity for cruise in July 1988. The symbols are same as in Fig. 5 for Co.

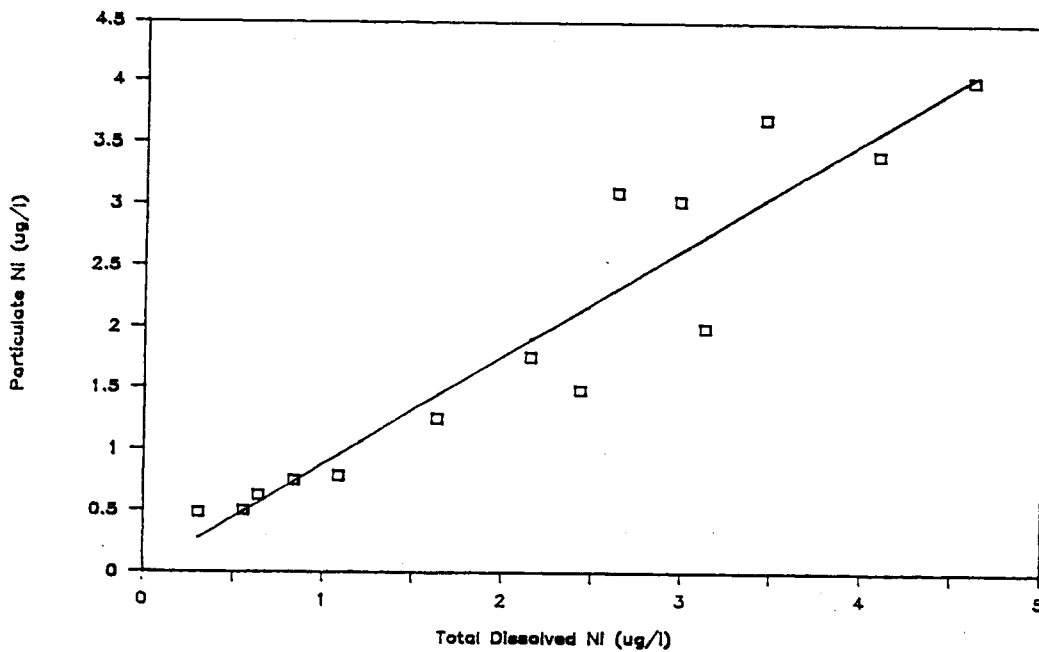


Fig. 8. Weakly bound particulate Ni concentration as a function of total dissolved Ni (cruise July 88).

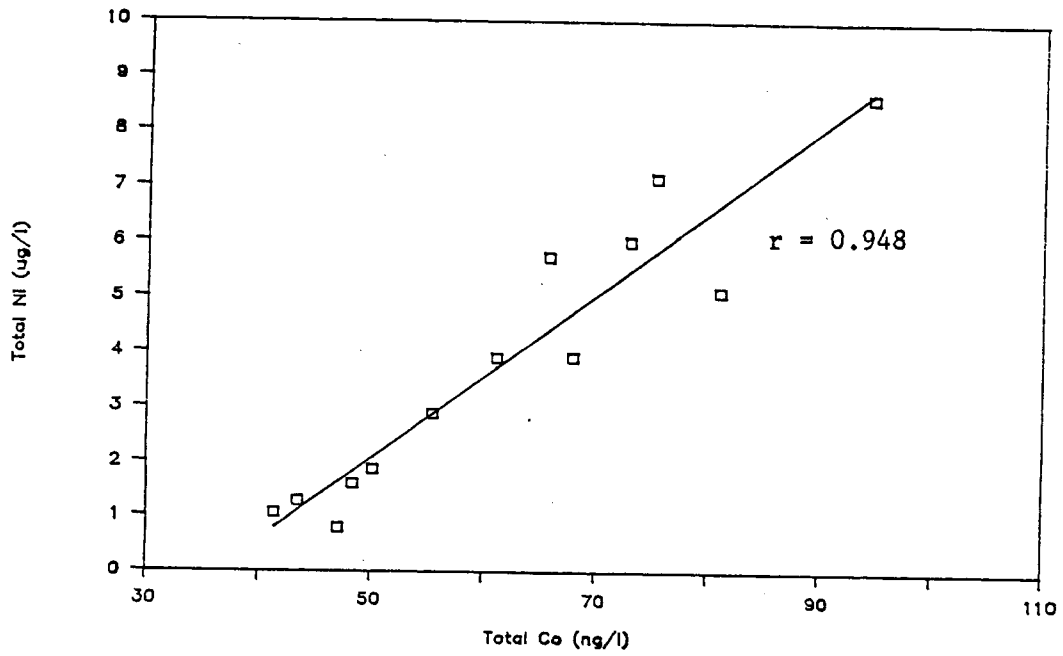


Fig. 9. Relation between total Ni and Co concentrations (cruise July 88).

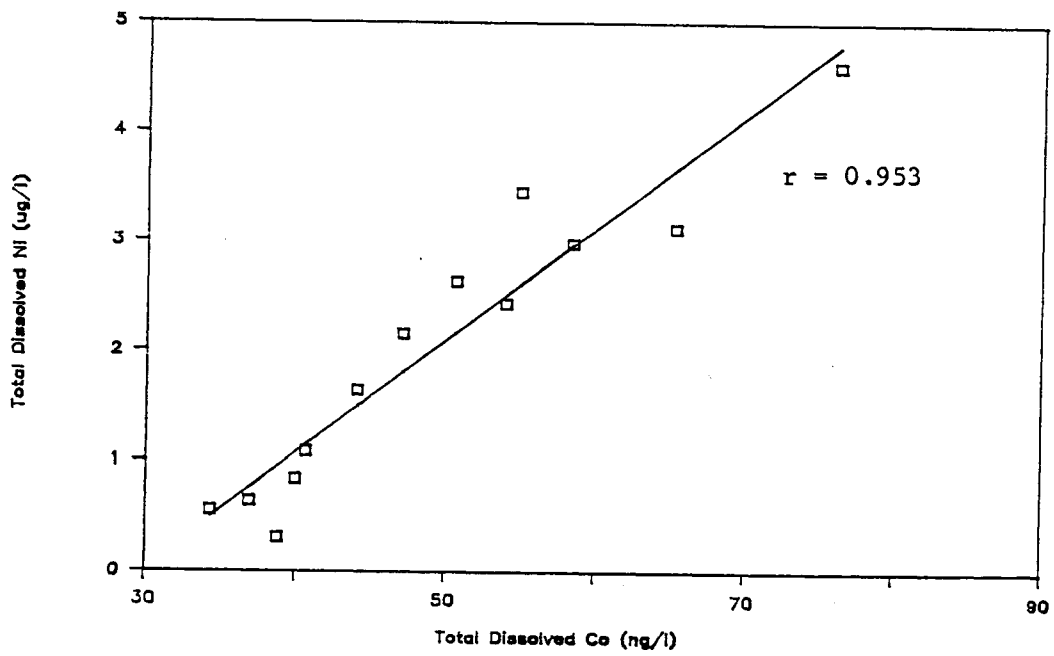


Fig. 10. Relation between total dissolved Ni and Co concentration (cruise July 88).

An experimental and theoretical work by Kurbatov et al. (1951) on the adsorption of cobalt by iron oxide shows a similar trend.

Nickel in the Scheldt estuary exhibits a comparable behaviour in terms of its speciation dominated by the inorganic dissolved fraction (Fig. 7). However in contrast to cobalt the weakly bound fraction of Ni to the particulate phase is much more significant and accounts for approximately 40 % of the total Ni. This is in agreement with the experimental results of Sholkovitz and Copland (1981) who have demonstrated that coagulation and precipitation of Ni in natural water is much more efficient and rapid than for Co. Also, the relation between total dissolved Ni and the particulate fraction measured according to our analytical procedure shows a linear relationship for all the concentration encountered (Fig. 8).

It is worth mentioning that due to the close similarity in electronic configuration between Co and Ni, they display some analogous properties and behaviour in natural waters which is supported by the strong linear relationship between Co and Ni for both dissolved and total concentrations (Fig. 9 and 10).

Co and Ni are mainly transported as dissolved species in the Scheldt estuary, either as free ions or labile inorganic complexes with Cl^- , CO_3^{2-} , HCO_3^- and OH^- (Nürnberg, 1982; Salomons et al., 1984; Goldberg, 1975).

The relatively small adsorbed fraction of Co is not surprising because cobalt, unlike other divalent elements is much less effectively adsorbed on particulate matters (Krauskopf, 1956). It may possibly be correlated with the greater polarizing ability of Co with its complete 18-electron shell.

3 CONCLUSIONS

The results of our study on the distribution and speciation of Co and Ni in the Scheldt estuary can be summarized as follows :

(i) Co and Ni distribution show similar trends with a maximum in Doel suggesting an input in this area very likely of industrial origin.

(ii) The seasonal variation of Co and to a lesser extent of Ni concentrations in relation with water discharge seems to confirm the existence of a possible large continuous anthropogenic input.

(iii) Both Co and Ni in the Scheldt estuary are present as dissolved inorganic species. However in contrast to Co, Ni is also largely in the form of weakly bound particulate species.

4 ACKNOWLEDGEMENTS

This work was partially supported by the EEC - Radiation Protection Programme, contract nr. B16-B191-NL. We are grateful to the Management Unit North-sea and Scheldt estuary for its logical assistance. We thank the Officers and the Crew of the